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THE PROPERTIES OF THE INTERSTITIAL COMPOUNDS OF GRAPHITE

II. THE STRUCTURE AND STABILITY OF GRAPHITE RESIDUE COMPOUNDS

by
Gerhart Hennig

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Chemistry

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ABSTRACT

1. Controlled decomposition of lamellar compounds of graphite produces substances intermediate in composition between graphite and lamellar compounds. These intermediate compounds have been termed residue compounds. They are much more resistant to decomposition than the lamellar compounds.

2. The x-ray pattern of residue compounds shows a very slight increase in the c spacing of the graphite lattice. The increase is entirely insufficient to account for the trapped reactant. Consequently, the bulk of the trapped reactant is believed to be situated at crystal imperfections.

3. Quantitative studies of the composition of graphite bromide residue compounds have shown that their composition is strongly dependent on the type and subdivision of the graphite used and the temperature to which the compounds have been heated.

INTRODUCTION

Graphite reacts with a large number of substances, such as bromine, ferric chloride, and potassium, to form compounds in which single layer planes of the reactant are wedged between the carbon layer planes of the graphite. These so-called lamellar compounds have been studied quite extensively.(1) Most of the reactant in the lamellar compounds can be removed by essentially reversing the procedure by which the lamellar compounds were formed. However, in all cases examined, it has been found that a considerable amount of reactant remains which cannot be removed without resorting to fairly drastic measures. The amount of reactant remaining is dependent on the amount of reactant present in the original lamellar compound. Compounds of this type, in which small

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(1) See for example the review article by H. L. Riley, Fuel in Science and Practice 24, 1, 43 (1945).

amounts of reactant are held very strongly in the graphite, have been termed residue compounds. These residue compounds were described in the preceding paper of this series,(2) and in a preliminary report(3) from this laboratory on the diamagnetism of graphite bromide. Furthermore, it is likely that Ganguli(4) who reported the magnetic susceptibility of lamellar graphite bisulfate, was actually measuring residue compounds instead. He washed his bisulfate compounds for two days in water; this treatment is known(1) to destroy the lamellar compound.

The purpose of the present paper is to describe experiments relating to the structure and stability of the residue compounds. It was pointed out in the preceding paper(2) that at least two different mechanisms can be postulated which will account for the ability of graphite to form residue compounds. The reactant may be trapped between the carbon planes as in the lamellar compounds, but in much lower concentrations. Alternately, the reactant may be trapped at imperfections of the crystal lattice. X-ray investigation of the residue compounds has been the most decisive method of distinguishing between these two mechanisms of trapping, as shall be shown. Molecules or ions trapped between the layer planes would cause a definite increase in the c axis of the graphite. Molecules trapped at imperfections would be unlikely to cause a change in the c axis of the graphite if the imperfections are randomly distributed. In fact, they would probably cause either no change in the diffraction pattern, or else only a line broadening if random imperfections are enlarged or new imperfections are formed.

The trapping centers have been characterized further by examining the residue compounds formed from various types of graphite which differ in the degree of perfection of the graphite crystallites.

The experiments to be described have been confined to the bromide and bisulfate residue compounds of graphite. The bromide is the easiest compound to prepare and is therefore best suited to quantitative studies. The bisulfate is of special interest for x-ray studies, since the bisulfate ion is particularly large.

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(2)G. R. Hennig, ANL-4579 (February 15, 1951).

(3)M. Goldsmith, J. Chem. Phys. 18, 524 (1950).

(4)N. Ganguli, Phil. Mag. (7), 21, 355 (1936).

EXPERIMENTAL

Materials. Six different types of graphite have been used. They will be identified by Roman numerals.

I. Pitch-bonded artificial graphite (Acheson). This material is very similar in properties to the National Carbon Company's Spectroscopic Electrodes. Similar material was used almost exclusively in the work reported in the previous paper of this series.

