II.—*On Paracyanogen and the Paracyanic Acid.* By JAMES F. W. JOHNSTON, A.M., F. R. S. E., Professor of Chemistry and Mineralogy in the University of Durham.

Read 4th April 1836.

INTRODUCTION.

THE history of the newer sciences presents many instructive examples of the progress of the human mind in developing the germs of natural knowledge, and building on a single observation entire departments of science. Few pursuits indeed are more interesting, even to the student of immaterial nature, than in the perusal of such a history to trace the footsteps of the several investigators, and to mark how far, and by what means,—whether by new methods or by greater patience of research,—each successive observer advanced the inquiry. We see the human mind, as it were, set free from the trammels of time, and developing its resources on a large and continuous scale, not limited by the powers of one intellect, the length of one life, or the means of one station. We see, at the same time, what varied gifts and opportunities are necessary for the elucidation of a single subject; how these gifts, though not all imparted to one man or to one generation, are yet wisely and beneficently bestowed on the entire species; and how all are thus enabled to co-operate, either in unfolding abstract truth, or in drawing forth those practical results which directly conduce to the amelioration and comfort of all.

These reflections are particularly suggested by the history of that branch of chemical science, to which the facts contained in the following paper are intended to form a small addition.

Early in the last century, about 1710, a solution of potash which had been employed by DIPPEL in the purification of his animal oil, and afterwards calcined, was accidentally mixed with a solution of sulphate of iron. A beautiful blue precipitate was the result, and by the repetition of the experiment a pigment was obtained, since known in commerce by the name of the Prussian blue. This single observation gave rise to a multitude of researches. WOODWARD, MACQUER, MORVEAU, LAVOISIER, and BERGMAN, successively experimented on the blue substance with little success. Upwards of seventy years elapsed before any light was thrown upon its true nature;—when in 1782 SCHEELE obtained from it the hydrocyanic or prussic acid. Five years later, his results were verified and ex-

tended by BERTHOLLET. In 1806, the characters and compounds of the new acid were more fully detailed by PROUST; and in 1815, its composition rigorously determined by GAY LUSSAC, in his admirable researches into the properties of cyanogen. Still it was not till 1819 that the exact constitution of the original pigment, Prussian blue, was established by BERZELIUS with any degree of certainty; and not till after the discovery of the red prussiates or ferro-cyanides by LEOPOLD GMELIN in 1822 that the last doubts were removed. Thus, from the time of its accidental discovery, a period of 112 years intervened, before our knowledge became so far extended that we could give a satisfactory reason for the various steps necessary to its production.

Yet the many more or less unsuccessful labours which this long period saw were not spent in vain. Almost every experimenter has recorded observations fitted to be the germ of new researches, and so many branches have already shot forth from the main trunk of investigation, as to render the department which includes cyanogen and its kindred compounds, by far the most complicated and difficult of the chemistry of the present day.

Among the more important memoirs to which we are indebted for the recent development of this branch of the science, may be enumerated those of PONNET on the ferro and sulpho cyanic acids; of LEOPOLD GMELIN on the suites of compounds formed on replacing the iron of the ferro-cyanides by other metals; of WÖHLER on the cyanic acid; of HOWARD, LIEBIG, and EDMUND DAVY on the fulminic acid; of SERULLAS on the cyanic acid, and many other interesting compounds of cyanogen; and of MOSANDER and others on the complicated combinations which the double cyanides are capable of forming with each other. To these must be added also the beautiful memoirs of LIEBIG and WÖHLER on the cyanic and cyanuric acids; of LIEBIG alone on mellon, and the curious compounds to which, by the action of acids and alkalies, it gives rise; and, most recently, of LEOPOLD GMELIN on the mellonic and hydro-mellonic acids, the investigation of which still remains to a considerable degree imperfect.

While, therefore, the history of this one department shews what lengthened and laborious research the illustration of some branches of nature requires, it shews, at the same time, how little the failures of even a succession of experimenters affects the ultimate advancement of knowledge,—how men may grope on in darkness year after year, perhaps age after age, despairing of success,—and yet may be all the while unconsciously laying the foundations and storing up the materials of future buildings, till at length accident or genius guides some philosopher into a new path, or puts into his hand a new instrument before which all obstacles give way.

I.—Preparation of Paracyanogen.

1. When pure dry bicianide of mercury is heated in close vessels, it gives off metallic mercury and a gas, which is wholly absorbed by solution of caustic potash. This gas is pure cyanogen. The pure dry salt gives off along with it no appreciable quantity of any other gas.

2. In all cases, however, when the pure bicianide is wholly decomposed, there remains in the retort a greater or less quantity of a black matter resembling charcoal, sometimes in the form of powder, light, porous, and void of lustre: at others more dense and coherent, and when it has been in contact with the sides of the retort exhibiting a shining metallic lustre.

