

XVI.—*On the Composition of a Carbonaceous Substance existing in Grey Cast Iron.*

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HAVING often noticed that the quantity of carbonaceous mass left in the vessels in which grey cast iron was dissolved, varied with the concentration of the acid used, I began in September, 1858, a series of experiments on the action of very weak acids on cast iron, in the hope of obtaining a quantity of the so-called graphite which it contains, and I believe that I have arrived at results which throw much light upon the chemical composition of this substance, proving it to be composed of iron, carbon, nitrogen, and silicium. This substance occupies exactly the same volume as the cast iron from which it is obtained, and is sufficiently soft to be easily penetrated by a blade. I shall now describe the method of experimenting.

Cubes, of one centimetre in dimension, of Staffordshire cold-blast cast iron were placed in corked bottles with eighty times their volume of the following weak acid solutions:—

Sulphuric acid,	1	alkalimeter	contained	10	grains of SO_3 anhydrous.	
Nitric	1	"		13·5	"	NO_5 "
Hydrochloric	1	"		9·12	"	HCl "
Acetic	1	"		12·75	"	$\text{C}_4\text{H}_3\text{O}_3$ "
Oxalic	1	"		9·00	"	C_2O_3 "
Tartaric	1	"		33·00	"	$\text{C}_8\text{H}_4\text{O}_{10}$ "
Gallic	1	"		10·00	"	cryst. acid.

The foregoing figures represent the equivalent quantity of anhydrous acid as compared with 10 grains of anhydrous sulphuric acid per alkalimeter.

Besides the above, phosphoric, carbonic, oleic acid, tannin, and acid peat-water were also used.

After three months of contact, I found that, although the external appearance of the cubes was not changed in any of the vessels, still those in contact with the weak sulphuric, hydrochloric, and acetic acid solutions, especially the latter, had become so soft externally that the blade could penetrate three or four millimetres into the cubes. I, therefore, removed the solutions from the vessels and replaced them by an equal bulk of each weak acid solution, and continued to do so every month for two years. I then found that the cubes in contact with the acetic acid ceased to yield iron to the acid, although they were still of the original size; they had, therefore, become transformed into the carbonaceous substance before mentioned. These are the results of the action of the various weak acid solutions, on the centimetre cubes of grey cast iron, after two years :—

Acetic acid	.	Complete.
Hydrochloric acid	.	Nearly complete.
Sulphuric acid	.	Ditto ditto.
Nitric acid	.	Action less complete than above.
Phosphoric acid	.	No similar action.
Oxalic acid	.	Ditto.
Tartaric acid	.	Ditto.
Tannin	.	Very slight action.
Carbonic acid	.	Ditto.
Gallic acid	.	Ditto.
Oleic acid	.	Ditto.
Acid peat-water	.	No similar action.

The action of acetic acid on grey cast iron is most interesting; for instead of ceasing when saturated with oxide of iron, as is the case with other acids, its action is continuous, if the precaution is taken to close the mouth of the vessel with an ordinary cork. Thus I have had cubes of cast iron in contact with the same quantity of acetic acid for two years, and the chemical action still existed when the contents of the bottles were examined. This action of acetic acid appears, therefore, to be analogous to that which it has on lead.

To examine the chemical composition of the cubes transformed by the action of acetic acid, they were reduced to fine powder in an agate mortar, and well washed with boiled water slightly acidulated with acetic acid. The powder was then dried at 115° C., in a dry atmosphere of carbonic acid or hydrogen, according to the nature of the body to be determined in the mass. The carbonaceous substance so prepared presented the following properties and composition :—

The cubes of grey cast iron, which originally weighed 15·324 grammes weighed only 3·489 at the end of the two years, and their specific gravity was reduced from 7·858 to 2·751. Their composition was as follows :—

Composition of the original cubes.		Composition of the carbonaceous substance.	
Iron . .	95·413		79·960
Carbon . .	2·900		11·020
Nitrogen . .	0·790		2·590
Silicium . .	0·478		6·070
Phosphorus .	0·132		0·059
Sulphur . .	0·179		0·096
Lost . .	0·108		0·205
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	100·000		100·000

These results lead to the following remarks :—

Nitrogen.—That the largest part of the nitrogen originally existing in the cast iron remains in the graphitoid substance, and only a small portion is transformed into ammonia. These facts tend to prove that the nitrogen of cast iron exists in it under two states, namely, that one portion is combined with the carbon, whilst the other is in a condition to unite with the hydrogen liberated from the water, and thus to form ammonia. This method of ascertaining the amount of nitrogen in cast iron, by determining the quantity of nitrogen in the state of ammonia, and that existing in the carbonaceous mass, appears to be the best process known, for I obtained 0·790 from the same cast iron which only yielded me 0·100 by the process lately published by M. Fremy. For ordinary analyses of cast iron, the slow action of acetic acid may be advantageously replaced by that of hydrochloric acid, taking care to use freshly distilled acid, water free from ammonia, and placing the whole in a flask provided with cork

and tube, so as to exclude the possibility of the ammonia existing in the atmosphere from interfering with the experiment. By this means the amount of nitrogen existing in cast iron can be easily and speedily ascertained.