II. Kish. These large flakes of graphite which form on molten steel were washed repeatedly with hydrofluoric and hydrochloric acids.

III. Flakes of Madagascar natural graphite. The diameter of these particles was approximately ten times their thickness. The crystals were cleaned thoroughly before use.

IV. Microfyne graphite (Dixon Crucible Company, New Jersey). This is a finely powdered natural graphite which has a particle size of a few microns. The material was purified before use.

V. Crystals of Ogdensburg natural graphite. These crystals were kindly furnished by W. Primak of this laboratory. The crystals had been leached from limestone rock, purified first by an acid treatment and then by heating in helium to 3000°C. For this work, a particle size of 160 microns was isolated by screening.

VI. SP-1 spectroscopic graphite powder (National Carbon Company, Cleveland).

Preparation of the Graphite Bisulfate Residue Compounds. Samples of graphite were oxidized for one day in a 12 M sulfuric acid solution 0.1 molar in nitric acid. The resulting lamellar-type compounds were converted slowly to residue compounds by washing with 8 M sulfuric acid for one hour and then with distilled water for from two to four hours. The samples were dried at 100°C and their composition was determined by weighing before and after treatment.

Preparation of the Graphite Bromide Residue Compounds. Graphite bromide lamellar compounds were first prepared in either of two ways. Graphite was reacted with bromine either in a vacuum line which included a thermostated trap containing bromine at a known temperature and therefore vapor pressure, or in tightly stoppered bottles above solutions of bromine in carbon tetrachloride. At any pressure the bromination was initially rapid, but the reaction was allowed to proceed for at least a day to approach equilibrium. The brominated samples were weighed in tightly stoppered bottles, and their composition was calculated from the weight of the bromine taken up.

Graphite bromide residue compounds were prepared by debrominating these lamellar compounds in an air stream for 24 hours at room temperature. Their composition was again determined by weighing. It was noticed that pitch-bonded artificial graphite and finely powdered graphite specimens usually attained a constant weight within one day of debromination. Heavily brominated, coarse graphite powders sometimes lost small amounts of bromine for several additional days.

Preparation of Samples for X-Ray Measurement. The solid graphite samples were ground in a mortar and the powder thus obtained was bonded with a small quantity of Duco cement for the diffraction measurements. The natural graphite samples were already in powder form and were not crushed further after the chemical treatment.

X-Ray Diffraction Measurements. The *a* and *c* spacings for thirteen different residue compounds, together with appropriate blanks, are given in Table I. It was found that the spacings of the residue compounds differed very little from those of graphite itself.

In addition to the measurements of Table I, it was noticed that the crystallite size of the residue compounds decreased with increasing concentration of impurity. Nevertheless the materials were still crystalline, of crystallite size 300A or larger.

Composition of the Residue Compounds. Four different factors were found to influence strongly the composition of residue compounds. These factors were the chemical composition of the parent lamellar compound, the type of graphite used, the subdivision of the graphite, and the temperature to which the residue compound had been heated.

The dependence of the composition of the residue compound on the composition of the parent lamellar compound was studied in some detail for pitch-bonded artificial graphite (Type I). The atom ratio of bromine in the lamellar compound has been plotted in Figure 1 against the atom ratio of bromine retained in the residue compound. It is apparent that the retention is an approximately linear function of the bromination for compounds whose atom ratio of retained bromine does not exceed ca. 0.006. Also included in Figure 1 are some data on rapid bromination in saturated bromine vapor followed after a few minutes by debromination. This method obviously reduced the retention in the residue compounds.

