



XLIII. Experiments on the alleged conversion of carbon into silicon

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XLIII. *Experiments on the alleged Conversion of Carbon into Silicon.* By R. H. BRETT, Ph. D., and J. DENHAM SMITH, Esq.

To Richard Phillips, Esq.

DEAR SIR,

IN the Transactions of the Royal Society of Edinburgh of this year, some experiments have been detailed by Dr. S. M. Brown, announcing the startling discovery, that carbon in certain states of combination is susceptible of conversion into silicon, and inviting a repetition of the trials made by the author.

Anxious to satisfy ourselves respecting the accuracy of the statements made by Dr. Brown, we instituted the subjoined experiments for the purpose of verifying the results which he details.

In his experiments Dr. Brown has made use of paracyanogen, obtained by the decomposition of the bichloride of mercury; the paracyanogen employed by us was produced by the decomposition of hydrocyanic acid; this was of a brownish black colour, and soluble in sulphuric acid, from which it was precipitated on the addition of water. It contained traces of sulphate of lime and iron.

We have deemed it unnecessary to repeat the whole of the numerous and, in many cases, prolonged experiments given in the paper, but have selected those which bore most directly on the stated transformation; the modes of procedure and the results arrived at by us, we shall describe without explanation or comment.

In page 231 of the Transactions we find it stated, that a tightly luted Berlin porcelain crucible, filled with paracyanogen, was imbedded in stucco paste and exposed to a white heat for an hour and a half. The residue of this experiment was a dark brown infusible substance like charcoal; this, when ignited with carbonate of potash, and the product treated with hydrochloric acid, is described as leaving a fine white gritty powder insoluble in acids and alkalies, infusible in microcosmic salt, and dissolving with effervescence in fused carbonate of potash, and then forming a solution in water, from which it was separable as a bulky gelatinous precipitate by acids, which precipitate was soluble both in acids and alkalies, and insoluble in either after ignition to redness. It is further stated, that "two grains of the dark ignited substance procured by the last process yielded 4.11 grs. of silicic acid; one grain, 2.06 grs., and 0.8 gr. 1.57."

This experiment was repeated in the following manner:—50

grs. of paracyanogen, obtained by the spontaneous decomposition of prussic acid, were stuffed into a small crucible of Berlin porcelain furnished with a cover; this covered crucible was completely imbedded in plaster of Paris made into a paste with water, in a Hessian crucible; a cover was then placed over the latter and luted with China clay.

This apparatus was placed in a sand-bath to dry, and afterwards submitted for three hours to a full red heat; when cold, the smaller crucible was carefully opened; there was found a perfectly black carbonaceous-looking residue, weighing 4 grs.; this black residue was ignited in a platinum capsule over a gas flame, and there remained a very inconsiderable light and grayish-coloured ash, which, when boiled in aqua regia, entirely dissolved. The ash in question consisted of sulphate of lime and traces of oxide of iron.—(R. H. B.)

Again, 50 grs. of paracyanogen were placed in a porcelain crucible under precisely similar circumstances to the last experiment. The crucibles in this case were exposed to a full white heat for two hours. When the smaller crucible was opened, a black residue, like that obtained in the former experiment, was found; this residue, when burnt in a platinum crucible with access of air, was consumed, with the exception of a trifling ash entirely soluble in aqua regia, and consisting of sulphate of lime and oxide of iron, as in the former experiment.—(R. H. B.)

Not content with the results of the two experiments just detailed, 50 grs. of paracyanogen were again subjected to an intense white heat in a furnace capable of fusing metallic iron and manganese, having previously rammed it tightly into a Berlin crucible, to which was adapted a suitable cover; these were luted together very carefully; when the luting, which then presented no cracks, was dry, this crucible was placed in an earthen one, and the vacant space filled up with a ferruginous sand; this again was covered and securely luted; after ignition for two hours it was withdrawn, when the residuum proved to be a perfectly black substance, exactly resembling that mentioned in the former experiments, weighing about 5 grs. The sand had agglomerated into a solid mass resembling soft white sandstone, and owing to a portion of this getting mixed with the black residue in the crucible, the exact weight could not be ascertained. The interior glaze of the crucible, to the level of the original bulk of the paracyanogen, had assumed a black colour with a shade of brown, which apparently penetrated to the depth of the glaze, but no further; on exposure to long-continued heat with free access of air, this black lining underwent but a very slight, if any,