Silicium.—I have ascertained by direct experiments that it is silicium, and not silica, that enters into the composition of the carbonaceous mass. Amongst other experiments I may state that I took 5·96 grains of the carbonaceous substance dried at 115° C. in a current of carbonic acid, and after having placed it in a small platinum dish, the whole was introduced into a porcelain tube, and submitted for several hours at a red heat to a current of pure and dry oxygen. I then found that the 5·96 grains had increased to 7·39 grains, or nearly the theoretical amount: for 5·96 grains of substance would lose 0·664 of carbon, and the remaining 0·338 of silicium would become 0·718 of silica, whilst the 4·692 of iron would become 6·702 of peroxide of iron, or both added together 7·420, being within 0·13 grain of the weight actually found. Now, if the iron in the mass had been in the state of protoxide, and the silicium in the state of silica, the 5·96 grains employed would, after the loss of carbon, have decreased to 5·551 grains, leaving, therefore, no doubt that the carbonaceous substance contained metallic iron and silicium. Finding, however, that the quantity of silicium in the carbonaceous substance, though high, did not represent the whole of the silicium contained in the cast iron employed, I passed the hydrogen liberated by the action of weak acids on cast iron through fuming nitric acid, and found, on the evaporation of this acid, a white deposit of silica. All acids which give off hydrogen when in contact with cast iron, also give rise to the gas discovered by Wöhler, namely, silicide of hydrogen.

Carbon.—Like silicium, the quantity of carbon found in the carbonaceous compound does not represent the whole of the carbon pre-existing in the cast iron employed, as carburetted hydrogens are given off during the slow action of acetic acid on cast iron.*

Iron.—As shown by the above analysis, the carbonaceous compound contains 79·960 of metallic iron, even when the acetic acid has ceased to act upon it. I have made several experiments to satisfy my mind that the carbonaceous mass contains metallic iron, and not oxide of iron. Thus, I passed hydrogen, at a dull-red heat,

* I am now engaged in preparing a sufficient quantity of these hydrocarbons to enable me to submit them to a careful examination.

over some of the carbonaceous substance previously dried at 115° , and obtained no water, and the experiment related under the head of silicium confirms this conclusion. All grey cast irons appear to yield the same relative proportions of carbon and iron; but as cast iron becomes harder and whiter, the amount of carbon decreases, and, in fact, nearly disappears in Welsh white cinder iron, being replaced by silicium. The relative amount of carbon and iron in the carbonaceous substance corresponds to $4C$ and $6Fe$, or are the same that I have found in some cast iron which had been saturated with carbon, by melting No. 1 cast iron in presence of a large excess of coke on a cupola, and called technically "keechy."

I do not, however, believe that the carbonaceous substance obtained by me is simply composed of $4C$ and $6Fe$, but that the nitrogen and silicium found in it must likewise enter into its composition. But, in the present state of my researches, it would be premature to attempt to assign any definite composition to this substance. As I am, however, still pursuing the subject, I shall be happy, if I arrive at any conclusion, to communicate the same to the Society.

When the *graphitoid* substance prepared by the above process, is exposed to the atmosphere, it absorbs oxygen with rapidity, and the temperature of the mass rises rapidly, protoxide of iron being first formed, which is converted into sesqui-oxide; but when this mass is placed in distilled water, a chemical action ensues similar to that described by M. Kuhlmann, namely, a portion of the carbon is converted into carbonic acid by the oxygen of the sesqui-oxide of iron, and the carbonic acid thus produced unites with protoxide of iron to form carbonate of protoxide of iron. The atmospheric action on the carbonaceous substance above described explains the difference of composition which I have found to exist between the body obtained by me, and that of a soft graphitoid mass which was found to replace a mass of iron buried for many years amongst coal cinders, and which had the following composition:—

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Mean of several Analyses.

Peroxide of iron	66·61
Carbon	12·03
Silica	18·13
Sulphur	0·79
Phosphorus	traces
Lime	2·14
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	99·70

Nitrogen was also present, but its amount was not determined.

I am aware that the latter curious and interesting change in cast iron has been several times noticed. Thus, Dr. Henry published a short notice on this subject in the "Annals of Philosophy." Mr. R. Mallet also described a similar substance in the "Transactions of the British Association." Mr. Warrington has also noticed the conversion of cast iron into a soft black substance which occurred in a brewery where it was in contact with sour beer. Lastly, Mr. E. W. Binney records, in the 11th volume of the "Memoirs of the Manchester Philosophical Society," a description of a similar substance found by him at the emptying of a deep coal-pit, in which the cast iron had remained submerged for a few years, and which yielded to Dr. Angus Smith the following composition:—

Iron and bases	38·8
Carbon	40·0
Silica	19·7
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	98·5

In conclusion, the conversion of the guns of the "Royal George," at Spithead, is so well known, that I merely refer to it to express the same opinion as Mr. Binney,—that it strongly behoves those who have charge of lighthouses, now so often erected in the sea upon cast-iron pillars, to carefully and frequently inspect such structures, for day by day their support must be weakened by the action of the salt-water. (See Memoirs of "Manchester Philosophical Society, Vol. II., page 28.)