QUARTERLY REVIEWS

LAMELLAR COMPOUNDS OF GRAPHITE

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Introduction

THE ability of graphite to form compounds by inclusion of foreign substances within its structure has been known for more than a century and many of the compounds so formed have been examined in considerable detail. Earlier investigations which are covered in Riley's excellent review[1] up to 1945 were mostly concerned with chemical and structural aspects of the graphite compounds. Although similar investigations have been conducted in recent years, more interest has also been shown in the manner in which intercalated substances are bonded within the graphite and the effect such bonding may have on the electronic properties of the latter. In all cases knowledge of the structure and properties of graphite has been a corner-stone in these studies; hence a brief description of the host substance, graphite, will add to appreciation of the researches to be described in this Review.

Macrocrystalline graphite consists of flat planes of carbon atoms stacked parallel to each other at regular intervals of 3·35 Å. Within each of the layer planes, carbon atoms are linked in a hexagonal network as in large planar molecules of aromatic compounds of carbon. Atomic order within the planes permits regular arrangement of atoms in one plane relative to those in adjacent planes, that is, layer planes are orientated as well as parallel. In all essentials, this generally accepted structure of graphite is the same as that deduced by Bernal.[2] Some uncertainties regarding minor variations in the stacking of planes still exist and have attracted the attention of a number of workers.[3-6]

As in the case of aromatic compounds, the graphite structure owes its existence to the possibility of binding the carbon atom at least as firmly with three bonds as with four. In graphite, such trigonal bonding is confined to atoms within the layer planes, each carbon atom being linked with its three nearest neighbours by sp^2 type σ bonds. The strength of the latter is increased above that of the normal single covalent C–C bond by superposition of other electronic structures involving non-localised electrons originally associated with the $2p_z$ orbitals of all carbon atoms in each plane. The considerable strength of this system of bonding is reflected

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[1] Riley, *Fuel*, 1945, **24**, (1) 8-15, (2) 24-53.
[2] Bernal, *Proc. Roy. Soc.*, 1924, *A*, **106**, 749.
[3] Laidler and Taylor, *Nature*, 1940, **146**, 130.
[4] Finch and Wilman, *Proc. Roy. Soc.*, 1936, *A*, **155**, 345.
[5] Lipson and Stokes, *Nature*, 1942, **149**, 328; *Proc. Roy. Soc.*, 1942, *A*, **181**, 101.
[6] Lukesh, *J. Chem. Phys.*, 1951, **19**, 1203; *Phys. Rev.*, 1950, **80**, 226.

in the high thermal stability of graphite. Beside increasing the binding energy between in-plane carbon atoms, the π electrons, because of their mobility, also account for the electrical and magnetic properties of graphite. The magnitude of both these properties depends on the distribution of free electrons between various electronic energy levels according to the energy of the system as determined by the state of the latter. Theoretical studies,[7-9] based on an ideal single crystal of graphite of infinite dimensions, show that there is sufficient accommodation in the lower energy levels at 0°K for all mobile electrons. However, excitation of electrons to upper levels occurs at higher temperatures, and conduction is then due to vacancies in the lower bands as well as to excited electrons. Wallace[7] calculates that, at room temperature, there are $2{\cdot}25 \times 10^{-3}$ free electrons per carbon atom. The anisotropic nature of the electrical and magnetic properties of graphite arises from limitation of free electron movement to the carbon layer planes. This restriction of electron movement draws attention to the nature of binding between carbon layer planes. It seems probable, in view of the distance between layer planes, that the latter are maintained in their relative positions by van der Waals forces. On this assumption, Brennan[10] calculated that the attraction between planes contributes only 3·99 kcal./mole to the stability of the graphite structure.

It is due to the considerable disparity between the strengths of forces maintaining the graphite lattice that foreign substances are able to expand and occupy the interplanar spaces of the graphite crystal without disrupting the carbon layer planes which they separate. Penetration of the graphite lattice in this manner is not a physical phenomenon comparable with that observed in the case of some zeolites.[11] This is supported by the remarkable specificity which graphite shows in its reactions with various substances. Many of the latter, although apparently suitable from the point of view of volatility and ionic or molecular size, fail to react with graphite. It has been confirmed that substances intercalated in graphite are linked with the carbon layer planes enclosing them, and Croft[12] has suggested that the feasibility of such bonding determines the possibility of intercalation when all other conditions are favourable. Bonding between intercalated substances may be either covalent or ionic. Covalent bonding is favoured by high electronegativity of the penetrating substance and the presence of conjugated double bonds within the carbon planes. When this type of bonding occurs the layer planes assume[13,14] a wavy form because of reversion of carbon bonding to the tetrahedral form. Also, because resonance in the bond system of the layer planes is eliminated, covalent

[7] Wallace, *Phys. Rev.*, 1947, **71**, 622.

[8] Bradburn, Coulson, and Rushbrooke, *Proc. Roy. Soc. Edinburgh*, 1948, **62**, *A*, 336.

[9] Coulson, *Nature*, 1947, **159**, 265.

[10] Brennan, *J. Chem. Phys.*, 1952, **20**, 40.

[11] Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130, 133.

[12] Croft, *Nature*, 1953, **172**, 725.

[13] Hofmann and Holst, *Ber.*, 1939, **72**, 754.

[14] Rüdorff and Rüdorff, *Chem. Ber.*, 1947, **80**, 417.

graphite compounds are light in colour. Ionic bonding between carbon layer planes and enclosed substances is possible because of the suitable electronic band structure of graphite. Excited electrons in the upper energy levels of the latter are, in some cases, capable of transfer to intercalated substances. In other cases, charge may be transferred from the invading substance to the unfilled bands of graphite. Whatever the direction in which electrons are transferred, the resulting change in the electronic state of the graphite can be readily detected by measurement of electrical or magnetic properties. It is probable that electrostatic forces as well as those due to charge transfer provide bonding in the ionic graphite compounds.

The various lamellar compounds of graphite can be classified according to the type of bonding between the intercalated substance and the carbon layer planes. The first group, in which bonding is covalent, includes graphite oxide and the graphite fluorides. The second, or ionic bonding group, contains the graphite salts, compounds of graphite with alkali metals, and the molecular compounds of graphite. For reasons already given, compounds of the first group are light in colour and except for their layer structure lack all the graphitic characteristics which are well preserved in the second group. The groups are also distinguished by reversibility of formation. For example, graphite oxide and graphite fluoride, when heated to sufficient temperatures, deflagrate and yield oxides and fluorides of carbon respectively together with finely divided soot-like forms of carbon. Graphite bromide, graphite–ferric chloride, and graphite–potassium, however, all decompose at appropriate temperatures yielding graphite and the intercalated substances in the free state. Compounds in both classes vary markedly in their stability to solvents. Graphite fluorides are hydrophobic like graphite, but graphite oxide possesses many interesting properties arising from the highly lyophylic nature of groups attached to the carbon layer planes. Compounds of graphite with the alkali metals and the graphite salts are rapidly decomposed by water and the alkali compounds react readily with ammonia and amines. The molecular compounds are generally more stable, but those containing chlorides of Group III elements react with water and the intercalated chlorides are hydrolysed *in situ.* Graphite–ferric chloride, although unaffected by most solvents, reacts with ammonia. Other general properties of, and major differences between, the various types of graphite compound will emerge from the following discussions which, in conformity with the above classification, commence with graphite oxide.

Covalent graphite compounds

Graphite Oxide.—Early observations by Brodie,[15] Staudenmaier,[16] and others provide ample evidence that treatment of graphite with certain oxidising agents results in the formation of a solid oxide of carbon which

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[15] Brodie, *Phil. Trans.*, 1859, **149**, 249.

[16] Staudenmaier, *Ber.*, 1898, **31**, 1481; 1899, **32**, 1394; 1900, **33**, 2824.

may vary from brown to light yellow. The yield depends on the crystallinity of the graphite. Microcrystalline graphite carbons which are generally structurally imperfect to a marked degree are mostly oxidised to gaseous oxides of carbon and give poor yields of the solid oxide. Macrocrystalline graphites on the other hand may, under suitable conditions of oxidation, give yields of oxide as high as 95% of the theoretical.[17]

The best known and still most generally used method of preparing graphite oxide is that due to Staudenmaier.[16] It consists in adding solid potassium chlorate to a suspension of graphite in a mixture of concentrated nitric and sulphuric acids (1:2 v/v). This procedure is slow and may require up to 10 days for a single treatment. Usually several such treatments are required. It is also necessary to keep the temperature below 50° because of the explosion hazard due to the formation of ClO_2. A final treatment with acidified potassium permanganate may be given to ensure complete oxidation. Graphite oxide obtained in this manner is pale lemon yellow but darkens rapidly on drying and storage. Clauss, Boehm, and Hofmann[18] succeeded in preparing pure white graphite oxide which darkened very slowly when dried and stored in daylight. This was achieved during the final oxidation stage by washing the product of initial treatments in the dark with water containing chlorine dioxide and hydrochloric acid. The final oxide was dried over phosphoric oxide. Recently, an entirely new method of preparing graphite oxide has been described by Hummers and Offeman;[19] graphite (100 g.) is treated with an anhydrous mixture of concentrated sulphuric acid (2·3 l.), sodium nitrate (50 g.), and potassium permanganate (300 g.). The permanganate is added slowly to a mixture of the other reactants at 0°, and the temperature kept below 20°. When addition is complete the temperature is held at 35° ± 3° for 30 minutes, after which water (4·6 l.) is added and the temperature allowed to rise to 98°. After 15 minutes the mixture is further diluted, residual permanganate is reduced by treatment with hydrogen peroxide, and the dispersed oxide finally filtered off. After redispersion of the filter cake in water, remaining salt impurities are removed by anion- and cation-exchange resins. Analytical data obtained by Hummers and Offeman given in Table 1 indicate that graphite oxide prepared by this method compares favourably with that obtained by Staudenmaier's method, both in degree of oxidation and in purity.

TABLE 1.

Method of prepn.	% (*w*/*w*)				*Atomic ratio*
	C	O	H_2O	Ash	C:O
Hummers and Offeman	47·1	28·0	23·0	2·0	2·3:1
Staudenmaier	52·1	24·0	22·2	1·9	2·9:1

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[17] Hofmann and Frenzel, *Ber.*, 1930, **63**, *B*, 1248.

[18] Clauss, Boehm, and Hofmann, *Z. anorg. Chem.*, 1957, **291**, 205.

[19] Hummers and Offeman, *J. Amer. Chem. Soc.*, 1958, **80**, 1339.