change of tint. Having carefully selected 3.5 grs. of the black residue so as to procure it free from the accidental admixture of sand, they were mixed with 20 grs. of carbonate of potash prepared from the bitartrate and free from silica; this mixture, which was perfectly black, was ignited for half an hour in a closed platinum crucible, which was itself placed in a covered earthen crucible carefully luted; the fused residue was black, and when treated with water left a black insoluble powder; this, washed, collected, dried, and ignited in a platinum capsule and in contact with air, glowed like ignited carbonaceous matter, and left an ash-coloured residue, which, treated with chlorate and carbonate of potash, gave a fused residuum entirely soluble in water; this solution, evaporated to dryness with the addition of hydrochloric acid in excess, and subsequently ignited, gave a slightly turbid solution with water, which became perfectly clear on the addition of hydrochloric acid; this solution contained traces of platinum. The first solution of carbonate of potash from the black residue treated in the manner described, gave not the least indication of silica.—(J. D. S.)

Having observed that the black lining of the crucible was precisely similar to the description given by Dr. Brown of the films of silicon mentioned by him as lining the porcelain crucible in which his experiment was made, and which process he recommends as likely "eventually to be an economical and convenient way of lining porcelain with silicon for experimental purposes," we were desirous of ascertaining whether a cheaper and more easily to be obtained substance containing carbon, could not be advantageously substituted for paracyanogen, so as to produce the desired object; we therefore placed some lamp-black, mixed with a trace of peroxide of iron, in a Berlin crucible, into which it was tightly rammed, and exposed this crucible, having previously put it into an exterior one, which was covered and luted, to a white heat for an hour and a half: when withdrawn it was found to be coated, as high as the lamp-black had reached, with a stain, differing only from that before alluded to as obtained from paracyanogen, in being quite black; this crucible was exposed to a red heat with free access of air for upwards of two hours, but the stain remained unchanged.—(J. D. S.)

We do not say that this is not silicon, but if it be, either lamp-black is as capable of lining crucibles with silicon as paracyanogen is, or at high temperatures the carbon is capable of reducing the silica of the glaze, and thus producing the same effect.

In page 235 Dr. Brown observes, that "before leaving the production of silicon from uncombined paracyanogen, there is another mode of operating to be mentioned, and it is equally remarkable for simplicity and freedom from any intelligible source of fallacy." "Triturate crude paracyanogen with an excess of carbonate of potash, and fuse the mixture two hours at a full white heat in a closed platinum crucible. Paracyanogen disappears; there is no free carbon in the white saline product; but it yields a conformable proportion of silicic acid when treated in the ordinary method of analysis for that compound." "This process is more striking when subborate of soda is substituted for potassa; for when the product is treated with acids, there is no effervescence of carbonic acid; and it must be remembered, once for all, that in every professed process of transformation, the disappearance of carbon has to be accounted for as well as the new formation of silicon." Dr. Brown further states, that his crude paracyanogen contains "nearly a third of its own weight of condensed cyanogen," and "that it yields a weight of silicon never less than an eleventh, and never more than a twelfth, under the calculable weight of the constituent carbon, the cyanogen of absorption being dissipated in the course of the processes;" by which we presume is meant, that from crude paracyanogen he always obtained between 27.5 and 28 per cent. of silicon, a proportion so large that, when converted into silicic acid, it is impossible it could escape observation, even when the quantities of paracyanogen subjected to experiment are very small.