TABLE I

The X-Ray Spacings of Graphite Residue Compounds

Sample No.	Graphite Type	Reactant	Concentration of Reactant (moles/g atom C x 10^2)	X-Ray Spacing (KX units)	
				a-axis	c-axis
1	III	Blank		2.4562 ± 0.0002	6.695 ± 0.005
2	III	H_2SO_4-HSO_4^-	0.27	2.456 ± 0.001	6.694 ± 0.001
3			0.56	2.457 ± 0.001	6.700 ± 0.004
4			0.78	2.458 ± 0.001	6.689 ± 0.006
5			1.39	2.456 ± 0.002	6.702 ± 0.005
6			2.49	2.456 ± 0.002	6.703 ± 0.004
7			3.56	2.456 ± 0.002	6.699 ± 0.004
8*			1.06	2.457 ± 0.002	6.701 ± 0.006
9*			0	2.458 ± 0.003	6.698 ± 0.005
10**	III	Br_2	0.345	2.457 ± 0.001	6.697 ± 0.003
11	V	Blank		2.4560 ± 0.0002	6.693 ± 0.002
12	V	Br_2	0.335	2.456 ± 0.001	6.692 ± 0.007
13			1.33	2.456 ± 0.001	6.748 ± 0.008
14	I	Blank		2.457 ± 0.001	6.696 ± 0.007
15	I	H_2SO_4-HSO_4^-	0.59	2.457 ± 0.001	6.68 ± 0.01
16			0.70	2.457 ± 0.003	6.70 ± 0.01

*Prepared from residue compounds by heating. The mole ratio was 0.025 before heating to 230°C (Sample 8) and 0.029 before heating to 450°C (Sample 9).

**Prepared from a residue compound by heating to 100°C.

The effect of graphite type on the composition of the residue compounds was investigated by preparing the most concentrated lamellar compounds obtainable in saturated bromine vapor, and subsequently determining the amount of bromine remaining in the residue compound after debrominating these lamellar compounds in the usual manner. The concentration of bromine in the resultant residue compounds obtained from four types of graphite increased in the order IV < I < III < II. This relationship is indicated

