

XXIII.—*Researches on the Atomic Weight of Graphite.*

BY B. C. BRODIE, F.R.S.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF OXFORD, AND PRESIDENT OF THE
CHEMICAL SOCIETY.

[For the numbers of the analyses given in this communication, and for other details, see the author's paper on the Atomic Weight of Graphite in the current number of the Philosophical Transactions.]

THE following research was undertaken with the hope of throwing light upon a very obscure problem, the nature of the allotropic conditions of the elemental bodies. My object was to ascertain whether this difference of condition was to be regarded as a purely physical, or as a chemical difference of matter. If it were a chemical difference, then different allotropic forms must exhibit different chemical reactions, and it was to be anticipated as not improbable that these different forms might even enter into combination with different combining weights. No fact of this nature has yet been ascertained; but among the physical properties of the allotropic forms of the elements, there was one which will hereafter be referred to, by which this result was indicated. In the great majority of cases the allotropic conditions of an element are

so easily convertible, and have so little permanence that we could hardly hope to discover any chemical difference between them, even if such exists. Certain instances, however, may be found of more permanent forms; of which the most remarkable is that of the forms of carbon. The forms of carbon are identified by the fact that by combustion in oxygen they can all be converted into one and the same substance, carbonic acid; but this transformation requires great heat; and within a very considerable range of temperature, the forms of carbon are unaffected by those causes which in other cases determine the transition of the allotropic forms of an element into its one most permanent state. I therefore examined with care the chemical reactions of carbon.

Some account of that remarkable substance which afforded the material of this inquiry may not be without interest. The term graphite has been applied indiscriminately to several varieties of native carbon, which have but little in common. Among these, however, two may be especially distinguished by their superior brilliancy and by their metallic streak. The one of these varieties possesses a distinct lamellar structure and the lustre of a metal; in appearance it resembles molybdenum; the other is amorphous, and appears as a powder of a silver-grey colour. The lamellar graphite is imported into this country chiefly from Ceylon, where it is found in large masses associated with quartz. It exists also in many other localities; at Travancore, and in Spain, and in small quantities is frequently discovered, associated with volcanic minerals.

The amorphous graphite is now chiefly procured from Germany; I believe from Passau, in Bavaria. Formerly mines of it existed at Borrowdale, in Cumberland, but these are nearly exhausted. It is of much less frequent occurrence than the other kind. In the following investigation, the term graphite is limited to these two varieties. The lamellar graphite is also formed artificially during the process of iron smelting, when it is dissolved by, and combines with, the iron. On dissolving cast iron in an acid, a residue is left of from 3 to 4 per cent. of graphite. I know of but one example of the artificial formation of amorphous graphite; the carbon which is deposited on the electrode during the passage of the electric light, is in this condition. This carbon is soft, amorphous, and has the streak of a fine black-lead pencil. This change is doubtless effected by the intense heat, the extremities of both poles being in the same condition. Of the other varieties of

native carbon, which have been vaguely termed graphite, at least two exist in large deposits. A deposit of carbon is found in New Brunswick, very similar in appearance to anthracite coal. In Greenland also there is a large deposit of carbon which is in its properties intermediate between this and the true graphite.

Several applications have been made of graphite in the useful arts. Mixed with clay it is employed in the manufacture of the crucibles used in gold refining. It is also extensively used for the glazing of certain varieties of gunpowder, specially that employed for blasting. The graphite is finely ground, and the gunpowder rolled with it in iron cylinders. It is also used for the protection of iron from rust, and, mixed with grease, for the lubrication of machinery. Its most important application is for the manufacture of pencils. For this purpose it is consolidated by pressure into blocks, from which the pencil is afterwards cut, or it is mixed with an aggregating material, made into a paste, and moulded into the required form. The ingenious process of the late Mr. Brockedon for the compression of black lead for pencils is well known.

The first experiment in which I succeeded in eliciting a difference in the chemical reactions of the different forms of carbon was in the action upon them of a mixture of concentrated nitric and sulphuric acids. When finely-divided carbon, in the form of lamp-black, or charcoal from the decomposition of sugar, is heated with a mixture of 1 of nitric and 4 of sulphuric acids, the carbon is rapidly oxidized, and a black substance is formed soluble in the concentrated acid, but precipitated on the addition of water. This substance is insoluble in acids and saline solutions, but is soluble in pure water and in alkalies. It is accompanied with other products which render its purification difficult. When the graphite of Ceylon is treated in a similar manner, the result is very different; the graphite becomes of a beautiful purple colour, and falls to pieces in the fluid. The substance, after the acid has been washed from it by water, has much the appearance of the graphite itself, but is darker in colour. It was found on analysis to contain the elements of sulphuric acid combined with oxygen, with hydrogen, and with a large amount of carbon. My efforts to procure this substance of a constant composition have been unavailing; it is insoluble in all reagents; it may be boiled with a strong solution of potash without separation of sulphuric acid, and with slight, if any, alteration of weight. When heated, it