As the two processes just quoted are strongly recommended by Dr. Brown for their "simplicity and freedom from any intelligible source of fallacy," and as they appeared to us to bear so directly upon the question of transformation as to be absolutely crucial experiments, we have followed the formula detailed by Dr. Brown with the greatest exactitude and care in the following experiments:—

Fifteen grs. of paracyanogen were mixed with 100 grs. of carbonate of potash prepared from the bitartrate: the mixture, placed in a closely covered platinum crucible, and this put into an earthen one, which was covered and carefully luted, was ignited at a full yellow heat for two hours; on examination when cold, a portion of the salt, probably cyanide of potassium, was found to have volatilized, cementing the cover to the platinum crucible, and the residual salt was white; this, treated with distilled water, gave a slightly opalescent solution, which, when a small portion was treated with a mixture of per- and protosulphate of iron and hydrochloric acid, gave an abundant precipitate of Prussian blue; to the solution,

hydrochloric acid was added in excess, which occasioned the evolution of the characteristic odour of hydrocyanic acid; this acid solution, evaporated to dryness, ignited to redness, and treated with water, left a trace of reddish matter entirely soluble in hydrochloric acid.—(J. D. S.)

Five grs. of paracyanogen were then mixed with about 40 grs. of dried borax, and exposed to a white heat for full two hours in a platinum crucible, covered and placed in a Hessian-luted crucible, as in the preceding experiment; when withdrawn, the Hessian crucible was completely glazed exteriorly, and had evidently been softened by the heat; in the platinum crucible there remained a glassy substance of a light sea-green colour; this, treated with water, gave an alkaline solution, which *precipitated lime-water and effervesced with hydrochloric acid*, evaporated the acid solution to dryness and fused the residue; again treated the residue with hydrochloric acid, and after evaporation to dryness, fused; the fused mass, treated with distilled water and hydrochloric acid, left a slight sediment; when this sediment was fused with carbonate of potash and the residue treated with hydrochloric acid, evaporated to dryness and ignited, the ignited chloride of potassium was wholly soluble, without any sediment whatever, in water acidulated with hydrochloric acid; the solution contained traces of lime.—(J. D. S.)

This experiment was repeated upon rather a smaller scale, with precisely the same results.

Notwithstanding the decisive nature of the experiments just detailed, we determined, in order to avoid every objection, to subject paracyanogen prepared from bicyanide of mercury—the paracyanogen employed by Dr. Brown—to the process indicated by him as simple and free from fallacy. Some bicyanide of mercury was powdered and shaken down closely in a porcelain crucible, which was then covered and firmly luted; this was placed in another crucible, also covered and subjected to a full red heat for half an hour; the residue was black and coherent; a portion of this ignited left a trace of oxide of iron, and it was almost entirely soluble in sulphuric acid.

Twenty grs. of this paracyanogen were mixed with 120 grs. of carbonate of potash and ignited for one hour and a half at a full yellow heat, the same precautions being taken as in the experiment before cited; when withdrawn, the residual salt was white, soluble in distilled water, gave with mixed per- and protosulphate of iron and hydrochloric acid a precipitate of Prussian blue, and evolved much hydrocyanic acid on the addition of hydrochloric acid, which occasioned no precipi

tate: this acid solution, evaporated to dryness, ignited, and again treated with hydrochloric acid and water, left no perceptible residue; whereas, from the statement of Dr. Brown (p. 236), if rightly understood by us, we ought to have obtained at least 11 grs. of silicic acid from this quantity of paracyanogen.—(J. D. S.)

We may here be allowed to remark, in explanation of the circumstance which seems to Dr. Brown so difficult to account for in the experiments just described, viz. “the disappearance of the carbon” of the paracyanogen when ignited with carbonate of potash, that it is probable that one portion of the paracyanogen decomposes the carbonate of potash forming carbonic oxide, mixed perhaps with carbonic acid, azote and potassium, and that the last-named substance combines with that portion of paracyanogen which is decomposed by heat into cyanogen, forming cyanide of potassium, a portion of which is volatilized, whilst, as we have seen, the remainder is found mixed with the excess of carbonate of potash used in the process: other explanations may be given, but this appears to us to be both the most feasible and the most in accordance with the facts we have noticed.

Although the foregoing experiments were as direct and, to us, as decisive as we could desire respecting the alleged transformation of carbon, we nevertheless determined to pursue the investigation further, so as to render it complete; we therefore turned our attention to the experiments of Dr. Brown (p. 236–7) on the formation of “compounds of silicon with copper, iron, and platinum, by the reaction of paracyanogen on these metals.”