3. Since pure bicianide of mercury consists wholly of cyanogen and mercury, and since, during the decomposition by heat, pure cyanogen and pure mercury are alone given off, the black residue, when freed from metallic mercury, can contain only carbon and nitrogen, in the same proportion in which they enter into the constitution of cyanogen. It must either be a new body having the same elementary constitution as cyanogen, or it must be a mixture of two or more substances which taken together have such a constitution.

4. This black substance did not escape the notice of GAY LUSSAC in his researches upon cyanogen. He recognised in it the presence of nitrogen, as many succeeding chemists have done, but he supposed the greater part to be carbon derived from the decomposition of a portion of the cyanogen. This opinion is still generally entertained.

5. Seven or eight years have now elapsed since, in a paper which I had the honour of reading before this Society, and which was afterwards published in Brewster's *Edinburgh Journal of Science* for 1829, p. 75, I endeavoured to shew that this black matter was not a mere mixture of two or more substances, but was in reality a new body, which, though differing so remarkably in physical and chemical properties, yet contained the same elements as cyanogen, and combined together in precisely the same proportion. Chemists, however, were not prepared at that time for the reception of so extraordinary an opinion. The only case of isomerism then clearly made out, was that of the cyanic and fulminic acids analyzed by LIEBIG, and even over that case the researches of EDMUND DAVY still threw some doubt. It was not surprising, therefore, that the result at which I had arrived should be regarded with a suspicion, which the many striking examples of isomerism since discovered has not yet wholly removed.

6. Dr THOMSON, in his *System of Chemistry*, has objected that I have not shewn the absence of hydrogen in the black matter; but, as the dry bicianide contains no hydrogen, it is obvious that none can be present in any residue it may leave. LIEBIG having prepared and analyzed a portion of this substance, concluded that

it was not a definite compound, and that the quantity of carbon was variable. The presence of some impurity had probably interfered with the accuracy of his results.

7. While on a visit to that eminent chemist at Giessen in the month of October 1835, he did me the favour to repeat his analysis in presence of Professor POGGENDORF and Dr GREGORY, and with a result on this occasion perfectly according with my own. Thus, burned with oxide of copper, and the gases separated by caustic potash—

99	vols. left	32.6	vols. of nitrogen.
92.9	— —	30.1	— —
293	— —	98	— —

Another portion burned with bichromate of potash, a method lately suggested by LIEBIG, gave the gases in a like proportion. Thus—

94.5	vols. left	33.5	nitrogen.
129	— —	43	—
108	— —	36	—
175	— —	58.5	—

8. My attention being thus recalled to the subject, I have since my return prepared this substance by a variety of processes; and have found, that not only has it, when pure, the same composition as cyanogen, but that, like it, it also exhibits with other substances many interesting reactions, and is capable of combining with oxygen to form a new cyanic acid.

9. Pure bicyanide, prepared by saturating prussic acid with peroxide of mercury, reduced to powder, carefully dried and decomposed in a retort gradually heated to redness, left a light bulky powder, which, when burned with oxide of copper, gave a gas, of which, treated with caustic potash,

102	vols. left	35	of nitrogen
86	— —	29	—
87.5	— —	29.5	—

This substance is remarkably difficult to burn. The quantity of nitrogen present is so great that I have only once or twice succeeded in burning it without the formation of a sensible quantity of nitric oxide.

10. When strong prussic acid is set aside, it speedily decomposes, and deposits a black powder in considerable quantity. Dried in vacuo over sulphuric acid or at 212° F., this substance still gives off, when heated in close vessels over a lamp, water, carbonic, and hydrocyanic acids, and ammonia. The black matter that remains, burned with bichromate of potash in large excess, gave a mixture of carbonic acid and nitrogen in the proportion of 2 to 1. Thus,

97.5	vols. left	32	of nitrogen.	92.5	left	30
95	— —	31	—	90.5	—	29.5

11. When a solution of cyanogen gas in water is allowed to stand for a considerable time, a similar black matter is deposited in smaller quantity. A portion of this substance, for which I was indebted to the kindness of Professor WÖHLER, after heating to redness, to free it from water, ammonia, &c., burned with oxide of copper, and the gases made to pass over a large surface of red hot metallic copper, gave still distinct traces of nitric oxide, and

263 vols. of the gas left 89 of nitrogen.

110	—	—	36.5	—
96	—	—	32	—
69.5	—	—	22.5	—

12. A strong solution of caustic potash absorbs cyanogen gas very rapidly, and when excess of the gas is present, speedily becomes coloured, forming a dark reddish-brown solution, from which a brown powder is precipitated on neutralizing with an acid. Solution of caustic ammonia has a similar action, but I have not yet prepared the matter in sufficient quantity by these processes to enable me to analyze it.

13. Ether absorbs cyanogen slowly, but in considerable quantity. The solution in close vessels remains colourless. Left in an atmosphere of the gas for thirty-six hours, it had absorbed sixteen times its volume, and began to be slightly coloured. After several days the absorption appeared to cease at twenty-eight volumes, it was of a brown colour, and had deposited a portion of a brown sediment. If water be added to the colourless solution, a black film gradually forms at the common surface of the two fluids.—Liquid ammonia and caustic potash cause a speedy deposition of the black matter.

