By B. C. Brodie, F.R.S., Professor of XIII. On the Atomic Weight of Graphite. Chemistry in the University of Oxford, and President of the Chemical Society.

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THE term Graphite has been indiscriminately applied to many varieties of native carbon Of very different properties. The graphite of New Brunswick differs but little in appearance from anthracite coal. The graphite of Greenland is not very dissimilar, but cossesses rather more metallic lustre. However, among these varieties of carbon, two anay be especially distinguished,—by a superior degree of metallic lustre, by their struc-Sure, and other well-defined properties. In the following paper, the term Graphite is Smited to these two varieties, which may be further distinguished as "lamellar" and mamorphous."
The lamellar graphite is found in great abundance in Ceylon, whence large quantities

are annually imported into this country. It appears in commerce in masses, someimes of the weight of many pounds, of a brilliant metallic lustre, and possessing a distinct fibrous structure. It is very difficult by mechanical processes to bring this grawhite to a fine state of division; however, by a prolonged grinding in water, it may be geduced to minute flat plates. This graphite is associated with quartz. The graphite The same variety of graphite has recently been discovered at Travancore. From Travancore has no fibrous structure, but is in the form of slightly coherent, minute plates. Specimens of a similar graphite have also been given to me, from Moreton Bay En Australia, in a matrix of quartz, and from Ticonderoga, in the State of New York, associated with olivine and sphene. When cast iron is dissolved in acid, a residue is eft of about 4 per cent. of carbon in the form of graphite. This graphite also consists of minute brilliant plates, and is perfectly similar in its appearance and properties to the lamellar variety of native carbon. Amorphous graphite is found in Borrowdale in Cumberland, and is also largely imported into this country from Germany, probably from Griesbach near Passau, but I am unable to speak with certainty as to the locality It appears as a powder of a silvery grey colour, soft to the touch, and whence it comes. which rubbed on paper gives a brilliant metallic streak. This graphite is much softer than the other variety, and therefore better adapted for the manufacture of pencils.

The graphite used in my experiments was in all cases carefully purified by boiling with acids, and by fusion with hydrate of potash in a silver crucible; unless otherwise mentioned, it is to be understood to be the variety from Ceylon. The graphite thus prepared leaves an almost inappreciable residue, and gave to analysis 99.96 of carbon. specific gravity was ascertained in two determinations as 2.25 and 2.26.

The following investigation was undertaken with the view of ascertaining the weight

with which carbon in the form of graphite enters into combination. With this end I examined its reactions.

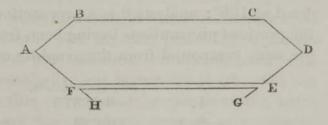
The first experiment in which I succeeded in eliciting a difference in the chemical reactions of the different forms of carbon, was, in the case of the action upon them, of a mixture of concentrated nitric and sulphuric acids. When finely-divided carbon, in the form of lampblack, or charcoal from the 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 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 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 most 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. A similar oxidation takes place when the nitric acid in the above experiment is replaced by other oxidizing agents, such as bichromate of potash and chlorate of potash. These experiments established one point of importance, the existence of a peculiar compound of carbon in the form of graphite. The discovery of this substance led me to turn my attention to the oxidation of graphite. I found that graphite, when 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. The analysis of the body resulting from different preparations, and with a difference in the time of oxidation, gave no constant result. These difficulties led me to further experiments. I found that when the substance formed by the treatment of the graphite with the oxidizing mixture was washed free from the salts produced in the reaction, and dried at 100° and again oxidized, it gradually underwent a change in appearance, until, after the fourth or 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 showed that this change was attended with a gradual alteration of the constitution of the substance, but that, finally, a time arrived when treatments with the oxidizing mixture produced no further change. It is remarkable that this result 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 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, Shirst in vacuo, and then at 100° C. A modification of the process which may be advanztageously 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.