Three grains of paracyanogen from decomposed prussic acid were tightly wrapped up in platinum foil and placed in a porcelain crucible, the bottom and sides of which were lined with platinum foil, so as to prevent the foil containing the paracyanogen from coming in direct contact with the glazed lining of the crucible; a cover was placed over the crucible, and the whole imbedded in plaster of Paris paste contained in a Hessian crucible; when dry, the apparatus was exposed to a white heat for two hours. The plaster of Paris had become vitrified by heat, and a portion of this vitrified matter found entrance into the porcelain crucible; the latter, however, when broken up, displayed the platinum of a brilliant colour, and of softer texture than foil not previously exposed to so high a temperature. It could hardly therefore be supposed that the platinum had been acted upon by silicon, which renders it brittle, and does not render the metal more brilliant; it was obviously useless to act upon the platinum by aqua regia for

the purpose of determining the quantity of silicon, if any, which it might contain, from the fact just noticed of vitrified matter having got accidentally into the crucible.—(R. H. B.)

Twenty grains of precipitated copper were mixed with five grains of paracyanogen, and placed in a covered and luted porcelain crucible; this was placed in another crucible, also covered and carefully luted, and the apparatus exposed to a white heat for one hour and a half; when opened, the contents consisted of numerous metallic globules, mixed with a black powder; these globules were malleable, and wholly dissolved in nitric acid, whilst the black powder was consumed when ignited in contact with atmospheric air.—(J. D. S.)

Another experiment was made by rolling up some very thin sheet-copper, so as to form a tube of considerable thickness, into which five grains of paracyanogen were tightly rammed, and each extremity of the tube secured by hammering; this was placed in an earthen crucible, covered and tightly luted, along with a platinum tube made of foil filled with paracyanogen, in the same way as the copper one above described, and exposed to a bright yellow heat for one hour and a half; when the crucible was withdrawn and opened, the contents were found to be fused into a button, which was only slightly malleable, breaking readily; having removed the exterior of this button, which adhered to the crucible, it was treated with nitric acid, which left a residue having the appearance of gray metallic particles mixed with black carbonaceous matter; by ignition with access of air the black powder burnt away, leaving a gray residue entirely soluble in nitro-muriatic acid.—(J. D. S.)

Having hitherto so completely failed in our endeavours to obtain results similar to those detailed by Dr. Brown in the paper under consideration, we resolved to conclude our experimental examination of it, by endeavouring to procure silicic acid, either with or without the admixture of carbonate of potash, from ferrocyanide of potassium. These experiments are not so satisfactory as the preceding ones, owing to the energetic action of the mixed ferrocyanide and carbonate upon wrought iron at the high temperatures, but are nevertheless useful as serving to confirm the results we had previously arrived at.

An experiment was made upon ferrocyanide of potassium, by drying it carefully, and pressing 700 grains of it into a covered porcelain crucible, which was then carefully luted, and when dry plunged into a paste of plaster of Paris contained in a Hessian crucible; this was well dried on a sand-bath, then covered, luted, and exposed to a white heat for five hours; when withdrawn from the fire and opened whilst still warm,

some portions of the contents glowed like a pyrophorus; the sulphate of lime had fused down, and had acted on the exterior of the porcelain crucible; the contents consisted of a light sooty spongy mass, very friable, and containing small globules of a metallic character, whilst the crucible itself was lined with a black enamel, similar to the stain noticed in the former experiments. Nine grains of this residue, from which the metallic globules had been separated, were mixed with 30 grains of nitrate of potash, and the same weight of carbonate of potash prepared from the bicarbonate, and the mixture fused in a platinum crucible; when cold, the fused mass, treated with water, afforded a solution of a deep purple colour, exactly resembling permanganate of potash; by rapid filtration this solution was obtained clear; decomposition appeared to be going on during filtration, for the liquid whilst on the filter was in a state of slight effervescence from the escape of a gas; by exposure to atmospheric air this solution rapidly decomposed, gradually losing its pink colour, becoming turbid, and finally deposited a reddish brown powder, leaving a colourless solution; this brown powder proved on examination to be peroxide of iron without a trace of manganese*.