14. Alcohol absorbs cyanogen rapidly, and in large quantity. When perfectly saturated and set aside, the smell of cyanogen disappears, a sweet penetrating ethereal odour takes its place, and the solution becomes coloured. It is now capable of taking up a second and larger doze of the gas, the smell of which again disappears, on standing for twenty-four hours—the ethereal odour, meanwhile, becoming stronger and the colour darker. The addition of gas may now be repeated, and by alternate changing and setting aside, an English pint of common alcohol may, in the course of a week or ten days, be made to absorb the whole of the gas given off by four or five pounds of bicianide of mercury. By this time, also, a large deposit will be formed at the bottom of the bottle, and the entire alcohol will have become dark and thick like treacle.

15. If this thick fluid be distilled, a colourless product passes over, having an ethereal odour, but from which water separates no ether, and which, on standing, gradually becomes dark coloured, and gives a further portion of the dark brown or black sediment. After the lapse of some weeks or months, according to circumstances, no farther evidence of decomposition shews itself, the deposi-

tion of black matter ceases, and the thick treacly fluid separates into a black powder, and a transparent and nearly colourless supernatant liquid.

16. It is unnecessary at present to inquire minutely into the nature of the complicated changes which take place during the mutual reaction of cyanogen and alcohol on each other. To this subject I shall have occasion to revert, in a future memoir, when describing certain new substances produced, partially at least, by this reaction, but of which the investigation is still incomplete. Ammonia and hydrocyanic acid are formed in considerable quantity, and probably more than one ethereal substance. The greater number of these appear to be decomposed in their turn, and the black powder is the ultimate and chief result.

17. When the thick alcoholic solution is thrown on the filter, and the substance dried without washing, it gives a mass, having a deep black colour and shining fracture; washed with hot water, it is of a brown, more or less dark, and if boiled in repeated portions of water, as long as any thing is dissolved and dried at 212° F. it is of a dark olive-brown colour. Heated over a lamp in a close tube, it gives off, like the substance deposited in prussic acid, water, carbonic and hydrocyanic acids and ammonia, leaving a black residue, which, at a dull red heat, gives off cyanogen, and slowly disappears.

The black residue burned with oxide of copper, gave a mixture of carbonic and nitrogen gases, of which

88.5 vols. left 30 of nitrogen.

85.5 — 29 —

This is as near the ratio of N : C₂ as can generally be expected.

18. When dry cyanate of silver is heated in a close tube, it is decomposed, giving off nitrogen and carbonic acid in the proportion of 1 : 2 by volume, and there remains behind a black matter mixed with metallic silver. This black substance has the same composition as that left by bicyanide of mercury, and its formation is accounted for by the following formula—

19. Rectified wood-spirit (bihydrate of methylene) also absorbs cyanogen rapidly and in large quantity. When it has absorbed upwards of thirty times its volume of the gas, it begins to be coloured, and the absorption goes on till it becomes dark brown and opaque, and begins to deposit a dark brown powder. In the course of an hour the quantity of gas taken up amounts to thirty or forty volumes, after the lapse of two days it has increased to between fifty and sixty volumes, and a portion of the deposit was observed. If the wood-spirit be not saturated with the gas, it exhibits no change of colour for some days, but ultimately assumes a reddish-brown colour, more or less dark, and gives a brown deposit.

20. When the ferro-cyanides, Prussian blue and prussiate of potash, are de-

composed by heat in close vessels, a black residue remains, which is generally supposed to be a carburet of iron. This, however, is not necessarily the case.

A portion of the best Prussian blue of the shops was gradually heated to redness in a retort for half an hour, water, hydro-cyanate and carbonate of ammonia, carbonic oxide and nitrogen, were given off. The black matter dissolved in sulphuric acid, with evolution of hydrogen gas, and the solution diluted with water, gave a precipitate of Prussian blue. Burned with bichromate of potash, it gave the carbon and nitrogen in the proportion of 2 to 1. Heated again to redness for half an hour, the carbon was found to be to the nitrogen as 4 to 1, and this proportion was not changed by a third heating for the same length of time.

It appears, therefore, that while water is present, the decomposition goes on in such a way as to remove *all the elements* of each atom of cyanogen as it is decomposed, without affecting the composition of what remains; and that, when all the water is drawn off, the affinity of the iron for carbon comes into play, and nitrogen is given off while a carburet of iron is formed.

Dry prussiate of potash, heated to redness in close vessels, as in the preparation of cyanide of potassium, undergoes a similar decomposition. A portion of the black matter remaining after the separation of the cyanide in this process, gave me the carbon to the nitrogen as 8 to 1. I have not satisfied myself, however, that the black matter thus formed contains paracyanogen at any stage of the process.