Another new method of preparing graphite oxide reported by Bottomley and Blackman[20] is principally of interest because aromatic compounds and not graphite are oxidised. For example, when phenol (0·1 g.) in a concentrated solution of boric acid (20 ml.) is treated with hydrogen peroxide (5 ml. of 100 vol.) and copper sulphate solution (0·1 ml., 0·1M) and the mixture is heated to 90°, a colloidal brown material is produced. Solid samples of the colloidal substance prepared by evaporation were found to possess chemical and physical properties similar to those of graphite oxide and to have the composition C, 55·9; H, 4·0; O, 40·1%. The authors' claim that similar substances can be obtained by anodic oxidation of aromatic compounds recalls Brown and Storey's electrolytic preparation[21] of graphite oxide from graphite. Although Bottomley and Blackman's discovery does not afford a useful method of preparing graphite oxide it suggests a connection between the production of graphite oxide "analogues" and the synthesis of humic acid, peat, and coal under natural conditions.

The unusual properties of graphite oxide, such as acid character, capacity for base exchange, and oxidising power, all of which have been described by Riley,[1] may be interpreted from its structure. Elucidation of the latter, however, has been delayed by difficulties. *X*-Ray diffraction, which has been employed successfully with many other graphite compounds, yields little information about graphite oxide because the regular disposition of carbon planes found in graphite is not preserved in the oxide. At most, this method only shows that graphite oxide is composed of parallel layers spaced at greater distances than are the carbon layer planes in graphite. Chemical methods of investigation are also handicapped by the considerable difficulty of completely removing reagents and solvents from the oxide. As a result, chemical analyses of oxides prepared in different ways were found to yield variable results, so much so that at one time it was doubtful whether a definite empirical formula could be assigned to graphite oxide.[17] In addition to problems arising from the strongly sorptive character of graphite oxide, it appears that many of the earlier investigators over-estimated its thermal stability. De Boer and van Doorn[22] have shown that decomposition commences at above 70°. As drying temperatures of 100 — 130° had been employed previously their observation may account for some of the inconsistencies in reported compositions. Both De Boer and van Doorn and Clauss, Boehm, and Hofmann[18] have shown that air-drying followed by drying *in vacuo* over phosphoric oxide, each operation being conducted at room temperature, yields oxides of constant composition. Their success made it possible to study, by chemical means, the nature of active groups in graphite oxide and to deduce probable structures for the oxide.

The acidic and basic exchange properties of graphite oxide draw attention

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[20] Bottomley and Blackman, *Nature*, 1953, **171**, 620.

[21] Brown and Storey, *Trans. Amer. Electrochem. Soc.*, 1928, **53**, 129.

[22] De Boer and van Doorn, Conference on Industrial Carbon and Graphite Soc., Chem, Ind., London, 1957; van Doorn, Proefschrift, Delft, 1957.

to the hydrogen content of graphite oxide. Part of the hydrogen found by analysis might be attributed to water which is readily imbibed by the oxide and causes swelling of the latter.[23] The interplanar spacing in air-dried graphite oxide is about 9 Å.[17] Drying over phosphoric oxide reduces this spacing to 6·3 Å but does not eliminate the exchangeable hydrogen ions, and the graphite oxide still contains OH groups which can be neutralised with sodium hydroxide or methylated with diazomethane.[13,24] Clauss, Boehm, and Hofmann[18] used a variety of reagents to determine the OH content of graphite oxide dried over phosphoric oxide. They found that neutralisation with aqueous sodium hydroxide and potassium hydroxide gave lower concentrations than alcoholic solutions of these alkali hydroxides. The largest OH content, *viz.*, 1050 mequiv./100 g., was found when the oxide was neutralised with sodium ethoxide solutions. A similar result, 1100 mequiv./100 g., was obtained by elution of the oxide with anhydrous dioxan[25,26] as used by Ruess[27] to determine water, separately from OH groups, included between layers of clay minerals. Attempts to confirm these data by methylation of graphite oxide by diazomethane resulted in only 515 mequiv. of OH groups being methylated. However the fact that the methylated oxide yielded a further 565 mequiv. on neutralisation with sodium ethoxide solution suggests that the reaction with diazomethane did not reach completion, possibly for steric reasons. The proportion of OH groups methylated with methanol and hydrogen chloride was much less than when diazomethane was used. Since it would be reasonable to suppose that the darkening of graphite oxide on exposure to light is indicative of decomposition, it is noteworthy that Clauss, Boehm, and Hofmann[16] found that a light-coloured oxide contained 1035 mequiv. of OH per 100 g. and that the corresponding figure for the dark oxide derived from it was 1050 mequiv. The sodium salts of graphite oxide resulting from neutralisation with sodium hydroxide or sodium ethoxide are hydrolysed by water.

The location of these reactive OH groups in the graphite oxide structure is indicated by the results of methylation experiments conducted by Clauss *et al.*[18] and Hofmann and Holst.[13] Thus methylation of the oxide with diazomethane in ether or dioxan caused an increase in lattice plane spacing of approximately 3 Å which may be interpreted as being due to the presence of methoxy-groups between the planes. From this it is concluded that the hydroxy-groups which react with diazomethane are distributed over the surfaces of the graphite oxide layer planes and accommodated in the inter-planar spaces of the oxide structure. *X*-Ray examination of graphite oxide methylated with methyl alcohol and hydrogen chloride showed no increase in inter-planar spacing as a result

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[23] Thiele, *Kolloid-Z.*, 1948, **111**, 15.
[24] Ruess, *Monatsh.*, 1946, **76**, 381.
[25] Ebert, *Angew. Chem.*, 1934, **47**, 305.
[26] Bull, *Angew. Chem.*, 1936, **49**, 145.
[27] Ruess, *Monatsh.*, 1946, **76**, 168.

of methylation. From this observation and the fact that fewer OH groups reacted (50–100 mequiv./100 g.), Hofmann and Holst concluded that these reagents react only with carboxyl groups at the peripheries of the oxide layer planes. The production of mellitic acid by oxidation of coal and other forms of carbon indicates that such peripheral groups probably exist in graphite oxide. Hofmann and Holst support their conclusion with evidence of a semiquantitative relation between the particle size of graphites from which oxides were prepared and the extent of methylation of the latter with methanol and hydrogen chloride. The ease with which methyl esters of graphite oxide obtained by methylation with methanol and hydrogen chloride could be hydrolysed with N-hydrochloric acid confirmed the strongly acid character of the peripheral groups which had been esterified and supports the view that they were carboxyl groups.

Clauss *et al.*[18] found that esters resulting from methylation of graphite oxide with diazomethane were only partly hydrolysed, and suggested that the unaffected fraction contained methyl esters of a phenolic type which are scarcely attacked by dilute mineral acids. However, if hydroxy-groups are attached directly to carbon atoms aromatically linked in the layer planes, as implied in this suggestion, it would be difficult to account for the acidity of these groups. Goldschmit, quoted by Clauss, Boehm, and Hofmann, points out that tertiary alcohols such as 9-hydroxydecalin do not have an acid reaction. On the other hand, if a carbon atom to which an OH group was attached, were linked to only two neighbours and to one of them by a double bond, an enolic structure possessing exchangeable hydrogen ions would be possible. The existence of enol groups in graphite oxide could account for the fact that darkening of the latter, by the action of light, heat, or alkali solutions, does not involve change of composition. If darkening is due to internal rearrangement, keto–enol tautomerism would be a reasonable explanation, particularly in view of the base exchange properties of the oxide as demonstrated by its reaction with alkalis.

The maximum hydroxyl content of dry graphite oxide determined by Clauss, Boehm, and Hofmann accounts for the hydrogen contained in this compound but not for the total oxygen and it must be assumed therefore that the balance of the oxygen (*ca.* 50%) is linked in a different manner. The structure proposed by Ruess[28] for graphite oxide indicates one manner in which this balance of oxygen may be bound. In this structure the hexagonally linked layer planes of graphite survive oxidation, but the fourth valencies of carbon atoms in them are saturated by statistically distributed hydroxyl groups, ether-like oxygen bonds, and double bonds between some carbon atoms. Because of the attachment of these groups the aromatic character of the carbon layer planes is lost. Bonds linking oxygen to carbon planes are presumed to be in the 1,3 position which is regarded on steric grounds as more probable than 1,2 or 1,4. Ideally, Ruess's

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[28] Ruess, *Monatsh.*, 1946, **76**, 381.

structure requires a C to O atomic ratio of 2 but this has not been attained. The lowest value obtained by Clauss, Boehm, and Hofmann for fully oxidised dry graphite oxides was 2·76 except for some very finely divided samples which gave 2·5. This low figure was probably due to the relatively high proportion of peripheral carboxyl groups in the finer material. The fact that the ratio of 2 cannot be achieved suggests that carbon–carbon double bonds are part of the structure of graphite oxide. The small number of carboxyl groups being neglected, it is calculated from Clauss, Boehm, and Hofmann's data that, on the average, fourth carbon valencies are distributed as follows: 46% for oxygen bridges, 21·5% for hydroxyl groups, and 32·5% for carbon–carbon double bonds.

The above considerations led Clauss, Boehm, and Hofmann to propose the structure shown in Fig. 1, in both keto and enol forms. The empirical formula corresponding with this structure is $C_8O_2(OH)_2$ for which the C to O ratio is 2·67 and the hydroxyl content 1240 mequiv./100 g. of oxide. The assumption that three out of every twenty pairs of hydroxyl groups are missing leads to the formula $C_8O_2(OH)_{1{\cdot}7}$ and a C to O ratio of 2·8 and a hydroxyl content of 1080 mequiv./100 g. The latter values agree with those obtained experimentally.

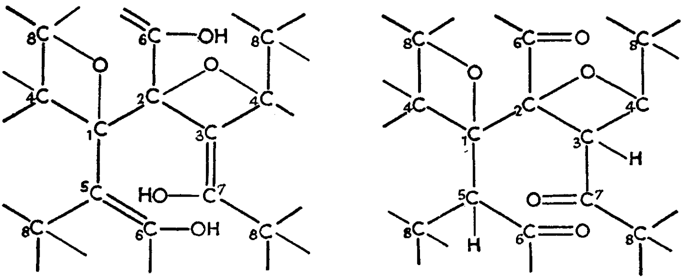

FIG. 1 *Structure of graphite oxide proposed by Clauss, Boehm, and Hofmann (keto and enol forms).*

[Reproduced with permission from *Z. anorg. Chem.*, 1957, **291**, 205]

The structure in Fig. 1 accounts very well for the chemistry of graphite oxide, but cannot be regarded as confirmed. Clauss, Boehm, and Hofmann admit the possibility that the oxide may contain tertiary hydroxyl groups which may be the groups which react with sodium ethoxide and acetic anhydride but not with aqueous sodium hydroxide or diazomethane. The opening of carbon–carbon bonds in the layer planes to permit formation of enol groups according to these investigators does not lead to larger faults in the planes. Hofmann and Frenzel[17] have demonstrated that in the case of well-crystallised graphite, the yield of graphite oxide is 95% of the theoretical yield based on carbon. The loss of 5% can be satisfactorily explained as resulting from cleavage of peripheral carbon atoms during oxidation.