The colourless and alkaline solution, tested in the usual way for silica, afforded a trace of this substance, which having reason to believe resulted from impurity in the carbonate of potash used in this experiment, it was tested for silica, and found to contain apparently the same quantity as that obtained from the alkaline solution just noticed; in each case the quantity was so minute as not to affect the most delicate balance, though appreciable by the eye. The oxide of iron, separated by filtration from the purple solution, and tested in the usual way for silica, did not afford the slightest trace of this substance.

The metallic globules before noticed were treated with hydrochloric and nitric acids; a black residue was obtained, which, ignited, left a light brown ash soluble in hydrochloric acid.—(J. D. S.)

Two hundred grains of carbonate of potash, heated in an iron tube to redness for three hours, and tested in the usual way for silica, gave 0.3 grain of this substance; when the quantity

* I believe that this combination of oxide of iron with an alkali has before been noticed, but I cannot remember the authority, nor do I think any investigation of the fact was attempted. It appears to me clearly to indicate the existence of iron in a state of oxidation, doubtless higher than any we are yet acquainted with, analogous to the acid oxides of manganese. I shall pursue this investigation, and endeavour to isolate, or at least ascertain the nature and composition of, this apparent *ferric acid*(?).—J. D. S.

[See *Journal de Pharmacie*, tom. xxvii. p. 97.—Ed.]

of silica contained in the carbonate of potash was thus ascertained, 200 grains of it were mixed with 50 grains of dry prussiate of potash, and ignited to redness in the same iron tube, closed with an iron plug and luted with China clay, for three hours; when cool, the contents of the tube were washed out with water and a little hydrochloric acid; a powerful odour of prussic acid was observed, and when the hydrochloric acid had been added to supersaturation, abundance of Prussian blue was formed; this was evaporated to dryness, and pure nitric acid added to the residue, the mixture transferred to a flask and heated; when the Prussian blue was entirely decomposed, the contents of the flask were evaporated to dryness, ignited, and boiled with water and hydrochloric acid; the colourless insoluble matter collected, dried and ignited, proved to be silica, and weighed 0.33 grain, showing a gain of 0.03 grain of silica, a quantity so small as readily to have been originally mixed with the 50 grains of ferrocyanide of potassium, or to be merely the error of experiment.—(R. H. B.)

When 30 grains of dried ferrocyanide of potassium were mixed with four times its weight of pure carbonate of potash and ignited in an iron box, inclosed in a closely covered and luted earthen crucible, to a white heat for three hours, the iron box was found on examination to have fused, and this fused iron quite malleable: this experiment was of course spoilt, and is merely mentioned to show the heat employed by us when we speak of a *white* heat.—(J. D. S.)

Another experiment, with twice the quantities of ferrocyanide and carbonate employed in the last experiment, and exposed to a full yellow heat for three hours, also failed from the energetic action of the fused contents on the iron box, by which the bottom of the box was corroded and perforated.—(J. D. S.)

Another experiment was tried upon 150 and 600 grains of the ferrocyanide and carbonate respectively, and ignited in a gun-barrel, protected by luting and well secured at the orifice, for six hours, at a full yellow heat. Notwithstanding the precaution of luting, the gun-barrel was corroded, and evidently from the action of the fused materials, and thus a great portion of the contents were lost; what remained was washed out by digesting water upon it for twenty-four hours, and the black insoluble matter separated from the alkaline solution, which latter evolved a strong odour of hydrocyanic acid on the addition of hydrochloric acid; the black residue, when ignited, was converted into a reddish brown powder, entirely soluble in hydrochloric acid: when these two solutions were evaporated together to dryness, and the Prussian blue formed decomposed by

nitric acid, the residuum was fused and then treated with hydrochloric acid, which left a trace of insoluble matter, probably silica, but which was so minute as not to affect a balance sensible to $\frac{1}{1000}$ gr.; this minute quantity was most probably accidental, and very probably was derived from the iron tube which was corroded. The weight of the residual chlorides, when evaporated to dryness, was 104 grs., so that if we admit that only one-seventh of the quantities originally employed were tested for silica, we should have above 20 grs. of ferrocyanide of potassium submitted to this trial, which, according to Dr. Brown (p. 245), should yield 3.6 grs. of silicic acid.—(J. D. S.)