II.—*Properties of Paracyanogen.*

1. It is of a black or dark brown colour, and occasionally has considerable lustre. It has no taste or smell, is insoluble in water and alcohol, has a density of about 2, and is a non-conductor of electricity.

2. Heated to redness in close vessels, it is slowly resolved into cyanogen. In the air or in oxygen, at a red heat, it burns away without residue, forming carbonic acid, and, according to the hygrometric state of the atmosphere, more or less ammonia and hydrocyanic acid. Heated to redness in a close vessel, and suddenly exposed to the air, it burns like tinder. Heated in a moist state in close vessels, ammonia, and carbonic and hydrocyanic acids, are first given off, and afterwards cyanogen.

3. Fused with sulphur or phosphorus, or heated to redness in the vapours of these substances, no apparent change takes place. With alkaline sulphurets containing an excess of sulphur, an action takes place at a red heat, but without the formation of any sulphy-cyanide. Heated to redness in an atmosphere of dry chlorine or iodine vapour, a very slight action takes place. Chlorine, if moist, disengages vapours which affect the eyes (chloride of cyanogen?), and among other products muriate of ammonia.

4. Heated with potassium in close vessels, a violent combustion takes place, and a compound is formed, which, when dissolved in water, gives with nitrate of silver a white precipitate. Dried and heated to redness, this precipitate gives off cyanogen and leaves metallic silver. The compound formed therefore is cyanide of potassium.

5. Prepared by heating bicyanide of mercury, it is exceedingly little soluble in a solution of caustic alkali, and is very slowly decomposed when boiled with it. During the boiling ammonia is evolved, and oxalic acid should remain in the solution for $\text{NC}_2 + 3\text{HO} = \text{NH}_3 + \text{C}_2\text{O}_3$. Prepared by heating to redness the deposit from cyanogen in alcohol, it is slightly soluble in a boiling solution of caustic potash, giving it a dark brown colour. Acids precipitate it apparently unchanged.

6. Fused with dry hydrate of potash, ammonia is evolved. Intimately mixed with caustic or carbonate of potash, and heated to incipient redness in the open air for some time, a salt is formed, possessing the properties of *cyanate of potash*. With nitrate of silver it gives a white flocky precipitate. With nitric acid, violent effervescence from the evolution of carbonic acid, while the filtered solution, evaporated to dryness, gives a mixture of nitrates of potash and ammonia.

7. Concentrated muriatic acid acts upon it very slightly, becoming pale yellow.

III.—*Action of Sulphuric Acid on Paracyanogen.*

Concentrated sulphuric acid ($\text{SO}_3 + \text{HO}$), dropped upon paracyanogen in the state of fine powder and gently heated, is absorbed by it, forming a dry mass. A larger quantity of acid, aided by heat, dissolves the paracyanogen without any sensible evolution of gas. The solution is of a deep brownish red colour, more or less thick. Water decomposes it, throwing down the paracyanogen *apparently* unchanged. It is difficult, by washing, to free the precipitate entirely from sulphuric acid. A portion of it boiled in water, dried and burned with oxide of copper, gave a gas of which 61.6 vols. left 20, and 82.5 left 26.5, so that the ratio of the carbon to the nitrogen is not sensibly altered.

If the temperature be raised too high during solution, or if the solution be heated to 400° or 500° F., the sulphuric acid and paracyanogen are mutually decomposed, sulphurous and carbonic acids are given off, and sulphate of ammonia is sublimed. The gases are evolved in the proportion *nearly* of one volume sulphurous to two of carbonic acid. This agrees with the formula,

During this decomposition, a portion of the paracyanogen becomes oxidised, *paracyanic acid* being formed, hence the volume of sulphurous acid obtained is gene-

rally in slight excess. That paracyanic acid is formed is proved by precipitating the brown solution with water, filtering the acid liquid, and adding a solution of nitrate of mercury, when a yellow precipitate falls more or less copiously of paracyanate of mercury.

If the solution in sulphuric acid be boiled for a sufficient length of time, it becomes colourless, and water gives no longer any precipitate; the paracyanogen, therefore, is wholly decomposed.

The black residue obtained by decomposing the bicyanide can rarely be freed entirely from the minute globules of mercury which adhere to it. If mercury be present in sufficient quantity when the paracyanogen is treated with sulphuric acid, the entire solution on cooling congeals into a mass of minute transparent crystalline needles of a brown colour, which are *possibly* a compound of the sulphates of oxide of mercury and of paracyanogen. They are decomposed by water, and have hitherto baffled my attempts to obtain them free from the great excess of concentrated sulphuric acid.

The action of this acid on paracyanogen seems to indicate, that the black substance is possessed of basic properties, and that it may be in some measure analogous to the carbo-hydrogens.