undergoes a remarkable change; gases are given off in the interior of the substance, which swells up in a singular manner, and is reduced to the minutest state of division. The residue consists of carbon which has the appearance and the structure of the lamellar graphite. This decomposition may be compared in its appearance with that which the chromate of ammonia undergoes by the action of heat.

The experiment may be applied to the disintegration and purification of graphite for purposes of the arts, with which view the process has been patented. Its details are as follows: One pound of powdered graphite is mixed with 4 pounds of concentrated sulphuric acid, with this is mixed 1 ounce of powdered chlorate of potash. The mixture is heated until chlorous fumes cease to be evolved; the residue is thrown into water, washed out, dried, and ignited. The ignited substance is washed in water, in which it floats, while the impurities fall to the bottom. It is then dried. By this process graphite may be obtained in a state of chemical purity.

These experiments established a point of considerable importance: the existence of a peculiar compound of carbon in the form of graphite. Its discovery led me to turn my attention to the oxidation of graphite. I found that graphite, heated with a mixture of nitric acid and chlorate of potash, increased in weight, and that the substance formed was, on the application of heat, disintegrated with evolution of gas. The disintegrated substance differed but little in appearance from the original graphite. I found, however, that when the substance formed by the treatment of graphite with the oxidizing mixture was washed free from the salts produced in the reaction, dried at 100° , and again oxidized, it gradually underwent a change in appearance, until after the fourth and fifth repetition of the process, the whole of the graphite was converted into a substance of a light yellow colour, consisting of minute, transparent, and brilliant plates. Analysis further showed that this change was attended with a gradual alteration of the constitution of the substance, but that finally a time arrived when further treatments with the oxidizing mixture produced no further change. It is remarkable that this change cannot be produced by one prolonged treatment; before the oxidation can proceed, the original conditions must be restored.

The details of this process are as follows:—A portion of graphite

is intimately mixed with three times its weight of chlorate of potash, and the mixture placed in a retort. A sufficient quantity of the strongest fuming nitric acid is added, to render the whole fluid. The retort is placed in a water-bath, and kept for three or four days at a temperature of 60° C. until yellow vapours cease to be evolved. The substance is then thrown into a large quantity of water, and washed by decantation nearly free from acid and salts. It is then dried in a water-bath, and the oxidizing operation repeated with the same proportion of nitric acid and of chlorate of potash until no further change is observed; this is usually after the fourth time of oxidation. The substance is ultimately dried, first in vacuo and then at 100°. A modification of the process which may be advantageously adopted, consists in placing the substance with the oxidizing mixture in flasks exposed to sunlight. Under these circumstances the change takes place more rapidly, and without the application of heat.

The analysis of this substance, when the necessary correction is made for the residual ash, gave the following numbers, the mean of nine concordant determinations.

Carbon . . .	61·04
Hydrogen . . .	1·85
Oxygen . . .	37·11
	100·00

These numbers correspond with the formula $C_{11}H_4O_5$ ($C = 12$) which requires

C_{11} . . .	132	61·11
H_4 . . .	4	1·85
O_5 . . .	80	37·04
	216	100·00

The crystals of this substance were ascertained by Professor Miller, of Cambridge, to belong either to the prismatic or the oblique system. It is insoluble in water containing acids or salts, but is very slightly soluble in pure water. It combines with alkalies and the crystals have an acid reaction. Agitated with dilute ammonia, it is converted into a transparent jelly, but the substance is not dissolved. On the addition of acids, it is separated unaltered from this combination, as a gelatinous mass

resembling silica. Treated with deoxidizing agents, it is readily decomposed. When a solution of sulphide of ammonium or of potassium is poured upon the dry substance, a crackling sound is heard, and a body is ultimately formed possessing the metallic lustre and general appearance of graphite itself. Changes similar in appearance take place on boiling the substance with an acid solution of protochloride of copper and of protochloride of tin.

The crystals on the application of heat are decomposed with ignition; gases are evolved, and a black residue is left of a body resembling in appearance finely-divided carbon. I propose for this substance the name, *Graphic acid*.