These crystals, when examined with the microscope, are perfectly transparent, and Sexhibit beautiful colours by the agency of polarized light. Professor MILLER of Cambridge, who was good enough to examine them, has communicated to me the following bservations:—"The crystals, though not absolutely too small to be measured, are too thin and too imperfect to admit of measurement with the reflective goniometer. I have Examined them under a microscope, for the purpose, if possible, of making out at least the system of crystallization to which they belong. Their system appears to be either the prismatic or the oblique,—most likely the former*. Sometimes the crystals appear

broken, as in the annexed figure. The straighteness of the fractured edges (in the direction EF) evidently indicated the existence of a cleavage in that direction. The crystals are so extremely thin in a direction perpendicular to Extremely thin in a direction perpendicular to the paper on which the above figure is traced,



that it is impossible to obtain any reflexion,

except from the faces parallel to the plane of the paper."

The crystals, on the application of heat, are decomposed with ignition. Gases are evolved, and a black residue is left of a substance resembling in appearance finely divided carbon. divided carbon.

I have not discovered any reagent by which these crystals may be dissolved, and they admit of no process of purification. The explosion which the crystals undergo on the application of heat render special methods of analysis necessary, and I have taken, with regard to the analysis, every precaution which suggested itself. Neither chlorine nor nitrogen could be detected.

The substance was placed in a platinum boat in a porcelain tube and burnt in a

^{*} Measurements of the crystals, by means of the microscopic goniometer, which have subsequently been made by Mr. A. H. Church, of Lincoln College, have determined with certainty that the crystals belong to the one or other of these systems.

current of oxygen, the gases evolved being passed over heated oxide of copper. At the extremity of the tube, where the oxygen entered, was placed a stopper of asbestos, and a second stopper between the substance and the oxide of copper. The ordinary potashbulbs were replaced by two tubes filled with pumice moistened with concentrated solution of potash.

In order to ascertain in the most rigorous manner the point at which the constitution of the compound became fixed, it was analysed after each successive oxidation. It will be seen that the analyses became constant upon the fourth treatment; after which, the

most prolonged action of the oxidizing mixture produced no further change.

The following are the results per cent. of the analyses of the same preparation of graphite, treated in the first instance once, in the second, twice, with the oxidizing mixture:—

Carbon		1. 69·67	67.79
Hydrogen		1.48	1.84
Oxygen		28.85	30.37
		100.00	100.00

The following are the results of analysis after the constitution of the body may be regarded as fixed. Analyses 1 and 2 are of a substance prepared by four treatments; analyses 3 and 4, of a substance prepared by five treatments; analysis 5, of a substance prepared by six treatments; analyses 6 and 7, of a substance prepared by seven treatments; analysis 8 is of a substance dried in vacuo, the previous preparations having beer dried at 100°; analysis 9 is a preparation from the amorphous graphite of Cumberland, the previous preparations having been from the graphite of Ceylon. I have also prepared the same compound from the graphite of cast iron.

1.	Substance taken. 0.23375	Carbonic acid formed. 0.52025	Water formed. 0.02925
2.	0.233	0.51875	0.03775
3.	0.24475	0.545	0.04175
4.	0.27275	0.609	0.0465
5.	0.209	0.46	0.036
6.	0.25275	0.5635	0.042
7.	0.23825	0.5325	0.04025
8.	0.2555	0.56875	0.0435
9.	0.216	0.48	0.0355

These analyses correspond to the following per-centage composition:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon	60.70	60.74	60.73	60.88	60.47	60.80	60.94	60.71	60.69
Hydrogen	1.37	1.80	1.89	1.88	1.91	1.80	1.87	1.89	1.75
Oxygen	37.93	37.46	37.38	37.24	37.62	37.49	37.19	37.40	37.56
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The mean of these analyses (omitting the hydrogen of the first analysis, which is evidently faulty) is-

Carbon . . 60.74 Hydrogen . 1.85 Oxygen. 37.41 100.00

A correction has yet to be made in these numbers. The graphite from which the substance is prepared leaves on combustion a slight ash, and during the prolonged treatment of the substance a further portion of incombustible matter is introduced, pro-

addition of acids it is separated unaltered from this combination in the form of a gelatinous mass resembling silica, which, dried under the air-pump, appears as a slightly yellow and spongy body of the same weight as the substance originally treated with ammonia. The crystals treated with deoxidizing agents are 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 substances formed in these processes admit of no process of purification, and I have not been able to procure them in a state of purity.