IV.—*Action of Nitric Acid on Paracyanogen—Paracyanic Acid.*

1. Paracyanogen, after heating to redness, as it is obtained from bicyanide of mercury, is very slightly acted upon by nitric acid. Boiled in this acid, a small portion is dissolved, and if the boiling be long continued, the insoluble matter gradually assumes a lighter colour, and ultimately becomes of an orange yellow. The acid solution, diluted largely with water, becomes turbid, and deposits a yellow precipitate in small quantity.

2. When the black deposit formed in an alcoholic solution of cyanogen, in strong prussic acid, &c. is treated with nitric acid in the cold, it dissolves slowly without any sensible evolution of gas, giving a dark reddish brown solution, from which water again precipitates it apparently unchanged. If, however, heat be applied to the solution, if a current of sulphuretted hydrogen be passed through it, or more rapidly and certainly, if the black matter be gradually added to the hot acid, as each successive portion dissolves, and the dark colour caused by it disappears, copious red fumes are evolved, and a transparent reddish yellow solution is obtained. From this solution water precipitates a bulky bright yellow powder, a further portion falls on saturation with an alkali, and a third, though much smaller quantity, by evaporating to dryness the supernatant yellow solution and washing the residue.

3. If the dark brown solution of paracyanogen in sulphuric acid be heated, and nitric acid gradually added, red fumes are evolved, and a yellow precipitate

gradually falls. If a sufficient quantity of nitric acid have been added to oxidize the whole, or if the solution be added to hot nitric acid slowly, and as the colour disappears, water, as in the former case, throws down a copious yellow precipitate.

4. When a solution of cyanogen in diluted alcohol, after becoming dark coloured, is acted upon by a current of chlorine gas, among other compounds formed is a portion of a yellow substance having the appearance and properties of that obtained by means of nitric acid.

5. The yellow matter obtained by these different processes, well washed and dried at 212° F., is without taste or smell, insoluble in water and alcohol, sparingly soluble in cold, more largely and with slight decomposition in hot nitric and sulphuric acids, and soluble to a certain extent in caustic alkalis.

Heated above 212°, it gradually becomes darker in colour; about 400° F. it begins to blacken and evolve ammonia; over the lamp, in a close tube, it gives off ammonia, hydrocyanic acid, and water, and a mixture of carbonic and nitrogen gases, in the proportion of two vols. of the former to one of the latter. It, therefore, contains water,—either hygrometric or in combination,—and oxygen. A residual black matter remains, which is paracyanogen, and which, by further heating, gives cyanogen gas.

6. Burned with bichromate of potash, it gave a mixture of carbonic acid and nitrogen gases, of which

76.75 left	26.5 of nitrogen,	100.5 left	33.1
83.5	— 28.4 —	189	— 63
103	— 34.5		

The ratio of the carbon to the nitrogen is therefore 2:1, as in cyanogen, and since it contains oxygen and combines with bases, I have given it the name of the paracyanic acid.

Like paracyanogen, it is exceedingly difficult to burn, either with oxide of copper or with bichloride of mercury, without the formation of binocide of nitrogen, but the presence of this gas in the above experiments does not produce any serious error, as the nitrogen in combining with the oxygen undergoes no change of volume, and the caustic potash employed to remove the carbonic acid absorbs very little of the binocide, until it has been a considerable time in contact with the gaseous mixture.

7. The small quantities I have yet obtained of this acid, have prevented me from submitting it in the uncombined state to a sufficient number of analyses, to establish its composition beyond dispute. 4.22 grs. dried carefully at 212° Fahr., and burned with Bichromate of Potash, gave

Carbonic acid,		1.3466 = 31.91	per cent.
Water,		1.13 = 26.777	per cent.

As this mode of analysis gives the water with great accuracy, we may deduct 1.13 from 4.22, and we have 3.09 of dry acid, containing 1.3466 of carbon = 43.481 per cent. And as the C : N :: 2 : 1, we have for the constitution of the dry acid,

	Calculation.	Experiment.
C ₈ = 611.496	= 43.074	= 43.481
N ₄ = 708.144	= 49.882	= 50.035
O ₁ = 100.000	= 7.044	= 6.484
<hr/>	<hr/>	<hr/>
Atom. = 1419.640	100	100

The quantity of carbon obtained is a little too high, which may be attributed to the absorption by the caustic potash of a small quantity of binoxide, which was recognised by the smell during the process. This excess of carbon necessarily causes an excess also in the nitrogen calculated from it, and a corresponding deficiency in the per-centage of oxygen.

If the water in the acid be 5 atoms, we have

	Theory.	Experiment.
Carbon,	= 30.85	= 31.91
Nitrogen and oxygen, =	40.78	= 41.303
Water,	= 28.37	= 26.777
	<hr/>	<hr/>
	100	100

As the acid, however, was dried only at 212° Fahr., I do not place much confidence in the *number of atoms* of water. It should probably retain, when fully dry, at this temperature, only four atoms of water, as the salt of silver appears to do, in which case the formula for the hydrated acid would be C₈ N₄ O + 4 HO.