Clauss, Boehm, and Hofmann suggest that graphite oxide may contain ether-like oxygen bridges between carbon atoms, carbon–carbon double bonds, tertiary hydroxyl groups, enolic groups, and keto-groups. They have been unable to detect any of these groups directly. However the structural model based on these groups affords a more satisfactory basis for interpretation of the properties of graphite oxide than do other models involving peroxide groups[29] or ionically attached hydroxyl groups.[30]

An independent chemical investigation of the constitution of graphite oxide conducted by De Boer and van Doorn[22] substantially confirms the conclusions reached by Clauss, Boehm, and Hofmann. Graphite oxides used in this investigation were prepared by Staudenmaier's method and after being dried *in vacuo* over phosphoric oxide at room temperature had the empirical composition $C_7H_2O_4$. Reduction, either by $TiCl_3$ or NaI in acetic anhydride, of an oxide having this composition showed that the latter contained 5 mequiv. of oxygen per formula weight. The empirical formula of the reduced oxide was C_7HO.

Acetylation of another portion of the same oxide sample indicated that the "molecule" of graphite oxide contains only one hydroxyl group capable of acetylation. Attempts at reduction after this treatment showed, furthermore, that acetylation of this one hydroxyl group resulted in the lowering of the oxygen equivalence to 3 mequiv. per formula weight. It seems therefore that, during reduction with $TiCl_3$, etc., the oxygen of the OH group must be present in some other form. Clearly a keto–enol equilibrium would comply with the requirements of providing 2 mequiv. of oxygen during reduction or 1 mequiv. of OH during acetylation.

In view of results obtained from acetylation experiments, it appears unlikely that there is another hydroxyl group in the reduced oxide, C_7HO. De Boer and van Doorn suggest that the hydrogen in this formula is the "aromatic" hydrogen from the keto–enol equilibrium. It is considered possible, as will be discussed later, that the unreducible oxygen in this formula is built into the carbon layer plane.

On the evidence for a keto–enol equilibrium in graphite oxide, the formula of the latter may be represented as

$$C_7(O_3H)(O)(H) \rightleftharpoons C_7(O_3H)(OH)$$

Further elaboration of the structure now rests on which O–H groupings for (O_3H) are possible. The various possibilities can be reduced by the requirements that, first, a suitable choice must contain 3 mequiv. of reducible oxygen; secondly, one oxygen atom will resist reduction; thirdly, the large expansion of graphite oxide does not permit interplane binding; and, fourthly, molecular oxygen is evolved during low-temperature decomposition of graphite oxide. According to De Boer and van Doorn, the only two groupings which satisfy these conditions are (–O–O–) (–OH)

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[29] De Boer and van Doorn, *Proc. k. ned. Akad. Wetenschap.*, 1954, **57**, *B*, 181.
[30] Franklin, *J. Chim. phys.*, 1953, **50**, *C*26.

and (–O·OH)(–O–). Discrepancies between calculated and observed densities of graphite oxide favour the view that one oxygen atom is built into the graphite layers as a heterocyclic atom and that the second grouping is the more probable. Accordingly, the structure of graphite oxide is represented as

$$(C_7O)(\text{–O·OH})(:O)(H) \rightleftharpoons (C_7O)(\text{–O·OH})(OH)$$

Both Clauss, Boehm, and Hofmann and De Boer and van Doorn have attempted to confirm their proposed structures for graphite oxide by infrared spectroscopy. Hadži and Novak[31] have conducted similar investigations independently. The results of all three investigations are in good agreement. All agree on the detection of –OH, C–O, and C=O groups. Clauss, Boehm, and Hofmann do not differentiate between carboxyl-carbonyl groups and ketonic-carbonyl groups, but De Boer and van Doorn demonstrated that carbonyl groups at the periphery do not play a quantitative role in the empirical composition of the oxide. Also, since it seemed improbable for steric and chemical reasons that carboxyl groups could be present internally in graphite oxide, as indicated in their proposed structure, De Boer and van Doorn concluded that the observed C–O and C=O vibrations relate to keto- and enol groups in the oxide. Measurements on acetylated graphite oxide and the potassium salt of the oxide support this interpretation. Apart from the above groups, both Clauss, Boehm, and Hofmann and Hadži and Novak noted an absorption band (10·2 μ) which could be attributed to epoxy- or peroxy-groups. Thus the oxygen bridges suggested by Ruess and adopted by Clauss, Boehm, and Hofmann in their structure appear to have some support.

While it cannot be said that the structure of graphite oxide has been determined with certainty, there is no doubt that the skilful chemistry and deduction of the above investigators has added considerably to our knowledge. The evidence obtained by Clauss, Boehm, and Hofmann for keto–enol equilibrium in graphite oxide is new and gains importance because it is supported by results of the independent investigation conducted by De Boer and van Doorn. Possibly, Hadži and Novak's inability to exchange hydroxyl groups of graphite oxide with D_2O might be argued as further evidence of this equilibrium. At present the choice appears to lie either with Clauss, Boehm, and Hofmann's structure

$$C_8O_2(OH)(:O)(H) \rightleftharpoons C_8O_2(OH)_2$$

or that of De Boer and van Doorn

$$C_7O(O\cdot OH)(:O)(H) \rightleftharpoons C_7O(O\cdot OH)(OH)$$

Franklin's structure[30] in which positively charged carbon layer planes enclose negatively charged groups of the general formula $(O_xH_y)_n^-$ does not account for the observation of C–O linkages by infrared examination nor does it accord with the behaviour of graphite oxide in water. The

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[31] Hadži and Novak, *Trans. Faraday Soc.*, 1955, **51**, 1614.

main uncertainties in the first two formulae concern the $O_2(OH)$ grouping in the first and the $O(O{\cdot}OH)$ in the second. It is to be hoped that future work on graphite oxide will resolve these and complete the excellent work already done by Clauss, Boehm, and Hofmann and De Boer and van Doorn.

The striking physical phenomena shown by graphite oxide are due largely to its ability to absorb various polar liquids. The latter penetrate between the oxide layer planes until these are finally dispersed as giant two-dimensional molecules.

Thiele,[23] who first noted the ability of graphite oxide to form a colloid ion, investigated some properties of sols and gels derived from graphite oxide. Using graphite oxide freshly prepared by Staudenmaier's method, he found that almost clear light yellow highly viscous sols could be prepared simply by shaking the oxide with water without the addition of peptizing agents. These sols were quite stable and could be kept for long periods in sealed vessels but were darkened by light.

As little as 0·006% of graphite oxide was found to raise the viscosity of water from 1 to 1·1. Thiele studied the variation of viscosity of aqueous sols with concentration of graphite oxide and found that the dependence is not linear. The curves obtained were typical of structurally viscous molecular colloids, resembling those for protein sols (although these reach the same viscosity at higher concentrations). The high viscosity observed at low concentrations is striking. For example, a sol containing 1% of graphite oxide will not flow from an inverted vessel. Although graphite oxide evidently belongs among the highly viscous sols, it is possible to prepare suspensions of this material, for example from artificial graphite, for which the viscosity is much lower and is linearly related to oxide concentration. Thiele found that such suspensions behaved normally like those of other colloids and concluded from his observations that the viscosity of graphite oxide sols was related to the surface area of dispersed oxide lamellae. This conclusion was tested by determining the minimum concentrations for various samples of oxides at which streaming birefringence was still recognisable, and the viscosities at these concentrations. These experiments indicated that viscosity increases and minimum concentration for observation of birefringence decreases with size of the oxide lamellae.

The addition of acids, salts, and other flocculating agents was found to increase the viscosity of graphite oxide sols when added in low concentrations but small quantities of ammonia and alkali hydroxides reduced it temporarily. Thiele's observation that the viscosity is the same whether yellow or brown graphite oxide is used to prepare the sol appears to be consistent with the suggestion made by Clauss, Boehm, and Hofmann[18] that this colour difference is due to internal structural rearrangement and not to change of composition.

Graphite oxide sols containing as little as 0·06% of the oxide gel rapidly on addition of flocculating agents. Multivalent ions of U, Fe, Mg, Cu, etc., as chlorides, sulphates, or nitrate are the most effective agents. Gel formation is simply the formation of a salt of graphite oxide by exchange of its hydrogen ions for one of the above metal ions. The process can be reversed by treatment of the gel with dilute acid, excess of which can be removed by dialysis. As observed by Clauss, Boehm, and Hofmann, exchange of hydrogen ions for metal ions during gel formation results in darkening of the graphite oxide. The elasticity of gels containing small amounts of graphite oxide is low and moderate mechanical agitation causes water to separate from them. Elasticity increases with concentration. Normally the gels are isotropic, but became anistropic under the influence of mechanical agitation or of an electric field. Slow coagulation of sols also produces structurally ordered anisotropic gels.

The imbibition of liquids by graphite oxide and the resultant one-dimensional swelling of the latter have been investigated by De Boer and van Doorn.[22] Isotherms obtained for the sorption by graphite oxide of nitrogen and water vapour obtained by these investigators show discrepancies which have been interpreted as being due to penetration of polar molecules between the layer planes of the oxide. Density determinations of graphite oxide containing water indicate that the oxide can absorb 4% of water without swelling, and *X*-ray measurements confirm that dry graphite oxide has the same interplanar spacing as that containing 4% of intercalated water. However, above this water content, results from the two methods disagree. *X*-Ray data indicate that the swelling is not large enough to account for all the water absorbed by the oxide. Density measurements, on the other hand, satisfactorily reconcile lattice expansion and water content. De Boer and van Doorn concluded that values obtained for the spacing between oxide lamellae by the *X*-ray method were incorrect because water molecules congregate in the peripheral regions of the interplanar spaces in which they are absorbed. Flexibility of the graphite oxide layer planes[32] makes this congregation possible. It appears, therefore, that *X*-ray measurements refer to the regions poorer in water and where layer planes are consequently closer together. The swelling of graphite oxide increases continuously and linearly with water content after the latter has exceeded 4·2%. The ability of graphite oxide to imbibe various other liquids is indicated by the specific volume of the oxide as determined in those liquids. Results of such determinations made by De Boer and van Doorn[22] are given in Table 2.