Subsequently to these experiments, it was observed in two or three instances, that when paracyanogen made from the bi-cyanide of mercury was submitted to the blowpipe flame in a tube of common flint-glass, closed at one end and drawn to a capillary at the other, that gaseous matter was evolved, and a small hole blown out at that end containing the paracyanogen, through which aperture the gas escaped, and invariably burnt with the characteristic flame of cyanogen.—(R. H. B.)

This experiment was followed by placing, in a tube of Bohemian glass, having a bulb at one extremity, a small quantity of paracyanogen, prepared by dissolving the dark-coloured product which results from the spontaneous decomposition of hydrocyanic acid in sulphuric acid, and precipitating by water, well washing, and drying at a temperature of 260° to 300° Fahr., and plugging up the opening of the tube with plaster of Paris. After causing the blowpipe flame to play upon the bulb containing the paracyanogen for a short time, a small hole was blown out as before, and cyanogen continued to burn for some time.

Some more paracyanogen, prepared in a similar manner, was placed in a similar tube of Bohemian glass, but in this instance the bulb was carefully coated with luting, the open extremity plugged as before, and the apparatus carefully dried; the flame of the blowpipe was then applied to the bulb for nearly half an hour without any aperture being made in it. When the contents of the bulb were removed, they presented precisely the appearance of precipitated peroxide of iron immediately after ignition, viz. a dark black glistening aspect; this residue, when burnt in a platinum capsule, was entirely dissipated, leaving no residue whatever.—(R. H. B.)

The disengagement of cyanogen in the last experiment but one is completely at variance with the statement of Dr. Brown in his paper 'On Paracyanogen,' p. 168, "that *pure* paracyanogen (precipitated by atmospheric moisture from the sulphuric acid solution of the common product) does not afford the

slightest appearance of cyanogen, warrants the conclusion that paracyanogen once formed from cyanogen or its elements cannot be rechanged into cyanogen by heat." For it can hardly, we apprehend, be argued that the paracyanogen employed in our experiment, prepared from the crude product resulting from the decomposition of hydrocyanic acid, solution in sulphuric acid, and precipitation by water, is less pure than that obtained from paracyanogen procured from bicyanide of mercury, dissolved in sulphuric acid, and gradually precipitated by the absorption of atmospheric moisture; nor can we see how it can be argued that the failure in effecting the transformation of carbon into silicon, in the experiment just detailed, can be attributed to the employment of an impure paracyanogen, or to a substance used not being paracyanogen, because it was not obtained by the action of heat on bicyanide of mercury.

As our object in performing the experiments we have detailed was simply an inquiry respecting the fact of the statement made by Dr. Brown, of the conversion of the carbon of paracyanogen into silicon, we have not entered into a critical examination of the paper, nor do we attempt to offer any explanation of the results arrived at by us in every one of our experiments (that *the carbon of paracyanogen is incapable*, by such of the processes as we have tried, which are recommended by Dr. Brown, *of conversion into silicon*), being in every instance in complete opposition to those published by that author. We leave those interested in this subject to decide whether Dr. Brown's experiments or ours are correct, and conclude this examination by stating that the terms "white heat" and "yellow heat," when employed by us, mean respectively temperatures at which malleable iron and manganese fuse in the first case, and at which copper melts in the second; whereas Dr. Brown's white heat is a temperature evidently below our yellow heat, as he speaks of exposing a copper tube to a white heat for upwards of an hour, and does not mention the fusion of the "gypsum" when kept at a white heat for one hour and a half.

Liverpool, Sept. 17, 1841.

XLIV. *Solution of a Geometrical Problem on the Form of the Black Cross in Biaxal Crystals.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

IN turning over some old papers, I have fallen upon the following very simple method of solving a geometrical problem which occurs in investigating the form of the black cross

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