8. Being insoluble in water, or nearly so, this acid does not affect litmus. In hot concentrated solutions of the caustic alkalies, it dissolves with partial decomposition and evolution of ammonia; in weaker solutions it is very sparingly soluble, and very little also is taken up by solution of caustic ammonia. It has a powerful affinity, however, for certain metallic oxides, especially for those of mercury and silver, with both of which it forms compounds very slightly acted upon by water, and with difficulty decomposable even by the mineral acids.

This acid, indeed, is remarkably distinguished from the cyanic (Cy O), and fulminic NC₂O acids by its great stability. It is decomposed very slowly by hot concentrated nitric and sulphuric acids, protracted boiling being necessary to produce complete decomposition. Its affinity for the oxide of mercury is so great, that a weak solution of nitrate of mercury throws down the paracyanate from a solution of the yellow acid in the nitric or sulphuric acid.

V.—Properties of the Paracyanates.

1. In powder they are all of a pale yellow or orange yellow colour, the salt of oxide of silver crystallizes in bright red crystals.

2. The salts of the metallic oxides are insoluble or sparingly so in water. They dissolve readily when heated in concentrated acids, and are in great part precipitated without apparent change by cooling, or by copious dilution with water. Acidulated solutions dissolve them more sparingly, and, in all cases, they dissolve more largely in hot than in cold solutions.

3. The alkaline salts are soluble in water, and the acid is precipitated in yellow flocks on the addition of a stronger acid. The metallic salts, if decomposed, are so with difficulty, and only by protracted boiling in solutions of the hydrates and carbonates of the fixed alkalies, or in liquid ammonia. They are partially soluble in such menstrua, giving yellow solutions from which they are in great measure deposited on cooling. By such action the salt of mercury becomes of a dark grey or chocolate colour.

4. Heated in close vessels they give off carbonic acid and nitrogen gases, leaving a black mass, which, at a full red heat, is *generally* resolved more or less completely into cyanogen gas. If the salt is moist, instead of carbonic acid and nitrogen, it gives carbonate of ammonia.

5. Heated in the air they become brown between 300° and 400° Fahr. Above that temperature they blacken and give off white fumes of carbonate of ammonia, which are more or less dense according to the hygrometric state of the atmosphere. At a dull red heat they burn like tinder, leaving only the metal, or if easily oxidizable its oxide.

VI.—Paracyanate of Mercury.

1. The paracyanic acid, as already stated, has a strong affinity for the oxides of mercury. A solution of nitrate of protoxide of mercury, though largely diluted, causes an immediate precipitate in solutions of the paracyanic acid, or of any of its soluble salts. It forms, in fact, an excellent test for this acid, where there is reason to suspect its presence.

2. The precipitate is of a pale, rarely of a bright yellow colour, and nearly insoluble in water. When thrown down from solutions of the acid in strong nitric or sulphuric acids, the yellow colour is generally more decided.

3. There appear to be several paracyanates of the oxides of mercury, not to be distinguished by their external characters, yet differing in composition as the basic and neutral salts of these oxides with the nitric acid do. Hence it requires great precautions and the use of carefully prepared nitrates, to insure precipitates of uniform composition.

4. These paracyanates are soluble in hot dilute nitric acid, from which they are again partially separated on cooling, or on the addition of water. By prolonged boiling in the acid, not only the salt, but the paracyanic acid itself, is in a great measure decomposed.

5. Concentrated sulphuric acid dissolves them slowly in the cold, giving a pale yellow solution; when heated, they dissolve more rapidly, in larger quantity, and with evolution of carbonic and sulphurous acids and nitrogen. On cooling, crystals are deposited, which are a mixture of bisulphate and paracyanate. From the liquid portion water separates a brownish precipitate, and the diluted supernatant liquid gives a white with a nitrate of mercury. Sulphuric acid, therefore, partly decomposes the salt, and retains the acid in solution, which it resolves into carbonic acid, nitrogen, and perhaps ammonia, when raised to the boiling temperature.

6. Muriatic acid dissolves them by the aid of heat, but if diluted with water a portion is again thrown down.

7. Solutions of caustic potash or ammonia immediately blacken the protoxide salts, especially if newly precipitated, forming a yellow solution, and leaving protoxide of mercury. Neutralized or rendered acid by nitric acid, the solution again gives a copious precipitate with nitrate of mercury.

8. The newly precipitated salt suspended in water is also rendered dark grey by binoxide of nitrogen and sulphurous acid. The latter forms a yellow solution containing a little mercury, and a considerable quantity of the paracyanic acid, which, when the excess of sulphurous acid is driven off by heat, again falls as a yellow paracyanate on the addition of a salt of protoxide of mercury.

9. Diffused through water, the salts of mercury are blackened by hydrosulphuret of ammonia, or by hydrosulphuric acid, without, however, being wholly decomposed, the black sulphuret, when sublimed, still leaving a residue of paracyanogen. Even when the salt is dissolved in muriatic, and precipitated by excess of hydrosulphuric acid, the sulphuret of mercury is apt to carry down with it a portion of the paracyanic acid, so powerfully do these compounds resist the decomposing action even of the mineral acids.