These data show that the specific volume of graphite oxide in polar liquids is smaller than in non-polar liquids, which must mean that molecules of polar liquids only can be accommodated in the interlamellar spaces of the oxide.

The effect of imbibition of organic liquids on the interplanar spacing of

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[32] Beckett and Croft, *J. Phys. Chem.*, 1952, **56**, 929.

graphite oxide was studied by MacEwan and Ruiz.[33] They found that, for aliphatic alcohols, intercalated molecules containing less than four carbon atoms lie flat between the oxide lamellae. However, between four and five carbon atoms per molecule, the orientation of occluded molecules changes from "lying down" to "standing up". This phenomenon is supposed by MacEwan and Ruiz to be due to the different modes of interplanar packing necessary for steric reasons to permit the reaction between short and long alcohol molecules with acidic groups on the surfaces of the graphite oxide layer planes, as in the equation

TABLE 2. *Specific volumes of graphite oxide in various solvents.*

Imbibed liquid	*Sp. vol. (ml./g.)*	*Imbibed liquid*	*Sp. vol. (ml./g.)*
Methanol	0·383	Nitrobenzene	0·446
1,4-Dioxan	0·399	Helium	0·465
Ethanol	0·400	(Reciprocal *X*-ray density)	0·466
Pyridine	0·412	Benzene	0·488
Water	0·423	Carbon tetrachloride	0·515

$$\underset{\text{(graphite oxide)}}{C_4O_9(OH)} + ROH \rightarrow C_4O_9(OR) + H_2O$$

These investigators do not define the nature of the acidic groups, except to suggest complex anions of the form $(O_xH_y)_n$ as proposed by Franklin.[30] The presence of such anions would permit a similar explanation for the behaviour of intercalated amines which also show this orientation phenomenon.

The possibility that oxygen bridging, as in the structure for graphite oxide proposed by Ruess,[28] would result in loss of structural rigidity of oxide lamellae compared with that of the carbon layers of graphite from which they were derived was investigated by Beckett and Croft.[32] Samples of dispersed graphite oxide lamellae 50—200 Å thick and dispersed flakes of colloidal graphite 70—150 Å thick were compared under an electron microscope. At a magnification of 50,000, photomicrographs showed the oxide lamellae to be much folded, but folds were rare in the case of graphite. This difference was attributed to the redistribution of valency linkages between carbon atoms in the layer planes of graphite occurring when the latter is converted into graphite oxide.

As yet there have been few attempts to exploit the properties of graphite oxide for useful purposes. Frechette and Yung Tao[34] have succeeded in increasing the density of artificial graphite blocks used in atomic reactors by impregnating them with graphite oxide sols and decomposing the latter *in situ* by pyrolysis. The fact that membranes of graphite oxide are permeable to water vapour, but not to gases such as nitrogen, is the basis

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[33] MacEwan and Ruiz, *Nature*, 1955, **176**, 1222.
[34] Frechette and Yung Tao, *Nuclear Sci. Abs.*, 1954, **8**, Abs. 161.

of a novel method, devised by Clauss and Hofmann,[35] of measuring the partial pressure of water vapour in a system.

The effect of heat on graphite oxide is of interest both because of the spectacular deflagration which marks decomposition of the oxide and because of the unique form of carbon which results from this decomposition. Such decomposition occurs at temperatures above 200°. Below this temperature decomposition proceeds more slowly. Many early analyses of graphite oxide were rendered inaccurate because investigators dried their oxide samples at or above 100°. De Boer and van Doorn's[22] experiments in which graphite oxide was heated at various temperatures and gases evolved were collected and analysed show that the oxide commences to decompose at about 70°. The results given in Table 3 also show that molecular oxygen is liberated freely in the vicinity of 70°, an observation which appears to have escaped other workers.

TABLE 3. *Thermal decomposition of graphite oxide.*

Temp. of decompn.	*Decrease of the weight of graphite oxide after heating for 6 hr.* (%)	*Composition of mixture of gases evolved* (%)			
		CO_2	H_2O	O_2	CO
72°	0·9	6·4	6·4	87·2	—
88	1·3	56·4	19·4	24·2	—
105	2·0	44·9	41·0	14·1	—
115	3·0	37·8	22·7	39·5	—
135	4·9	41·5	22·6	35·9	—
150	7·2	46·1	25·2	28·7	—
180	32·2	62·1	24·3	7·8	5·7

The effect of heat on graphite oxide as reflected by changes in weight and interplanar spacing has been studied by Matuyama.[36] Curves obtained from thermal-balance data confirm the observation that there is a substantial loss of weight when the oxide is heated to 100°. Matuyama attributed this decrease to loss of absorbed water but did not verify his assumption by analysis. He observed other regions of rapid decomposition in the ranges 150—190° and 190—220°. Beyond 220° decomposition proceeds slowly and is amost complete at 280°. Corresponding with the loss of weight of graphite oxide during heating there is a decrease in interplanar spacing. This decrease was observed to be abrupt at 190° and 220°, that is, at the ends of the first and the second stage of rapid decomposition. During the progressive decrease of interplanar spacing, other structural changes were also found to occur. The layer planes at first expanded by 0·5%, then contracted by the same amount, both changes being measured relative to normal C–C distances in graphite planes. The

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[35] Clauss and Hofmann, *Angew. Chem.*, 1956, **68**, 522.
[36] Matuyama, *J. Phys. Chem.*, 1954, **58**, 215.

planar expansion was attributed to variation in C–C distances, but the contraction was presumed to result from unevenness of layer planes and the displacement of carbon atoms from the latter.

By determining the deflagration temperatures of various preparations of graphite oxide when heated under similar conditions, Ruess[37] was able to fix the maximum temperature of the heating which takes place in the centre of the objective in the Siemens electron microscope at high magnification as 264—278°. The value calculated by Borries and Glaser[38] was 270°.

The finely divided form of carbon obtained by rapid thermal decomposition has been discussed by Riley.[1] Recent application of the techniques of *X*-ray diffraction, electron diffraction, and electron microscopy by Ruess[39] and Beyersdorfer[40] give the following account of this unique form of carbon. Thermal decomposition of graphite oxide in the region 250—300° yields a light soot of high specific area. Electron micrographs reveal a structure best described as resembling a heap of crumpled sheets of paper. *X*-Ray and electron-diffraction measurements indicate varying dimensions for these carbon sheets; Ruess gives minimum basal plane diameters of 500 Å and thickness of individual sheets of the order of 20 Å. Beyersdorfer on the other hand measured diameters ranging from 1000 to 2000 Å and set maximum thickness of sheets at 100 Å. It is evident that sheet dimensions will be determined by the nature of the graphite oxide from which they are derived, for it is a reasonable assumption that the explosive escape of gases from single flakes of graphite oxide tears apart and crumples sheets of graphite a few layer planes thick, but bearing some relation in area to the basal dimensions of the oxide flake. Structural determinations by Ruess and Beyersdorfer confirm that carbon is linked hexagonally within layer planes making up sheets of graphite oxide soot. This likeness to graphite is also supported by observations on anomalous change of specific resistance of the soot with applied pressure made by Ruess. Since the conductivity of graphitic carbon is less by a factor of at least 100 in the direction normal to carbon layer planes than in the planes themselves, the fact that the orientating effect of pressure on sheets of graphite oxide soot is accompanied by an increase of specific resistance confirms the graphite layer structure proposed for this soot.

The magnitude of data obtained by Ruess[41] from absorption tests with Methylene Blue and experiments to determine catalysis of synthesis of hydrogen bromide cannot be reconciled with the view that active areas of the carbon sheets of graphite oxide soot are located solely at the peripheral regions of these sheets. The yields of acid surface oxides produced on the carbon surfaces by oxidation by treatment with moist oxygen

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[37] Ruess, *Kolloid-Z.*, 1944, **109**, 149.
[38] Borries and Glaser, *Kolloid-Z.*, 1944, **106**, 123.
[39] Ruess, *Monatsh.*, 1948, **78**, 222.
[40] Beyersdorfer, *Optik*, 1950, **7**, 192.
[41] Ruess and Ruston, *Fuel*, 1946, **25**, 156.

at 480° or concentrated nitric acid at 100° support this conclusion. That these yields were amongst the highest values found for active carbons, although other forms of active carbon have a far higher ratio of prismatic face area to basal plane area, supports Ruess's view. Hofmann's observation[42] that catalytic activity of the soot declines with formation of surface oxides indicates that the active carbon centres responsible for catalysis are the same as those at which surface oxidation occurs.

Graphite Fluorides.—*Carbon monofluoride.* Like many other elements, carbon burns in fluorine to yield a variety of carbon fluorides. An important feature of this reaction, however, is that the nature of the fluorides is in some degree dependent on the character of the carbon used. Pursuing this observation, Ruff and Brettschneider[43] discovered that by selecting reaction temperatures and fluorine pressures, it was possible to cause the elements to react without combustion and that the product so obtained was a grey hydrophobic solid of low electrical conductivity with the formula $(CF)_n$. *X*-Ray examination indicated that, when graphite was used, the distance between carbon layer planes was increased to about 8 Å by intercalation of fluorine atoms between them. W. and G. Rüdorff[44] confirmed these observations, particularly the fact that $(CF)_n$ can be formed from the elements in the range 420—550°. The compositions of homogeneous compounds prepared by them ranged from $CF_{0\cdot68}$ to $CF_{0\cdot99}$. Preparations containing the highest proportion of fluorine were pure white, transparent in thin layers, and virtually non-conducting.