This body belongs very distinctly to the class of acids, but from the insolubility of its salts and the facility with which they are decomposed, I have not been able to procure them pure. The following determinations, however, indicate it to be bibasic. A portion of the moist substance shaken up with baryta-water, washed out, and dried at 100°, gave a compound containing 21.19 per cent. of barium. The same substance suspended in water, and decomposed by a current of carbonic acid, gave a substance

2 M

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which, dried at 100°, contained 13·30 per cent. of barium. The formula C₁₁ H₃ BaO₅ requires 24·13 per cent. of barium. The formula C₂₂ H₇ BaO₁₀ requires 13·73 per cent. of barium. These substances are excessively hygroscopic, and when heated, explode with yet greater violence than the original body. The compound itself may be termed graphic acid.

The residue which is left upon the decomposition by heat of graphic acid, although resembling carbon in appearance, is not that element, but contains a considerable amount of oxygen. I made many experiments with a view of procuring this substance in a pure state,—both by decomposing the compound, alone, in an atmosphere of nitrogen. and by decomposing it mixed with a large quantity of chloride of sodium, with the view of moderating the violence of the decomposition, and causing it to take place at the lowest My endeavours were unsuccessful, until it occurred to me to effect possible temperature. the decomposition in a fluid medium, by which the particles of the substance would be 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. It was purified by rectification over sodium, and boiled at about 270°C. When graphic acid is heated in this fluid, a considerable quantity of water is formed, which distils over between 100° and 200°, and which is accompanied at first by a slight, and ultimately by a brisk evolution of gas. This gas was in one experiment collected and examined: it consisted solely of carbonic acid. But water and carbonic acid are not the exclusive products of this reaction. The hydrocarbon becomes of a deep red colour, and when filtered and distilled, leaves a black carbonaceous residue. I have found no means of separating the body formed from the naphtha in which it is dissolved.

In the following experiments the substance was heated in the naphtha for three or four hours, at about 250° C., until all perceptible evolution of gas had ceased. The graphic acid employed was weighed, and also the residue of its decomposition. The residue was collected on a weighed filter, washed out with ether and with alcohol, and dried at 100°.

Expt. I. 1.024 grm. of graphic acid gave 0.684 grm. of residue.

Expt. II. 1.0854 grm. of graphic acid gave 0.7248 grm. of residue.

Expt. III. 2·1805 grms. of graphic acid gave 1·4607 grm. of residue.

This corresponds to a loss on 100 parts of the substance taken—in Experiment I. of 66.78, in Experiment II. of 66.77, in Experiment III. of 66.98 parts.

These substances, burned in a current of oxygen, gave the following results. In these and all following analyses the residual ash was weighed, and its amount deducted from the substance taken.

1.	Expt. I.		ostance taken. 0.311	Carbonic acid formed. 0.9147	Water formed. 0.0148
2.	Expt. II.		0.4237	1.2372	0.022
3.	Expt. III.		0.3573	1.0404	0.0178
4.	The same		0.3391	0.9857	0.0185

These results correspond to the following per-centage composition:-

			1.	2.	3.	4.
Carbon .			80.19	79.64	79.40	79.27
Hydrogen			 0.52	0.57	0.55	0.60
-		*	19.29	19.79	20.05	20.13
			100.00	100.00	100.00	100.00

When this substance was carefully examined under the microscope, traces of trans-parent crystals could still be perceived, similar in appearance to the original substance.