10. A current of chlorine gas causes a very interesting reaction when passed through water, holding the salt in suspension. It decomposes both the salt and the acid, causing the evolution of carbonic acid, and forming bichloride of mercury, sal ammoniac, and carbonate of ammonia, which remain in solution. The action in this case is represented by the following formula:—

11. When a solution of iodide of potassium is digested on a protoxide salt, the latter becomes dark green, grey, and finally black, from the separation of me-

tallic mercury. The solution is yellow or orange coloured, and contains biniodide of mercury, and *probably* paracyanate of potash. Such a reaction is thus explained.

and it is probable that the haloid salts in general would act in a similar manner.

11. Heated to 230° F., these paracyanates are decomposed, and, from the sudden evolution of gas, appear to decrepitate. Mercury is sublimed, and carbonic acid, nitrogen, and cyanogen gases may be collected. 67.6 vols. of the mixture collected over mercury gave

7.1	vols. of cyanogen absorbed by alcohol,
33.5	— carbonic acid — — caustic potash,
17.0	— nitrogen, remaining.
<hr/>	
57.6	

A black residue remains behind, which, by further heating, gives cyanogen only.

12. Burned with bichromate of potash, it gives also carbonic acid and nitrogen gases in the proportion of two to one.

Thus 97.5 vols. left 32.5 of nitrogen, and 95 vols. left 31.5. A portion of a beautifully yellow ($HgO + C_8N_4O$) gave a gas, of which 88.5 left 30 vols.

13. It was not till I came to subject this salt to analysis that I was made fully aware of the necessity of attending minutely to the circumstances under which it was prepared, and to the nature of the mercurial solutions employed. I have analyzed only two portions. The first precipitated from a neutral solution of the acid, dried at 212° F., and burned with bichromate of potash, gave from 24.08 grs. 7.74 grs. of carbonic acid, and 1.32 of water = 5.48 per cent. This gives for the composition of the anhydrous salt

$$C = 9.402 \quad N = 10.888 \quad O = 1.529 \quad HgO = 78.181$$

16.57 grs. of the same salt dissolved in muriatic acid, and precipitated by hydro-sulphuric acid, gave 13.83 grs. of bi-sulphuret = 11.933 of metallic mercury, or 72.016 per cent. This gives for the anhydrous salt 79.200 of protoxide of mercury. This, therefore, was a basic salt, and its constitution

		Calculation.	Experiment.	(1.)	(2.)
C ₈	= 611.496	= 9.150 . . .	9.402 . . .		
N ₄	= 708.144	= 10.599 . . .	10.888 . . .		
O ₁	= 100.000	= 1.499 . . .	1.529 . . .		
2HgO	= 5263.288	= 78.752 . . .	78.181 . . .	79.200	
		<hr/>	<hr/>	<hr/>	<hr/>
		6682.928 100	100		

The water amounts only to about 1.7 atoms.

14. The second portion analyzed was thrown down from an acid solution. 10.88 grs. burned with bi-chromate of potash, and the gases made to pass over red hot copper, gave 4.62 of carbonic acid and 1.09 grs. of water.

10.87 grs. dissolved and boiled in aqua regia, and precipitated as before, gave 7.56 grs. of bi-sulphuret of mercury = 60.003 per cent. of metallic mercury.

These give for the constitution of the *anhydrous* salt,

	(1.)	(2.)
Carbon,	= 13.094 . . .	
Nitrogen,	= 15.163 . . .	
Oxygen,	= 2.141 . . .	
Protoxide of Mercury, =	69.602 . . .	69.3738

Boiled in diluted nitric acid, and dried *in vacuo*, the salt gave me 61.13 per cent. of mercury: it had therefore undergone little change.

A neutral compound ($C_8N_4O + HgO$) would contain 15.088 of carbon and 64.958 of protoxide of mercury per cent.

The difference, amounting to 2 per cent. in the quantity of carbon obtained by analysis, may be accounted for by supposing it to contain a portion of the basic salt

VII. *Paracyanate of Silver.*

1. When metallic silver is introduced into a solution of paracyanic in nitric acid, a yellowish-brown powder falls down as the silver dissolves. A similar precipitate is obtained by dissolving solid nitrate or carbonate of silver in such a solution; and the more neutral the solution is rendered, the more completely is the paracyanate thrown down. If allowed to stand in this acid solution, the precipitate sometimes forms minute prismatic or acicular crystals of a deep red colour, grouped into small radiated globules. The supernatant liquid still retains much of the salt in solution, a large portion of which is thrown down as a beautiful bulky yellow powder, on the addition of water. After it ceases to be troubled by further dilution, the nitrate of protoxide of mercury throws down a copious precipitate of paracyanate of mercury, shewing how much less soluble it is than the salt of silver.