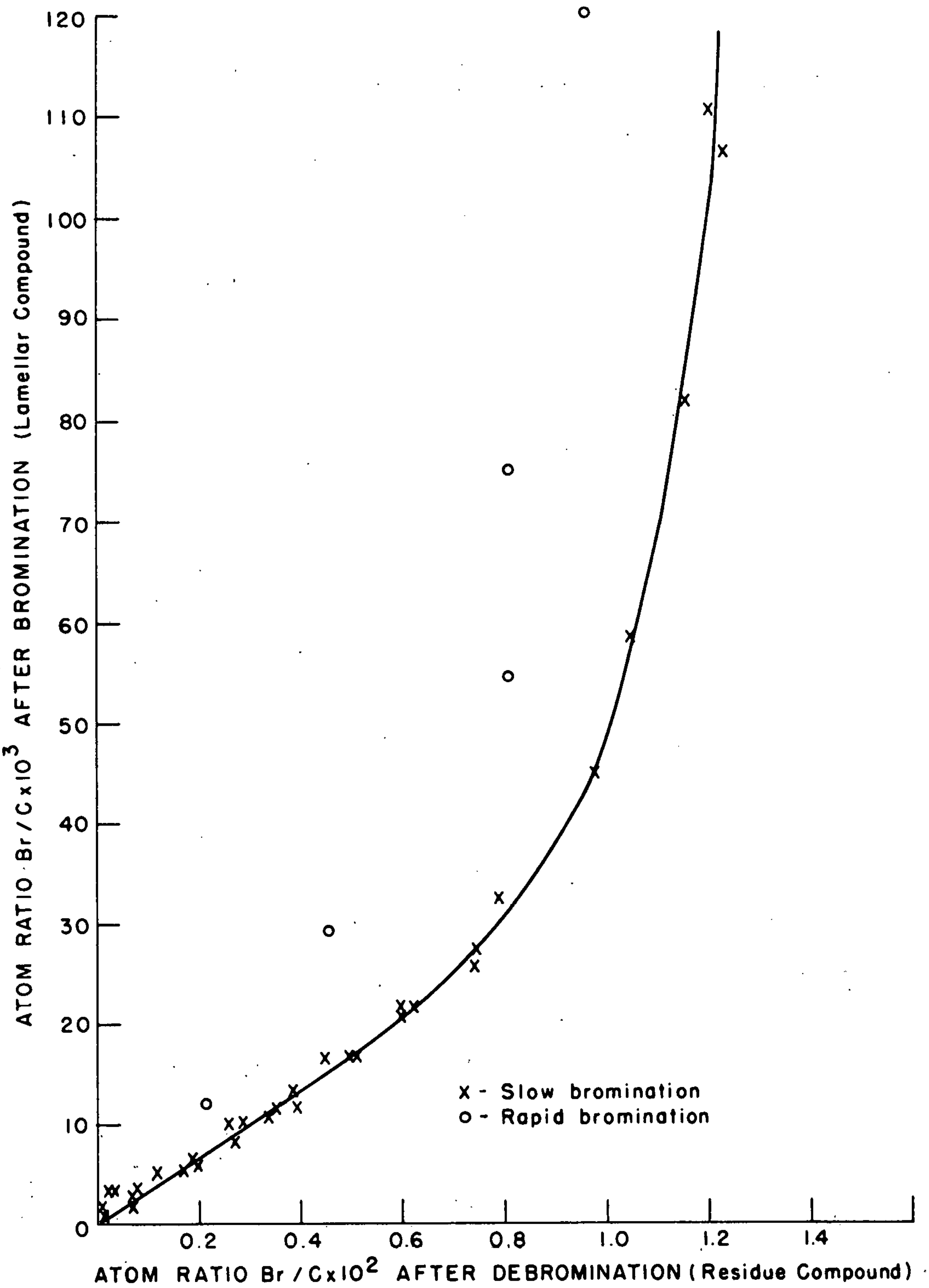

Figure 1

Composition of the Graphite Bromide Residue Compound as a Function of the Composition of the Parent Lamellar Compound (Pitch-bonded Graphite) on the left side of Figure 2. At least part of the difference between various graphite types can be traced to the effect of particle size since the particle size of the materials used also increased in the above order. This effect of subdivision of the graphite on the composition of the residue compounds was studied on powders of natural (Type III) and artificial (Type VI) graphite. The results have been plotted in Figure 3 as compositions of the parent lamellar compound against compositions of the residue compounds. It is apparent from Figure 3 that finely divided graphite retained considerably less bromine than larger particles. On the other hand, there did not appear to be much difference between artificial and natural graphite powders of comparable particle size.

The composition of these residue compounds after heating to various temperatures is also shown in Figure 2. It is evident that only Type I graphite forms residue compounds which remain reasonably stable at elevated temperatures. The composition of the residue compounds after heating at elevated temperatures was not particularly dependent on the subdivision of the samples. The retention of bromine at 310°C for numerous powders of natural and artificial graphite can be approximated by one curve (Curve A, Figure 3) regardless of the particle size of the powder.

Chemical Reactions of Residue Compounds. Incidental to the measurements on the stability of residue compounds, some anomalous reactivities were observed. The graphite bromide residue compounds were found to show a higher chemical reactivity than graphite. Chlorine reacted quite rapidly with the residue compound although graphite itself reacts very slowly with chlorine. A few samples of standard artificial graphite were suspended in the saturated vapor above boiling liquid chlorine for 30 minutes, quickly transferred to potassium iodide solutions, and allowed to stand for at least 30 minutes. The amount of chlorine taken up was determined by titration with standard thiosulfate. It was found that the graphite had acquired only about 0.3 atom per cent of chlorine. On the other hand, residue compounds containing about one atom per cent of bromine gained between 3 and 4 atom per cent of chlorine, or roughly ten times the amount acquired by pure graphite under similar conditions.