		Substance taken.	Carbonic acid formed.	Water formed.
1. Expt. IV		. 0.377	1.1126	0.0210
2. The same .	7.0	. 0.4766	1.4068	0.0255
3. Expt. V		. 0.3835	1.1327	0.022

			1.	2.	3.
Carbon .	*		80.48	80.50	80.56
Hydrogen			0.62	0.59	0.63
Oxygen.			18.90	18.91	18.81
			100.00	100.00	100.00

substance for the ten additional hours had been to increase the per-centage of carbon in the residue from about 0.5 to 1 per cent. It is evident that the decomposition is arrested at about this point; and if we take the mean, as may reasonably be done, of three analyses of the first and the three of the second series of experiments, as representing the constitution of the body, we have the following as its per-centage composition:-

Carbon .			80.13
Hydrogen			0.58
Oxygen .			19.29
			100:00

This corresponds to the formula C22 H2 O4, which has the following composition:

C_{22}		264	80.00
H,		2	0.60
O ₄		64	19.40
		330	100.00

There is every reason to believe that, although the decomposition is difficult to regulate, this same body is formed by the simple application of heat to the substance without the intervention of the naphtha. The result of one experiment, in which the graphic acid had been carefully heated in an air-bath to 280° until it ceased to lose weight, gave to analysis—carbon 80·36, hydrogen 0·71. In other experiments numbers approximating to these were obtained.

We have not the data to determine with certainty the precise mode of the formation of this body. The simplest hypothesis which coincides with the ascertained facts, is that 7 equivalents of the graphic acid give by their decomposition 6 of the new body. We have $7(C_{11} H_4 O_5)=1512$ and $3(C_{22} H_2 O_4)=990$ and $1512:990::100:65\cdot48$, $65\cdot48$ being the amount of residue found.

On this view it would be possible to form the new substance by the elimination of water, carbonic acid, and carbonic oxide from the original body, according to the equation

$$7(C_{11} H_4 O_5) = 3(C_{22} H_2 O_4) + 6H_2O + 6CO_2 + 5CO.$$

The slight excess of carbon in the last series of analyses indicates the presence of some compound containing a higher per-centage of carbon. It will be rendered evident, by the following experiments, that we have only to heat this substance under slightly different circumstances to determine a further decomposition. Portions of the substances last analysed were placed in a platinum boat in a glass tube, through which was passed a current of nitrogen, and which was heated in an air-bath to a temperature of 250°. The substance was weighed before and after the experiment.

Expt. 1. '9087 grm. of the substance resulting from Expt. IV. gave a residue of 0.883 grm.

Expt. 2. 0.9209 grm. of the substance resulting from Expt. V. gave a residue of 0.8968 grm.

This corresponds to a residue on 100 parts of the substance taken—in Expt. 1 of 97·16, in Expt. 2. of 97·38 parts.

Water is given off from the substance during the process, which was collected in a sulphuric acid tube and estimated. It corresponded, in the two experiments, to 2.26 and 2.30 per cent. The quantity formed was, however, too small for correct estimation, and these numbers are undoubtedly too high. Traces of probably carbonic oxide, amounting to something under 1 per cent., are also given off. The action is perfectly definite. The experiment was continued until the substance ceased to lose weight; in the last two hours the loss in weight was not above 1 milligramme.