Ruff concluded from *X*-ray examination of $(CF)_n$ that the graphite structure is retained in the carbon layer planes of this compound and that these planes are separated to a distance of 8·17 Å. He assumed that fluorine atoms acquired electrons from the carbon planes and that the fluorine ions so formed were close-packed in six parallel layers between each pair of carbon planes. Bigelow[45] cast doubt on the stability of such a structure and suggested instead one in which fluorine atoms lie in parallel planes about each carbon plane and to which they are linked by polarised covalent bonds. Palin and Wadsworth[46] examined samples of $(CF)_n$ prepared from Acheson graphite and concluded from their *X*-ray diffraction patterns that the spacing of carbon planes is about 6·0 Å, which compares favourably with 6·3 Å, the spacing calculated from a determined density of 2·78. Difference between ratios of the spacings corresponding to (100) and (110) reflections for graphite and $(CF)_n$ led these authors to suggest that, although the carbon atoms in $(CF)_n$ are arranged similarly to those in graphite there is an expansion of C–C distance and also a slight distortion of the true hexagonal arrangement in this compound. They support their hypothesis with spacings calculated from weak (200)

[42] Hofmann and Lemcke, *Z. anorg. Chem.*, 1932, **208**, 194.
[43] Ruff and Brettschneider, *Z. anorg. Chem.*, 1934, **217**, 1.
[44] Rüdorff and Rüdorff, *Chem. Ber.*, 1947, **80**, 413.
[45] Bigelow, *Chem. Rev.*, 1947, **40**, 83.
[46] Palin and Wadsworth, *Nature*, 1948, **162**, 925.

and (120) reflections and give a calculated average C–C distance of 1·49 Å. The latter value suggests a loss of double-bond character and therefore also supports Bigelow's suggestion of a polarised C–F covalent link. Palin and Wadsworth noted an absence of general (*hkl*) reflections and ascribed this to turbostatic arrangement of the carbon planes. W. and G. Rüdorff[44] obtained results essentially similar to those of Palin and Wadsworth. They found an interplanar spacing of 6·6 Å for the compound $CF_{0 \cdot 99}$ and interpreted prism diffractions satisfactorily by assigning the customary single-bond length of 1·54 Å to the in-plane carbon distances. Examination of compounds containing lower proportions of fluorine revealed another anomaly, namely, an increase in interplanar spacing up to 8·9 Å as the fluorine content fell from the maximum value. W. and G. Rüdorff[44] proposed a structure for $(CF)_n$ in which they assumed covalent linkage of fluorine and carbon atoms and tetrahedral disposition of single carbon bonds. These assumptions imply complete loss of aromatic character of the carbon layer planes, which is consistent with the colour and electrically insulating character of the fluoride, and are expressed in a structure consisting of wavy or corrugated planes of carbon atoms flanked on either side by similar planes of fluorine atoms. Although it was not possible to locate the positions of fluorine atoms in $(CF)_n$ by *X*-ray diffraction, the C–F distances were assumed to be of the usual order, *viz.*, 1·4 Å. It is possible that this structure for $(CF)_n$ is oversimplified. Palin and Wadsworth report a marked change in the reflection-intensity ratio for (100) and (110) reflections in graphite and $(CF)_n$ which is difficult to reconcile with Rüdorff's "giant hydroaromatic molecule". Although discussion of intensities permits of other structures such as that suggested by Ruff, the available evidence is in favour of Rüdorff's model.

W. and G. Rüdorff[44] found that hydrogen fluoride catalyses the reaction between graphite and fluorine below 400° where graphite is practically inert to fluorine. In the presence of hydrogen fluoride $(CF)_n$ was produced at temperatures in the range 250—360°. As in the reaction involving only carbon and fluorine, the nature of the carbon was also found to be a determining factor in the reaction catalysed by hydrogen fluoride. Thus the reactivity of macrocrystalline graphite is almost entirely dependent on the partial pressure of hydrogen fluoride in the gaseous mixture; for example, the partial pressures of hydrogen fluoride required to maintain reaction at 250° and 360° were 200 and 20 mm. Hg respectively. On the other hand the reactivities of aggregates of microcrystalline carbon (average crystallite size 40 Å) such as retort carbon depend more on reaction temperature than on partial pressure of hydrogen fluoride. This form of carbon is very resistant to fluorination at 250°, even with a high partial pressure of hydrogen fluoride, but at 320° it becomes even more reactive than flake graphite. The following explanation is offered to account for the difference in behaviour of these two forms of carbon. Reaction in the case of macrocrystalline graphite is governed by the rate of diffusion of fluorine through readily accessible prismatic faces of the flakes. However, with aggregates of microcrystalline graphite, random arrangement of crystallites confines reaction to the surface of the aggregate where prismatic faces of the crystallites are exposed and not protected as within. When the reaction temperature is raised, volume increases resulting from enhanced surface reaction cause loosening of surface crystals which have reacted and render new crystals accessible for reaction. Because of their size these crystallites undergo complete fluorination more rapidly than large single flakes of graphite. These observations make it apparent that, although the temperatures of fluoride melts from which fluorine is generated electrolytically do not exceed 260—270°, the presence of a high hydrogen fluoride concentration in these melts may result in the formation of substantial quantities of $(CF)_n$ if graphite anodes are used. Anodes of coke-oven or retort carbon, on the other hand, are likely to be more resistant to fluorination. Experimental confirmation[44] of this argument has greatly reduced the explosion hazard, due to the accumulation of $(CF)_n$, which was once a problem in the large-scale generation of fluorine.

Tetracarbon monofluoride. During their investigation of the catalytic effect of hydrogen fluoride on the reaction between carbon and fluorine, W. and G. Rüdorff[47] found that gaseous mixtures of fluorine and hydrogen fluoride (200 mm. Hg. partial pressure) react with finely divided graphite at room temperature to give the compound C_4F. Contrary to the effects of temperature observed in the preparation of $(CF)_n$, yields of C_4F were found to decrease as reaction temperatures were raised. The reaction ceases at 100°. As in the case of formation of $(CF)_n$, reaction is favoured by high partial pressures of hydrogen fluoride. To account for the formation of C_4F the Rüdorffs suggest that, at low reaction temperatures and high partial pressures of hydrogen fluoride, condensation of the latter on graphite is likely and would be followed by the formation of graphite bifluoride which because of its relative instability would be oxidised readily to C_4F. Cessation of condensation of hydrogen fluoride on graphite with increase of temperature may be the reason for inability to form C_4F at temperatures above 100°.

The only point of resemblance between C_4F and $(CF)_n$ is their chemical inertness; they are not attacked by acids or alkalis. In appearance C_4F is velvet-black, sometimes showing a bluish tint. It is less stable to heat than $(CF)_n$. Slow heating causes progressive loss of fluorine from C_4F but rapid heating results in deflagration and the production of volatile carbon fluorides CF_4, C_2F_6, etc., as happens with $(CF)_n$. C_4F cannot be converted into $(CF)_n$ by heating the former in a gaseous mixture of fluorine and hydrogen fluoride; this only results in loss of weight or deflagration of the C_4F.

C_4F is less dense than $(CF)_n$. The density measured pycnometrically varies with the liquid used. For example the density obtained under heptane

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[47] Rüdorff and Rüdorff, *Chem. Ber.*, 1947, **80**, 417.

was 2·06 whereas corresponding figures for xylene and bromobenzene were 2·09 and 2·11. This variation is similar to that reported by De Boer and van Doorn[22] for graphite oxide and shown by them to be due to imbibition of polar liquids. Although Rüdorff expected similar imbibition in the case of the graphite fluorides, this has not yet been confirmed. The specific electrical resistance of C_4F under a pressure of 750 kg./cm.^{2} is about 2—4 ohm/cm. and is therefore much less than that of $(CF)_n$. Rüdorff questions whether the resistance of C_4F can be attributed entirely to the intercalation and binding of fluorine in the graphite lattice or whether it is due to an increase in intercrystalline resistance resulting from effects of fluorination of external surfaces of the original graphite flakes.

Structural features of C_4F have been examined by W. and G. Rüdorff.[47] The *X*-ray diffraction pattern obtained for this compound was quite distinct from that for $(CF)_n$ and contained fewer reflections. It showed, however, that the distance between carbon planes is 5·4 Å and that the in-plane carbon–carbon distances are the same as in graphite. Although the pattern did not permit determination of the complete structure of C_4F, intensities of the (001) lines indicated that fluorine atoms are not arranged in a single layer between the carbon planes, but are probably disposed in two layers, one above and one below each carbon plane at approximately 1·4 Å which corresponds to the C–F bond length. Densities calculated from *X*-ray data lie in the range 1·97 to 1·99, and are slightly lower than pycnometric values which range from 2·05 to 2·09.

The similar chemical behaviour and mode of thermal decomposition of C_4F and $(CF)_n$ suggest that fluorine is linked in the same manner in both compounds. It is also probable that carbon atoms linked to fluorine in both compounds exhibit tetrahedral bonding, perhaps strained in the case of C_4F. Recognising this possibility, the Rüdorffs note that the C–C distances determined for C_4F may be projected distances and that the carbon layer planes may not be completely flat. The good electrical conductivity of C_4F indicates that the carbon layer planes in this compound have retained a substantial amount of aromatic character and that there has been little displacement of carbon atoms from their original planar positions. The total loss of aromatic character of carbon planes in $(CF)_n$ is due to the greater number of fluorine linkages, and the assumption that carbon planes are corrugated in this compound appears reasonable. Perhaps one of the more important distinctions between C_4F and $(CF)_n$, noted by the Rüdorffs, is that carbon layer planes are orientated with respect to each other in the former, but not in the latter.

Ionic compounds of graphite

Graphite–Alkali Metal Compounds.—Fredenhagen and his co-workers[48] were the first to show that graphite reacts strongly with potassium, rubidium, and cæsium in the molten or vapour state. At 300° they obtained

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[48] Fredenhagen, Cadenbach, and Suck, *Z. anorg. Chem.*, 1929, **178**, 333.

a bronze-coloured product of the approximate composition C_8M. The bluish product obtained at reaction temperatures in the range 360—400° had, according to these investigators, the composition $C_{16}M$.

Schleede and Wellmann[49] showed by *X*-ray diffraction that both the above reaction products were formed by intercalation of alkali-metal atoms between carbon layer planes of the graphite. As a result of this intrusion the interplane spacing of graphite was increased from 3·34 to 5·34 Å in the case of potassium and to 5·7 Å in the case of rubidium and cæsium. Schleede and Wellmann found that when an interplanar space is filled to capacity the metal atoms form layers parallel to, and midway between, the carbon layers. Also the metal atoms are regularly arranged in a triangular pattern so that they lie over the centres of alternate carbon hexagons. The carbon layer planes are orientated and superimposed relative to each other as in graphite. These X-ray studies confirmed the formula of the compound richer in alkali metal as C_8M and, in accordance with the triangular arrangement of metal atoms, showed that each carbon plane of the graphite is separated from its neighbours by a plane of metal atoms. The structure of the compound to which the formula $C_{16}M$ was assigned differed in that metal atoms were intercalated in every second interplanar space of the graphite, that is, every layer of metal atoms was separated by two carbon lamellae.