Aluminum trichloride does not normally react with graphite at room temperature. At 200°C in vacuo it did not cause any swelling of a graphite sample and the sample retained only 0.07 molecules of trichloride per 100 carbon atoms, probably due to surface contamination. A graphite bromide residue compound containing 1.44 bromine atoms per 100 carbon atoms reacted rapidly with aluminum trichloride, swelling first, and then falling apart. Its weight increase corresponded to 1.97 molecules of trichloride per 100 carbon atoms.

Iodine and pure graphite did not react, but small amounts of residual bromine in the graphite induced an uptake of iodine which was measurable

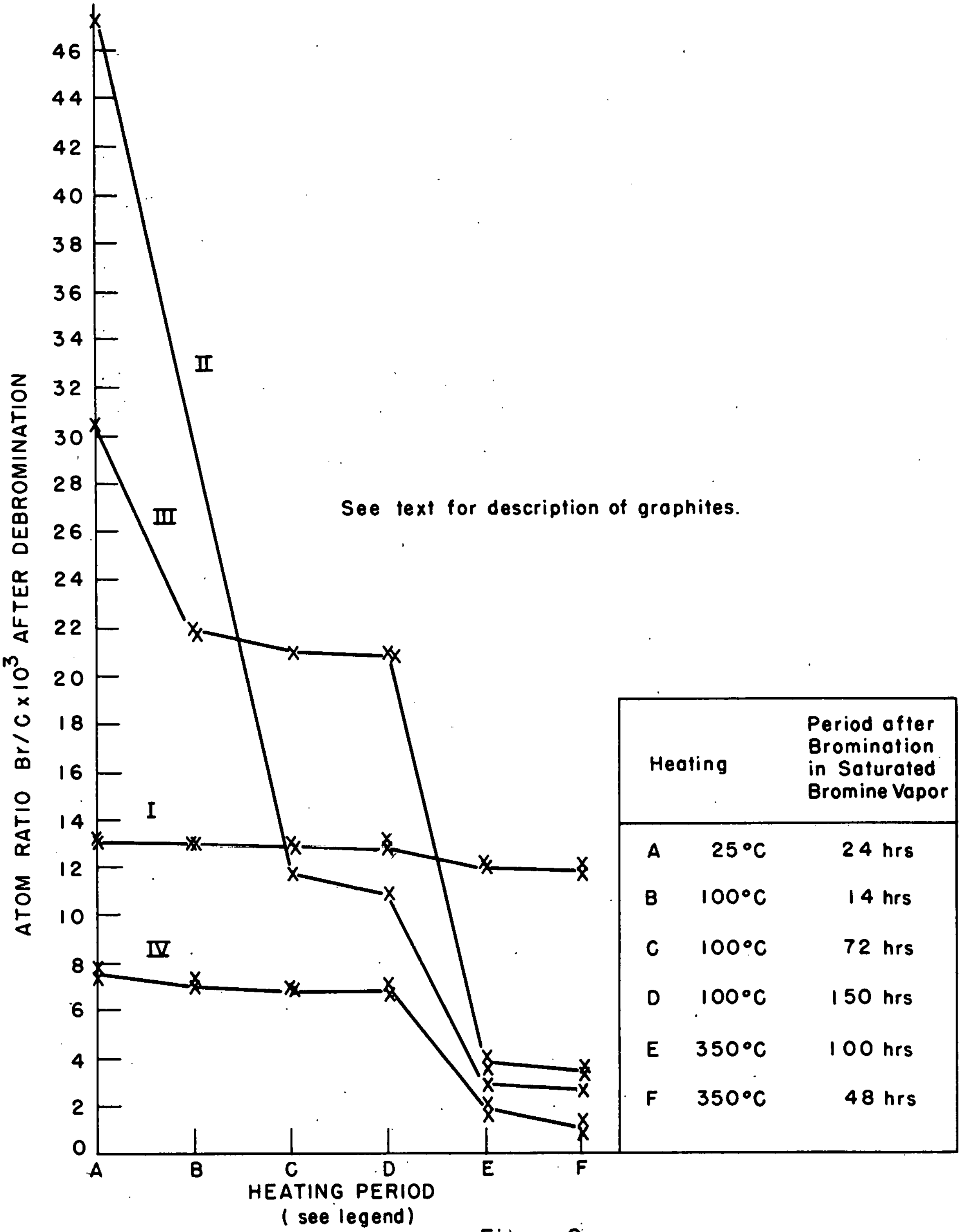

Figure 2

The Effect of Temperature on the Stability of Graphite Bromide Residue Compounds for Several Types of Graphite