I have in vain attempted to procure the product of the decomposition by heat of the graphic acid, until it occurred to me to effect the decomposition in a fluid medium by which the particles of the substance were separated from one another and elevation of temperature precluded. The fluid which I selected for the experiment was the mixture of hydrocarbons of high boiling points from the Rangoon naphtha. When graphic acid is heated in this fluid to a temperature of about 270° , water is given off, and a brisk evolution ensues of carbonic acid, the hydrocarbon at the same time becoming of a deep red colour. The residual substance resembles graphite, and gave as the mean of several analyses, the following numbers

Carbon . . .	80.13
Hydrogen . . .	0.58
Oxygen . . .	19.29
	100.00

which correspond with the formula $C_{22}H_2O_4$.

C_{22} . . .	264	80.00
H_2 . . .	2	0.60
O_4 . . .	64	19.40
	330	100.00

When this substance is heated in a current of nitrogen to a temperature of 250° , a further change ensues; water is given off

accompanied by a small quantity of carbonic oxide. An analysis of the resulting substance gave the following numbers

Carbon . . .	81·80
Hydrogen . . .	0·44
Oxygen . . .	17·76
	100·00

which corresponds with the formula $C_{66}H_4O_{11}$ which requires

C_{66} . . .	792	81·48
H_4 . . .	4	0·41
O_{11} . . .	176	18·11
	972	100·00

This substance would be derived from the preceding by the elimination of 1 atom of water from 3 atoms of the original substance. On a greater elevation of temperature, carbonic acid, carbonic oxide, and water are again evolved, but the body may be exposed to a red heat for several hours in a current of nitrogen, and only undergo a very partial decomposition, the residual substance still containing a considerable portion both of hydrogen and oxygen.

Buff and Wöhler have recently discovered a remarkable series of compounds derived from the graphitoidal form of silicon,* among which is a compound of silicon, hydrogen, and oxygen, of the formula $Si_4H_4O_5$. The general properties of this substance correspond very closely with those of the graphite compound, as separated from its combinations by an acid. It is described as a white and voluminous body which floats upon water, in which it is very slightly soluble. We may therefore reasonably infer, that the graphite-compound is the same term in the system of carbon, as the silicon-compound in the system of silicon. When we proceed to state this analogy in the formula of the substance, we are led to very remarkable conclusions.

The total weight of graphite, which in the compound is combined with 4 atoms of hydrogen and 5 of oxygen, is 132. If we assume that this weight is, like the corresponding weight, 84 of silicon, to be divided into 4 parts, we arrive at the number 33, as the atomic

* Ann. Ch. Pharm. vol. civ. p. 94.

weight of graphite. Representing this weight by the letters Gr., the formulæ of the substances $C_{11}H_4O_5$, $C_{22}H_2O_4$ and $C_{66}H_4O_{11}$ become $Gr_4H_4O_5$, $Gr_8H_2O_4$ and $Gr_{24}H_4O_{11}$.

There is a property of graphite by which these formulæ may be tested.

According to the law of Dulong and Petit, the specific heats of the elemental bodies vary inversely with their atomic weights. The elements are divided into two classes, the one in which the product of the specific heat into the atomic weight is approximately 3.3, the other in which this product is approximately 6.6. This law expresses the only common physical property by which these weights are characterized. The specific heat of carbon however presents a remarkable exception to it. It differs in the different allotropic forms of carbon. The specific heat of native graphite as determined by Regnault is 0.20187. Now $6 \times 0.201 = 1.206$ and $12 \times 0.201 = 2.412$, which are not within the limits of error. But if we assume the atomic weight of graphite as 33, we have for the products of the specific heat into the atomic weight, the number 6.6 which is according to the law, this product being the same as the product of the specific heats into the atomic weights of the elements phosphorus, antimony, arsenic, bismuth, and iodine.

The relation also which exists between the atomic weights of boron, silicon, and zircon, and that form of carbon for which a place may be claimed as a distinct element, *graphon*, is precisely the kind of numerical relation which is found to exist between the weights of analogous elements. We have

Boron	.	.	.	11
Silicon	.	.	.	21
Graphon	.	.	.	33
Zircon	.	.	.	66

These considerations lead to the remarkable inference that carbon in the form of graphite functions as a distinct element, that it forms a distinct system of combinations into which it enters with a distinct atomic weight, the weight 33. Analogy would lead us to a similar conclusion with regard to the elements boron and silicon. How far this inference is to be extended to the allotropic forms of other elements, experiment alone can decide.