This earlier work has been re-examined by both Hérold[50] and Rüdorff.[51] The former studied the graphite–potassium system using an "isobar" method. In this method a bulb containing potassium metal maintained at 250° was connected to another bulb containing either purified Ceylon flake graphite or Acheson graphite the temperature of which was held at some predetermined value above 250°. After equilibrium was reached in approximately 12 hr. the whole tube was cooled and the graphite compound analysed. Repetition of this experiment over a range of temperatures for the graphite bulb permitted Herold to plot composition of the graphite compounds against the difference between the temperatures of the bulbs containing the graphite and the potassium. The resulting curve showed two plateaux corresponding to the compositions C_8K and $C_{24}K$. An uncertain composition of $C_{40}K$ was also observed. Calorimetric determination of the heat of reaction of graphite with an excess of potassium at several temperatures in the range 66° to 95° gave a mean value of 81 ± 2 cal./g.[52] Although this figure is for a high-density Acheson graphite, it differs considerably from the value of 125 cal./g. reported by Fredenhagen, Cadenbach, and Suck for natural graphite.[48]

X-Ray studies conducted by Hérold on compounds C_8K and $C_{77}K$ prepared by his "two bulb" method confirmed Schleede and Wellmann's structure for C_8K. In the case of $C_{77}K$ it was also confirmed that only

[49] Schleede and Wellmann, *Z. phys. Chem.*, 1932, **18**, *B*, 1.
[50] Hérold, *Bull. Soc. chim. France*, 1955, **187**, 999.
[51] Rüdorff and Schulze, *Z. anorg. Chem.*, 1954, **277**, 156.
[52] Quarterman and Primak, *J. Amer. Chem. Soc.*, 1952, **74**, 806.

half of the interlamellar spaces of the graphite were occupied and that separation of carbon lamellae by planes of metal atoms was 5·34 Å, the same as in C_8K.

The structure of C_8K and so-called $C_{16}K$ was studied by Rüdorff and Schulze[53] who prepared these compounds by heating finely divided crystalline graphite with weighed quantities of potassium in highly evacuated vessels. Their results are in good agreement with those of Hérold. However Rüdorff and Schulze's more detailed structure examination revealed in addition that the carbon layer planes which are normally offset in graphite are exactly superimposed when directly adjacent to potassium layers. In addition, distinct phases having the compositions $C_{36}K$, $C_{48}K$, and $C_{60}K$ were also shown to exist. These compounds, which may contain rubidium or cæsium instead of potassium, are formed by intercalation of alkali metal in only each third, fourth, or fifth interlamellar space of graphite respectively. Again, in each case, the ratio of atoms in the alkali-metal plane to those in the adjacent carbon plane was concluded to be 1 to 12. In these compounds, carbon lamellae adjacent to alkali-metal planes were found to be superimposed as in C_8K and $C_{24}K$.

McDonnell, Pink, and Ubbelohde[54] measured the electrical conductivity and magnetic susceptibilities of several graphite compounds including those of potassium to determine the effect of intercalated substances on the π electrons of graphite. Their results referring to graphite potassium are given in Tables 4 and 5.

TABLE 4. *Conductances of graphite and its compounds.*

Substance	*Bulk density* (g./c.c.)	*Conductance* (ohm^{-1}cm.$^{-1}$)	
		90°K	288°K
Graphite (A.E.R.E.)	1·19	26·5	35·2
Metallic K (compact)	0·86	—	150,000
$KC_{8\cdot46}$	—	1302	980
$KC_{8\cdot46}$	1·40	—	1271
$KC_{27\cdot8}$	1·05	—	565

TABLE 5. *Magnetic susceptibilities of graphite and its compounds* (c.g.s. × 10^{-6})

Substance	90°K		195°K		288°K		*Bulk density in Gouy tube*
	χ_s	χ_m*	χ_s	χ_m*	χ_s	χ_m*	
Graphite (A.E.R.E.)	−7·909	−94·81	−6·757	−81·08	−6·04	−72·48	0·783
Metallic K	+0·540	+21·1	+0·538	+21·0	+0·539	+21·1	0·849
$KC_{8\cdot47}$	+1·01	+16·78	+1·01	+16·78	+1·00	+16·61	0.730
$KC_{7\cdot79}$	+0·953	+16·23	+0·951	+16·17	+0·953	+16·23	0·713

*Calculated per g.-atom of carbon.

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[53] Rüdorff and Schulze, *Z. anorg. Chem.*, 1954, **277**, 156.
[54] McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191.

It is evident from these data that graphite–potassium compounds are "more metallic" than graphite. Also the penetration of potassium into graphite destroys the paramagnetism of the latter and increases its electrical conductance. These effects are attributed to the transfer of electrons from intercalated potassium atoms to the carbon layer planes of the graphite. Subsequently to these investigations, Ubbelohde[55] obtained samples of natural and synthetic graphite[56] in which large single crystallites showed excellent alignment of their crystal axis. Changes of the electrical conductivities of these samples resulting from intercalation of potassium (also ICl and bromine) in them were determined. It was found that introduction of potassium to give the compound C_8K reduced the resistance of the graphite in the direction of the *a*-axis by a factor of about 10. A reduction of 100 to 200 times was observed in the direction perpendicular to the carbon planes. This remarkably large change supports the existence of "quasi-metallic" bonds[55] between intercalated potassium atoms and graphite layer planes. Such bonds would permit metallic conduction paths in the direction of the *c*-axis.

Rüdorff and Schulze[53] measured the magnetic susceptibility of each of the five stages of graphite–potassium and graphite–rubidium (Table 6).

TABLE 6. *Molar susceptibilities of potassium- and rubidium-graphite compounds at* 295°K.

	Potassium compounds		*Rubidium compounds*	
		$\chi_m{}^*$		$\chi_m{}^*$
Graphite		-110		—
1st Stage	$CK_{0\cdot120}$	$+10\cdot0$	$CRb_{0\cdot119}$	$+5\cdot0$
2nd Stage	$CK_{0\cdot037}$	$+\ 8\cdot7$	$CRb_{0\cdot040}$	$+5\cdot1$
3rd Stage	$CK_{0\cdot027}$	$+\ 8\cdot5$	$CRb_{0\cdot028}$	$+5\cdot6$
4th Stage	$CK_{0\cdot021}$	$+\ 5\cdot7$	$CRb_{0\cdot019}$	$+6\cdot2$
5th Stage	$CK_{0\cdot015}$	$+\ 4\cdot0$	$CRb_{0\cdot014}$	$+3\cdot7$

*Calculated per g.-atom of carbon.

The weak paramagnetism displayed by both compounds in all stages is in accord with previous evidence that graphite becomes "more metallic" upon the introduction of alkali metals.

It had long been accepted that potassium, rubidium, and cæsium are the only alkali metals capable of intercalation in graphite. However, several recent investigations confirm that both sodium and lithium react with graphite under rather different conditions from those employed with the above metals. Asher and Wilson[57] found that stirring of finely divided graphite with molten sodium at about 400° yields a deep violet

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[55] Ubbelohde, Blackman, and Mathews, *Nature*, 1959, **184**, 454.

[56] Brown and Watt, Conference on Industrial Carbon and Graphite, Soc. Chem. Ind., London, 1957.

[57] Asher and Wilson, *Nature*, 1958, **181**, 409.

product having the composition $C_{64}Na$. *X*-Ray examination confirmed that this compound corresponds with a pure phase. The composition is also in accord with that given by Rüdorff for the phase in which every fifth interplanar space of graphite is occupied by metal atoms.

Hérold[50] detected reaction between sodium and graphite by the bluish colour assumed by the latter after the reactants had been heated in a closed steel tube at 900°. No reaction was observed when the experiment was repeated with an equi-atomic ratio alloy of sodium and potassium instead of sodium. However, a similar sodium–cæsium alloy reacted with resultant intercalation of both sodium and cæsium.

Small amounts of lithium were intercalated in graphite when the latter was made the cathode during electrolysis of a molten equimolar mixture of potassium chloride and lithium chloride at 400°. However, Hérold found heating of lithium with graphite in a high vacuum at 500° to be more effective. Under these conditions C_2Li_2 was the sole product after prolonged heating. Shorter heating periods however yielded intermediate products. One of these, C_4Li, is appreciably harder than graphite and gives a homogeneous golden-yellow powder when crushed. Beyond the Li:C ratio of 1:2, the intermediate is black. Hérold states that the intercalation of lithium is partly reversible and that heating of the C_4Li compound in a high vacuum at 700° liberates lithium vapour.

Yet another method of intercalating sodium and lithium in graphite was devised by Rüdorff.[58] Graphite is allowed to react with solutions of the various alkali metals in liquid ammonia or methylamine. According to the concentration of alkali metal in solution and particle size of the graphite used, one obtains a bluish alkali-rich compound, of approximate composition $C_{12}M(NH_3)_2$, or a black graphite compound having the ideal formula $C_{28}M(NH_3)_2$. Every interplanar space of the graphite crystal is occupied by alkali-metal atoms and ammonia in the first compound, and every third layer of the graphite layer is replaced in the second. Intercalation increases the interval between carbon layer planes from 3·35 Å to 6·6 Å in the case of metal–ammonia compounds and to 6·9 Å for the metal–methylamine compounds. Arrangement of alkali-metal atoms and ammonia molecules in the graphite interplanar spaces could not be determined from Debye diagrams. Nevertheless the latter showed that atoms in carbon layer planes between which intercalation occurs, occupy identical positions while the planes remain orientated to one another as in graphite.

At ordinary temperatures compounds of graphite with amines of potassium, rubidium, and cæsium can be stored in dry nitrogen for months without decomposition. However, the compounds containing sodium decompose in a matter of days and the lithium compounds even more rapidly. Liberation of hydrogen leads to the formation of metal amides. The decrease in stability of the graphite compounds with lowering of the

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[58] Rüdorff, Schulze, and Rubisch, *Z. anorg. Chem.*, 1955, **282**, 232.

atomic weight of the alkali metals is reflected in the behaviour of the compounds to liquid ammonia. Those containing potassium, rubidium, and cæsium can be washed at —40° whereas liquid ammonia extracts the alkali metal from those containing sodium and lithium.

Compounds of Graphite with the Halogens.—Although much of the chemistry of the halogens demonstrates a steady gradation in the properties of these elements, this is not at all true as regards their reactivity towards graphite. Only two members of the group, fluorine and bromine, react readily and then only to form different types of compound.[54] Iodine does not react with graphite at all, but chlorine has been observed to react slowly under favourable conditions.