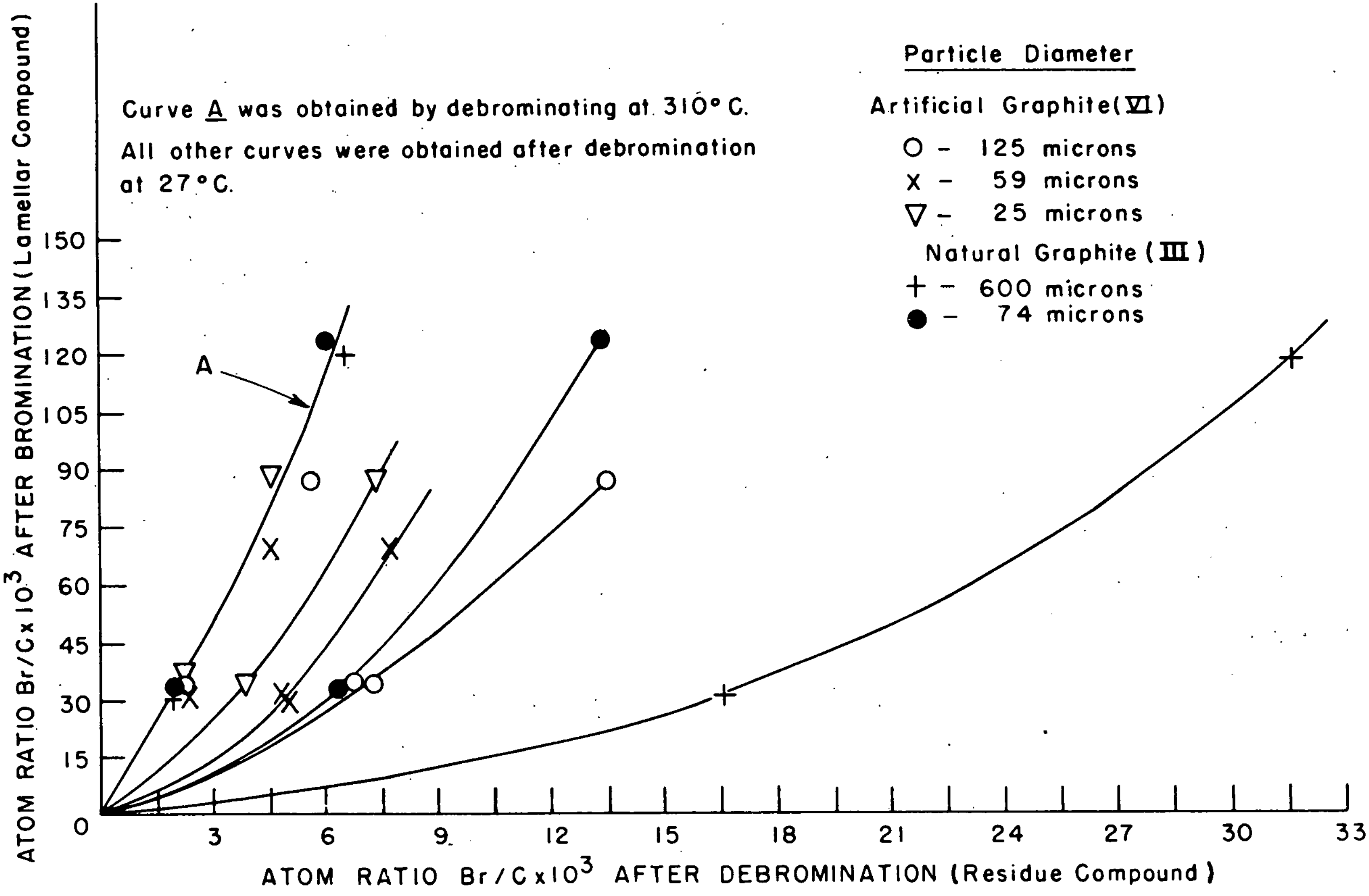

Figure 3

Effect of Particle Size on the Relation between the Composition of the Parent Graphite Bromide Lamellar Compound and the Corresponding Residue Compound after an hour in saturated iodine vapor at 183°C. The reaction was very pronounced in samples reacted with iodine vapor at room temperature for 6 months. In these samples the presence of one atom per cent of residual bromine induced enough iodine uptake to decrease the electrical resistance by more than 50 per cent.

DISCUSSION

The conversion of graphite to residue compounds changed the <u>a</u> and <u>c</u> axes very little (Table I). Actually the change in the <u>a</u> axis never exceeded the limits of error of the measurements. The <u>c</u> axis, however, seemed to increase rather consistently. From this increase the quantity of interlamellar impurity was calculated by suitable assumptions regarding the size of bisulfate ions or bromine molecules between the planes. A volume of 95A^3 was used for a bisulfate ion or a sulfuric acid molecule. The bromine atom was assumed to have an average volume of 40A^3. These volumes are the average volumes occupied by the respective molecular species in their compounds with heavy cations. They are also in fair agreement with the molecular volumes calculated from the density of the corresponding liquid, and furthermore agree with the volumes deduced from the x-ray spacings(5,6) of the graphite bromide and bisulfate lamellar compounds. The concentration of interlamellar impurities in the residue compounds, calculated from the data of Table I, have been tabulated in column 5 of Table II. Column 3 shows the total concentration of impurities determined gravimetrically. The fraction of the impurities thus found to be interlamellar, i.e., accessible to x-ray measurement, has been tabulated in column 6, together with the probable error inherent in the x-ray measurements. It is apparent that only 