2. The paracyanate of silver is precipitated by caustic ammonia from its solutions in acids; but the precipitate does not dissolve in an excess of the alkali. Even when boiled in it, no sensible change is produced. The solution, indeed, acquires a yellow colour, but contains no silver.

3. It undergoes no sensible alteration in the sun's rays.

4. It is soluble in hot dilute nitric acid, from which it partly separates again on cooling.

5. In the air, it may be heated to 300° F., without much change of colour.

At incipient redness, it blackens, and at a red heat burns like tinder, leaving metallic silver.

6. When heated in close vessels, it gives off water, carbonate of ammonia, carbonic acid, and nitrogen, and leaves a black residue, which, at a red heat, yields cyanogen. The carbonic acid and nitrogen are in the ratio of 2 to 1, as they are also when the salt is burned with oxide of copper or bi-chromate of potash.

7. *a.* 3.33 grs. dried at 212° F. in LIEBIG'S tube, left of metallic silver 1.34 = 40.24 per cent.

b. 7.16 grs. burned with bi-chromate of potash gave 0.96 grs. of water = 13.40 per cent.

c. 9.08 grs. burned with oxide of copper gave 6.49 grs. of carbonic acid = 1.7945 of carbon, or 19.702 per cent.

These give for the constitution of the salt,

	Calculation.	Experiment.
8C . . = 611.496	= 18.412 . . .	19.702 <i>c</i>
4N . . = 708.144	= 21.322	
O . . = 100.000	= 3.017	
AgO . = 1451.607	= 43.705 . . .	43.217 <i>a</i>
4HO . = 449.918	= 13.544 . . .	13.400 <i>b</i>
	<hr/>	
	3321.165	100

Here, as in the analysis of the uncombined acid, the carbon obtained is in excess, and probably from the same cause,—the formation of oxides of nitrogen,—which in burning paracyanogen and its compounds, it seems almost impossible wholly to prevent.

Paracyanate of Iron.—When a solution of sulphate of protoxide of iron is poured into one of paracyanic in nitric acid, a yellow precipitate falls, not very copiously, which is soluble in hot dilute nitric acid, and falls in great part on cooling. Heated in the air it becomes brown, blackens, then burns like tinder, leaving metallic iron, which rapidly oxidizes.

Paracyanate of Lead may be formed by mixing together a solution of nitrate of lead with one of the paracyanic, evaporating to dryness, and washing the mass with cold water.

The washings of both these salts give copious precipitates with nitrate of protoxide of mercury.

Alkaline Paracyanates.—The affinity of this acid for the alkalies seems to be singularly small. In large excess they partially decompose the metallic salts, and dissolve small quantities of the uncombined acid forming yellow solutions; but they exhibit little inclination to form neutral salts. Perhaps it is, that the neutral paracyanates of the alkaline bases are also but sparingly soluble in pure

water, and hence the difficulty of obtaining a neutral solution. But this is a matter for future investigation.

Rendered neutral by an acid, the solutions of the alkaline paracyanates are precipitated by the salts of oxide of silver and of protoxide of mercury; an excess of acid decomposes them, and throws down the paracyanic acid.

In my paper published in 1829, I suggested that the nitrogen known to exist in certain varieties of coal, might be present in them in the state of paracyanogen. I find that fine caking coal from Killingworth colliery near Newcastle, which contains nitrogen equal to about one-ninth of the weight of carbon, and leaves only 0.95 per cent. of ash, dissolves completely in hot nitric acid, with copious evolution of red fumes, giving a dark brown solution. Water throws down a reddish-brown powder, and the yellow supernatant liquid gives a reddish-brown precipitate with nitrate of mercury. The substance thrown down by water when burned with bichromate of potash, gave a mixture of gases containing about eight per cent. of nitrogen. The subject, therefore, is worthy of future investigation.

In concluding this paper, I would draw the attention of chemists to the very remarkable discordance between the properties of cyanogen and paracyanogen and their several compounds; a discordance certainly more striking than any other with which we are yet acquainted among isomeric bodies. I have already adverted to the analogy which this black substance seems to exhibit in some of its chemical relations to the hydrocarbons. It also agrees with them in the multiple ratio of the elementary atoms existing in its equivalent as compared with that of cyanogen; and in the less stability and more difficult formation of its compounds, as is the case with the hydrocarbons of greater density. For though in its relation to the acids, the paracyanic is much more stable than the cyanic acid, yet in relation to heat the latter is by far the more permanent.

We have therefore three compounds of carbon with nitrogen in the proportion of two atoms to one.

Cy . . .	Cyanogen.
C ₂ N . . .	The radical of the fulminic acid.
C ₈ N ₄ . . .	Paracyanogen

forming with oxygen the acids CyO, C₂NO, and C₈N₄O respectively.

If we allow ourselves to reason from the obscure analogy of paracyanogen to the hydrocarbons, we may expect a compound C N₄ to fill up the gap between it and cyanogen, and which may possibly be a liquid.