The following are the results of the analysis of the bodies:-

		Sul	stance taken.	Carbonic acid formed.	Water formed.
1. Expt. I			0.367	1.1051	0:0163
2. The same			0.3783	1.1366	0.0139
3. Expt. II.			0.3979	1.1938	0.0158
4. The same			0.3927	1.1724	0.0155

These numbers give the following per-centage composition:-

Carbon .		1. 82·12	2. 81·95	3. 81·80	4. 81·41
Hydrogen		0.49	0.41	0.44	0.43
Oxygen .		17.39	17.64	17.76	18.16
		100.00	100.00	100.00	100.00

C66 .	792	81.48
H4 .	4	0.41
On .	176	18.11
	972	100.00

covered a remarkable series of compounds derived from it. When hydrochloric acid gas is led over this form of silicon at a low red heat, a volatile liquid is formed containing silicon, chlorine, and hydrogen, to which they assign the formula Si₂ H₂ Cl₃. hydriodic acid gas a similar reaction takes place, with the formation of the corresponding compound Si₂ H₂ I₃. In water, these substances decompose with the production of a compound of silicon, hydrogen, and oxygen, of the formula Si₄ H₄ O₅. analyses are unfortunately neither so concordant nor so exact as might be desired; but the formulæ are derived from the consideration of a system of decompositions, which

hardly leaves room for any other hypothesis. The general properties of the substance Si₄ H₄ O₅, 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. Heated to a temperature of above 300°, it is decomposed with ignition and evolution of hydrogen. The ratio of the number of equivalents of hydrogen to those of oxygen is as 4 to 5. It is formed exclusively from graphitoidal silicon, as the graphite compound from graphitoidal carbon. From these considerations we may 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 this compound is combined with the 4 atoms of hydrogen and the 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 weight of graphite. Representing this weight by the letters Gr, the formulæ of the substances $C_{11}H_4O_5$ and $C_{22}H_2O_4$, and $C_{66}H_4O_{11}$, become

 $Gr_4 H_4 O_5$ $Gr_8 H_2 O_4$ $Gr_{24} H_4 O_{11}$.

We are acquainted with a property of graphite by which this theory may be tested.

According to the law of Dulong and Petit, which has been confirmed by the exact researches of Regnault, the specific heats of the elemental bodies vary inversely with their atomic weights. With the atomic weights of the elemental bodies, as generally received, 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. To this law, however, there is one remarkable exception, namely, the specific heat of carbon in its various forms. The following are the specific heats of carbon as determined by Regnault:—

Diamond	Specific heats. 0.14687
Native graphite	
Graphite from the blast furnace	
Carbon from gas retorts	
Carbon from anthracite	. 0.201
Wood charcoal	. 0.2415
Animal charcoal	. 0.26085

In no single case, whether the atomic weight of carbon be assumed as 6 or as 12, does carbon conform to the law. The product of the specific heat of graphite into the atomic weight is with the weight 6, 1.2, with the weight 12, 2.4. If, however, we

assume the atomic weight of graphite as 33, we have for the product 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.

This form of carbon should be characterized by a name marking it as a distinct element. I propose to term it Graphon.

In the formulæ assigned by Buff and Wöhler to the compounds of silicon, the atomic weight has been assumed as 21. If the atomic weight of silicon be assumed as 28, these relations no longer appear; the atomic weight of graphite must be assumed as 44, and the product of the specific heat into the atomic weight would be 8.8. 44, and the product of the specific heat into the atomic weight would be 8.8. We are thus enabled to decide upon the atomic weight of the graphitoidal silicon. It is greatly to be regretted that those chemists who have had a sufficient quantity of this substance in their possession have omitted to determine its specific heat. There is much reason to believe that in its other forms silicon, like carbon has a distinct atomic weight. The The to believe that in its other forms silicon, like carbon, has a distinct atomic weight. The The weight 21 of silicon must be considered as still open to correction. The results arrived at by Deville*, from the oxidation of graphitoidal silicon, indicate a higher number.

Finally, these considerations lead us 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. 5 vapour-density of the chloride of silicon leads us to the weight 28; and it is worthy of

Boron .		(4)	11
Silicon .			21
Graphon			33
Zircon .		100	66

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.

^{*} DEVILLE obtained from 100 parts, 205.3 of silica. Calculated from these numbers, the atomic weight of silicon would be 22.7, approximating to the former atomic weight of Berzelius, 22.5. The subject requires further investigation.