1% or less of the impurities are trapped between the planes with the one exception of compound 13, a heavily brominated compound in which about 6% of the bromine is still interlamellar. Apparently the bulk of the impurities are always trapped at imperfections where x-rays do not detect them.

The imperfections which trap the impurities are very probably the crystallite boundaries, because no other type of imperfection is known to be present in sufficient concentration to account for the extent of trapping. The definition of crystallite boundary should probably also include the edges of the mosaic blocks of perfect regions within the crystallites.

A number of observations have been made with allow some conclusions about the mechanism of trapping. It was found (Figure 2) that small particles retained less bromine per mole of carbon than large particles. This makes it probable that the imperfections are quite large, at least

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(5) W. Rüdorff, Z. anorg. u. allgem. Chem. <u>245</u>, 383 (1941).

(6) W. Rüdorff, Z. physik Chem. <u>B45</u>, 42 (1940).

TABLE II

The Fraction of Reactant Present in Interlamellar Positions in Graphite Residue Compounds

Sample No.	Reactant	Total Concentration (moles/g atom C x 10^5)	Fractional Change in c Spacing ($\Delta c/c$ x 10^4)	Concentration of Interlamellar Reactant from X-Ray (moles/g atom C x 10^5)	Interlamellar Fraction of Reactant (x 10^3)
2	H_2SO_4-HSO_4^-	270	+ 1.5	1.4	5 ± 30
3	H_2SO_4-HSO_4^-	560	+ 7.5	6.9	12 ± 22
4	H_2SO_4-HSO_4^-	780	- 9.0	(- 8.3)	(-11 ± 20)
5	H_2SO_4-HSO_4^-	1390	+10.4	9.6	7 ± 10
6	H_2SO_4-HSO_4^-	2480	+12.0	11.1	4 ± 5
7	H_2SO_4-HSO_4^-	3560	+ 6.0	5.6	16 ± 36
8	H_2SO_4-HSO_4^-	1060	+ 9.0	8.3	8 ± 8
9	H_2SO_4-HSO_4^-	0	+ 4.5	4.2	--
10	Br_2	345	+ 3.0	3.3	10 ± 40
12	Br_2	335	- 1.5	(- 1.7)	(- 5 ± 45)
13	Br_2	1330	+76.2	84	63 ± 12
15	H_2SO_4-HSO_4^-	590	-23.9	(-22.1)	(-37 ± 39)
16	H_2SO_4-HSO_4^-	700	+ 6.0	5.6	8 ± 32