Several theories have been suggested to account for the varied behaviour of the halogen towards graphite. Rüdorff, Sils, and Zeller[59] suggest that although chlorine has a high electron affinity, its polarisability is low. The reverse is true for iodine. Bromine on the other hand apparently exhibits both these properties to a sufficient degree. Hérold[50] recognised the importance of electron affinity and likewise cites this as the reason for the inactivity of iodine. In the case of chlorine he suggests that smallness of the chlorine ion limits the number of carbon atoms with which it may be closely associated. This according to Hérold would localise the chlorine ion with respect to one or so carbon atoms and not permit stabilisation of the chlorine carbon association by resonance as he suggests occurs in the case of bromine. Hérold has proposed a similar argument to account for reluctance of lithium to form lamellar compounds with graphite. This analogy between the halogens and the alkali metals seems reasonable since, like that of the lithium ion, the radius of the chlorine ion is less than that of the sodium ion. Seemingly the low ionic radius of the fluorine ion is also responsible for formation of compounds such as C_4F and $(CF)_n$ rather than the C_8F type. Detailed discussions of individual compounds will permit evaluation of these theories.

Graphite chloride. Evidence of reaction between chlorine and graphite was first obtained by Hennig[60] who observed that the resistance of graphite fell to one tenth of its original value after immersion for 3 days in liquid chlorine at —33°. Reactions conducted at room temperature in heavy-walled glass tubes were faster but always ceased at an early stage of chlorination. Repeated chlorination at temperatures below —30° after dechlorination in a stream of helium gas at —78° gave the most reproducible results.

In view of Hérold's suggestion that chlorine and bromine are unlikely to form similar types of compound with graphite, it is of particular interest that Hennig's measurements of relative electrical resistances and Hall coefficients for graphite compounds with either halogen agree closely (see Fig. 2).

[59] Rüdorff, Sils, and Zeller, *Z. anorg. Chem.*, 1956, **283**, 299.
[60] Hennig, *J. Chem. Phys.*, 1952, **20**, 1443.

Attempts by Hérold to study the formation of graphite chloride by the "isobar" method as used for the alkali metals, failed to reveal any intercalation of chlorine in purified natural flake graphite. The small amount of chlorine retained by the graphite was attributed to adsorption on the surface of the latter. Some condensation of chlorine in the pore structure of artificial graphite was detected.

Magnetic investigations conducted by Juza, Jönck, and Schmeckenbecher[61] support Hennig's conclusions. These investigators studied the change of magnetic susceptibilities of both natural and artificial graphites in contact with chlorine at various temperatures. Graphite was found to react with chlorine at —78° to the extent that its anomalous diamagnetism (—9·08 × 10^{-6} at —78°) was reduced to —0·4 × 10^{-6} c.g.s. unit. With purified natural graphite flakes measuring 0·5—1 mm. in diameter, this stage was reached in approximately 5 days. Fine-grained graphite samples and artificial graphite in which the flake size was of the order of 0·02 mm. reacted more rapidly. Temperature was found to influence the rate of change of susceptibility particularly in the case of coarse-grained graphite. This rate was found to be at its maximum at —12° but uptake of chlorine could not be detected magnetically at 0°.

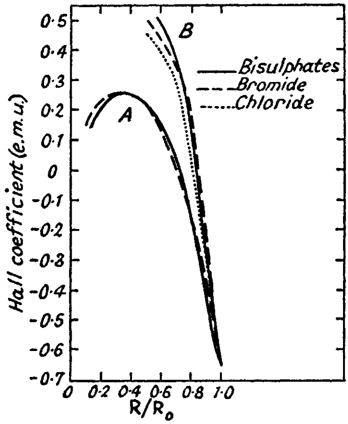

FIG. 2. *Relation between the Hall coefficients and the relative electrical resistances* (R/R_0) *of graphite compounds.*

A, Lamellar compounds. *B*, Residue compounds.

——— Bisulphates. - - - - Bromide. .... Chloride.

[Reproduced with permission from Hennig, *J. Chem. Phys.*, 1952, **20**, 1443]

Again, contrary to ion-size theory that chlorine would be more likely to follow fluorine than bromine in the type of compound it formed with graphite, it was found that at —78° the susceptibility of graphite ceases to decrease approximately at the composition C_8Cl. Isobaric thermal

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[61] Juza, Jönck, and Schmeckenbecher, *Z. anorg. Chem.*, 1957, **292**, 34.

degradation of graphite chloride at 65 mm. Hg also indicated a distinct stage corresponding with 0·11 g.-atom of chlorine per g.-atom of carbon or an approximate composition of C_9Cl. Although no structural datum is yet available to confirm that the carbon layer planes are separated by the inclusion of chlorine, pycnometric measurements at —78° show that the volume of the graphite is increased 42% when this occurs.

Impurities intentionally introduced into graphite exercise a marked influence on the inclusion of chlorine in graphite. Juza and Schmeckenbecher[62] have shown the accelerating effect of intercalated bromine and bisulphate ions on this inclusion. Figs. 3 and 4 refer to 12 hr. periods during which graphite–bromine residue compounds were (*a*) immersed in liquid chlorine at —78° and (*b*) heated with iodine at 142°. Although they will be discussed later, it may be helpful to note here that graphite residue compounds result when lamellar compounds are decomposed. Thus,

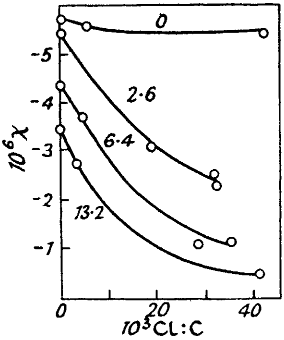

FIG. 3. *Occlusion of chlorine by bromine residue compound of Ceylon graphite.*

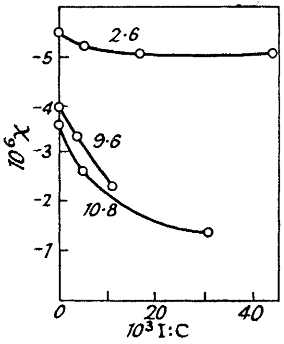

FIG. 4. *Occlusion of iodine by bromine residue compound of Ceylon graphite.*
[Reproduced with permission from Juza and Schmeckenbecher, *Z. anorg. Chem.*, 1957, **292**, 46]

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[62] Juza and Schmeckenbecher, *Z. anorg. Chem.*, 1957, **292**, 46.

while most of the intercalated substance can be removed from the graphite compound small quantities varying according to experimental conditions are not recovered, but remain trapped at imperfections in the graphite crystal. The various curves in Figs. 3 and 4 refer to bromine–graphite-residue compounds originally containing 2·6, 6·4, and 13·2 mg.-atom of bromine per g.-atom of carbon. The upper curve in Fig. 3 shows the action of chlorine on pure graphite. The curves clearly demonstrate the increase in chlorine sorption, as reflected by decrease in diamagnetic susceptibility of the bromine–graphite-residue compound, caused by increase of bromine in the latter. Iodine is also taken up in substantial quantities by the residue compounds, the amount increasing with bromine content of the latter (see Fig. 4). It should be noted however that since the quantity of iodine occluded may be as much as three times the bromine content, this is not a case of sorption of IBr.

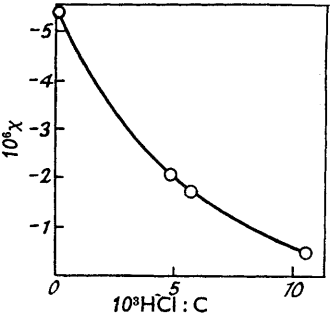

FIG. 5. *Effect of hydrogen chloride on the formation of graphite chloride by Ceylon graphite.*

[Reproduced with permission from Juza and Schmeckenbecher, *Z. anorg. Chem.*, 1957, **292**, 46]

Though not as effective as bromine, the bisulphate ion present in graphite–bisulphate-residue compounds also accelerates the occlusion of chlorine. A similar effect was observed when the residue compound resulting from decomposition of graphite chloride was rechlorinated.[63]

The effect of impurities on occlusion of chlorine discussed above appears due to some stabilising interaction between the chlorine and the residual impurities in the graphite. This may be so, but postulation of any such mechanism is made difficult by the fact that hydrogen chloride, which does not form a lamellar compound with graphite, also promotes sorption of chlorine by the latter. Juza and Schmeckenbecher[62] confirmed that hydrogen chloride has no influence on the magnetic susceptibility of graphite. However they found that at −78°, in the presence of excess of liquid chlorine, increasing quantities of hydrogen chloride cause proportionate increases in the amounts of chlorine occluded by the graphite as indicated in Fig. 5.

[63] Seidel, Dilplomarbeit, Kiel, 1957.

Compounds of graphite with iodine mono- and tri-chloride. During measurement of the electrical properties of the halogen compounds of graphite Hennig[60] observed that a graphite sample suspended in iodine monochloride vapour at room temperature gained up to 73·5% in weight and that its resistance relative to the original value for the graphite fell by almost 90%. On pumping, the weight gain was reduced to 8·03%. Although no structural examination was made, physical examination indicated that intercalation of ICl in graphite had occurred.

Further examination of the reaction between iodine monochloride by Rüdorff *et al.*[59] showed that at 30° graphite absorbed 2·5—2·6 g. of ICl from the gaseous phase per g. of carbon, *i.e.*, 1 molecule of ICl to 5·4—5·1 atoms of C. *X*-Ray diffraction confirmed that intercalation of ICl in the graphite interplanar spaces had occurred. Density measurements showed that occlusion of iodine monochloride caused the graphite lattice to expand 3·16 times in the *c* direction. This value and the identity period $Ic = 21{\cdot}15$ Å determined by *X*-ray diffraction indicates that ICl is occluded only after every second carbon plane in the graphite crystal.

A similar reaction between graphite and iodine trichloride has been reported by the Reviewer.[64] Immersion of graphite in liquid iodine trichloride at room temperature yielded a compound which after being washed with carbon tetrachloride contained *ca.* 30% of ICl_3.

Graphite bromide. When graphite is left in contact with bromine either in the vapour or the liquid form, it occludes 82—84% of its own weight of the halogen or approximately one bromine atom per 8 carbon atoms. On standing in the open air the graphite compound C_8Br rapidly loses bromine. Hérold[50] has confirmed the composition of graphite bromide and studied its formation and decomposition by the isobar method. Hysteresis curves obtained by him confirmed the ready desorption of bromine from C_8Br and also demonstrated the existence of residual compounds of graphite and bromine. Artificial graphites were also shown to form a compound of the formula $C_{10}Br$. The shape of initial sections of the curves relating to natural graphite suggests the existence of the unstable compound $C_{16}Br$.