along the average a direction of the crystallites composing the particles, so that an appreciable fraction of the imperfections communicate with the surface and therefore a fairly sizeable area at the periphery of the particle is able to expel its impurities to the surface. This area will be free of trapped bromine and, since it constitutes a larger fraction of the total volume in small particles than in large ones, will result in an effective decrease in the retention of bromine by small particles.

Actually, the width of the bromine-free area and therefore the average length of the imperfections can be estimated from the data in Figure 2. Disregarding altogether the c direction of the crystallites, one can consider each particle as a disk of radius r. The imperfections which do not communicate with the surface are found in an area $a = (r-x)^2 \pi$ where x is the average length of the imperfections. The retention of bromine is $\bar{R} = ab/r^2\pi$ where b is a proportionality constant. Combining the values of the retention for large and medium sized spectroscopic crystals at high and at intermediate brominations, one calculates an approximate imperfection length of 10 microns. Actually the calculated length of the imperfections increased somewhat with the particle size. The dependence of the retention of bromine on the particle size of the graphite powders decreased after debromination at 310°C. It appears, then, that a much larger fraction of the imperfections becomes accessible to the outside, and that the remaining inaccessible imperfections are much smaller than the particle diameters, because for small x, the retention $((r-x)^2/r^2)b$ becomes nearly independent of r. Furthermore, the imperfections are probably much smaller, and more confined, in pitch-bonded graphite than in unbonded graphite, because bromine is retained much more tenaciously in the pitch-bonded material, as is shown by reference to Figure 3.

Another observation which requires explanation is the fact (Figures 1 and 2) that the retention of bromine depends strongly on the composition of the parent lamellar compound. Two quite different explanations are possible. It may well be that the imperfections are quite short in the average c direction of the particles, so that an incompletely brominated lamellar compound contains a considerable number of imperfections which have simply not yet become accessible to bromine and which will only become accessible on complete bromination. In this connection it must be remembered that in all the lamellar compounds known(1) incomplete reaction implies that layers of reactant and layers of unreacted graphite alternate with great regularity. Any imperfections in those unreacted carbon layers are also unlikely to contain reactant unless they are wide enough to communicate somewhere with a layer of reactant. The rather abrupt change in the slope of Figure 1 would occur at the point where bromination has proceeded far enough to fill most of the imperfections.

The alternate explanation which would explain the composition of the residue compounds implies that the imperfections are long in all directions, but that the concentration of bromine in the imperfections is pressure dependent. On this model the change in the slopes of Figures 1 and 2 could be attributed to a decrease in the volume of the imperfections caused by the swelling of the crystallites. The observation (Figure 1) that rapid bromination resulted in abnormally low retention of bromine probably indicates that invasion of the imperfections by bromine is slower than the formation of lamellar bromine layers.

It is hoped that a detailed study of the residue compounds derived from other lamellar compounds than the bromide and bisulfate will elucidate further the structure of the residue compounds.

ACKNOWLEDGEMENT

The author is particularly indebted to Professor W. H. Zachariasen, Dr. S. Siegel and H. A. Plettinger for their invaluable help in taking the x-ray photographs and interpreting the patterns. Without this important assistance the interpretation of the nature of the residue compounds would have been impossible.

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