Confirmation of the lamellar character of C_8Br is due to Rüdorff[65] who, by *X*-ray diffraction measurements, showed that while the hexagonal layer planes of graphite are preserved in this compound, bromine is intercalated in every second place between the planes and these spaces expand to 7·05 Å as a result of bromine penetration. Since the formation of C_8Br occurs only in the presence of saturated bromine vapour, and since the intercalated bromine is easily given off again, it might well be assumed that the graphite compound is simply a solution of bromine molecules in the graphite lattice. However, Rüdorff points out that the

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[64] Croft, *Austral. J. Chem.*, 1956, **9**, 184.

[65] Rüdorff, Fiat Rev. German Sci. 1939-46, Part I, 244; *Z. anorg. Chem.*, 1941, **245**, 354.

expansion of interplanar spaces to 7·05 Å is greater than the sum of the effective diameters of graphite plus a bromine atom layer. The value of the bromine increments, calculated from the molar volumes of graphite bromide after deduction of the graphite volume, is 23·5 c.c., which is closer to the ion increment of 25 c.c. than to the atomic increment of 19·2 c.c. Graphite bromide therefore appears to possess some salt-like character. This view is supported by the decrease of diamagnetism of graphite with increase of bromine contained in the latter. Goldsmith[66] found that at 298°K graphite containing 0·051 g. of bromine per g. of carbon had a susceptibility of $-4{\cdot}14 \times 10^{-6}$ compared with $-5{\cdot}29 \times 10^{-6}$ c.g.s./g. for the original graphite. For bromine contents of 0·67 g. and 0·71 g. per g. of carbon the susceptibilities were $-3{\cdot}1 \times 10^{-6}$ and $-0{\cdot}31 \times 10^{-6}$ c.g.s./g. respectively. Using Peierls's theory[67] of diamagnetism of free electrons in a solid and Wallace's theory[68] of the band structure of graphite, Smoluchowski[69] derived an expression connecting change in magnetic susceptibility with change in the number of electrons in the Brillouin zones. Goldsmith's results agree well with this expression if it is assumed that bromine ionises by accepting electrons from graphite when intercalated in the latter.

Hennig[60] and Hennig and McClelland[70] investigated the partial salt-like character of graphite bromides with the object of establishing the formula of the latter. From relative resistance data for graphite containing different amounts of bromine, it was estimated that the ratio of un-ionised to ionised bromine lies close to 6. This figure leads to the probable formula $C_nBr,3Br_2$. This formula was used in the process

$$C + 3{\cdot}5mBr_{2(g)} \rightarrow C^{m+}(3Br_2,Br^-)_m$$

to derive an expression for the free energy of formation of graphite bromide under various partial pressures of bromine. It was assumed that the work involved in moving graphite layers apart and inserting bromine is largely independent of the number of bromine molecules present and is essentially the difference between a van der Waals carbon–carbon bond and a carbon–bromine bond. Since no mixing occurred, it was also assumed that entropy changes would be independent of bromine concentration. The same independence of concentration was assumed for the dissociation and ionisation of intercalated bromine molecules. In the case of the graphite, however, it was recognised that ionisation of bromine by transfer of electrons from graphite would result in lowering of the Fermi energy of the latter. The effects of electrostatic interaction of intercalated ions and of distortion of the electronic band structure of graphite being neglected,

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[66] Goldsmith, *J. Chem. Phys.*, 1950, **18**, 523.

[67] Peierls, *Z. Physik*, 1933, **80**, 786.

[68] Wallace, *Phys. Rev.*, 1947, **71**, 622; Haering and Wallace, *J. Phys. and Chem. Solids*, 1957, **3**, 253.

[69] Smoluchowski, *Rev. Mod. Phys.*, 1953, **25**, 178.

[70] Hennig and McClelland, *J. Chem. Phys.*, 1955, **23**, 1431.

$$\Lambda{\cdot}F_m = -\sum_{1}^{m}\epsilon i - 3{\cdot}5mRT\ln(pm/pe) + m\,(3{\cdot}5B + E)$$

gives the total free energy of the above reaction. In this equation ϵ represents the energy of the *i*th electron in graphite, *E* the free-energy of dissociating and ionising the bromine, *p*m the reaction pressure and *p*e the saturation pressure of bromine. The term *B* is proportional to the work involved in moving graphite layers apart and inserting layers of bromine molecules. Modification of this equation to include Wallace's calculation of the energy spectrum of electrons in two-dimensional graphite permitted Hennig to plot in Fig. 6 the lowering of the Fermi level of graphite resulting from intercalation of bromine.

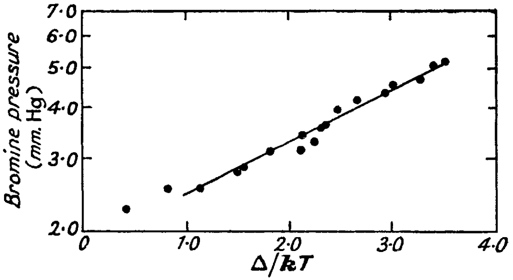

FIG. 6. *Lowering of the Fermi level of graphite by bromine.*
[Reproduced with permission from Hennig and McClelland, *J. Chem. Phys.*, 1955, **23**, 1431]

Hennig suggests that the fact that only part of the bromine in graphite bromide is ionised may be due to mutual electrostatic repulsion of negative bromine ions, this requiring uncharged molecules to act as "spacers" between the latter. Hérold[50] on the other hand does not consider that any particular bromine atoms form ionic bonds with the carbon layer planes. It appears more probable to him that the ionic bond resulting from the transfer of an electron from a carbon plane to intercalated bromine resonates between all atoms of the latter and the carbon atoms in contact with them. According to this hypothesis the C–Br bond should be substantially metallic in character.

Investigations conducted by McDonnell, Pink, and Ubbelohde[54] demonstrate clearly that graphite bromide is "more metallic" than graphite. They show that the diamagnetism of graphite is lowered considerably by intercalation of bromine: from $-6{\cdot}04 \times 10^{-6}$ for graphite to $-0{\cdot}403 \times 10^{-6}$ c.g.s. units/g. for $C_{9{\cdot}98}Br$ at 288°K. The corresponding change in conductance for the same samples was found to be 35·2 to 38·4 $ohm^{-1}cm.^{-1}$. Measurements of the thermoelectric voltages of graphite and $C_{9{\cdot}9}Br$ against brass for the difference between liquid-air and room temperature also illustrate the more metallic nature of the lamellar compound: the voltage for graphite was $-0{\cdot}5$ v and for $C_{9{\cdot}9}Br$ $-2{\cdot}4$ v.

Concurrent investigation of the compound C_8K by these authors established a fair measure of similarity between C_8K and C_8Br and the complete work on these two compounds provides an excellent demonstration of the amphoteric properties of the carbon layer planes of graphite, taking up electrons from potassium atoms on the one hand and donating them for the ionisation of bromine on the other.

Graphite bisulphate. When graphite is treated with concentrated sulphuric acid and one of a number of oxidising agents, *e.g.*, concentrated nitric acid, it swells and assumes an iridescent dark blue colour. Subsequently this was found to be due to the intercalation of bisulphate ions and sulphuric acid molecules between the carbon layer planes of the graphite. The compound resulting from the oxidation of graphite as described therefore became known as graphite bisulphate. Most of the chemical aspects of formation, properties, and also of structure were investigated before 1945 and details of these investigations are to be found in Riley's review.[1]

Recent interest in graphite bisulphate has been largely in connection with the electronic constitution of carbons and graphite. Kmetko,[71] for example, made use of the increase of conductivity, which results when a graphitic carbon is converted to the bisulphate, to follow changes in the properties of carbons caused by heat-treatment. Conductivity and Hall coefficient measurements indicated that the influence of chemical oxidation on the electrical properties of graphitic carbons depends upon crystallite sizes in the latter, being greater for carbons composed of larger crystals. Mrozowski[72] suggested that study of the electronic properties of such compounds as graphite bisulphate in relation to bisulphate ion content of the latter might provide a means of investigating the Brillouin zones in graphite. He developed this idea both theoretically and by examination of Hennig's experimental data and concluded, first, that simple electronic models are unsatisfactory for the interpretation of electrical properties of ionic compounds of graphite and, secondly, that it is probable that large graphite crystals possess slightly overlapping Brillouin zones.

Krishnan and Ganguli[73] verified experimentally that introduction of bisulphate ions into graphite has the effect of reducing the abnormal diamagnetism of graphite parallel to the layer planes (from -22×10^{-6} to -2×10^{-6} c.g.s. units/g.) but causes virtually no change in the susceptibility in the direction normal to the carbon planes.

Hennig[74] determined the electrical resistance, its temperature dependence, and the Hall coefficients of graphite bisulphate compounds at various states of oxidation. This author's results indicate that the resistance of graphite is lowered and the sign of its Hall coefficient

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[71] Kmetko, *J. Chem. Phys.*, 1953, **21**, 2152.
[72] Mrozowski, *J. Chem. Phys.*, 1953, **21**, 492.
[73] Krishnan and Ganguli, *Z. Krist.*, 1939, *A*, **100**, 530.
[74] Hennig, *J. Chem. Phys.*, 1951, **19**, 922.

changed by oxidation. Both effects are consistent with the general view that the electrons in graphite fill one conduction band except for a small number of electrons which are excited into a nearly empty band. Current carriers therefore consist of excited electrons and vacancies in the lower band. According to Hennig, oxidation further depletes the lower band thereby increasing the number of unpaired electrons therein, but reduces the number of excited electrons in the upper band to a lesser extent. As a result the total number of current carriers increases with consequent lowering of resistance. Since the greater number of carriers is in the lower band, the Hall coefficient is positive. Also, since temperature has only a slight effect on the number of positive carriers the temperature coefficient of resistance becomes small and changes sign because temperature disturbances of the lattice eventually increase the resistance beyond the point where it can be compensated by thermal excitation of electrons into the empty band. Because of the smaller number of permanent scattering centres[7] the already positive temperature coefficient of the graphite increases further with oxidation. Hennig failed to obtain a quantitative correlation of his experimental results with data calculated from Wallace's band theory of graphite and concluded that a two-dimensional model of graphite is inadequate for calculation of the effect of oxidation on the electronic structure of the latter.

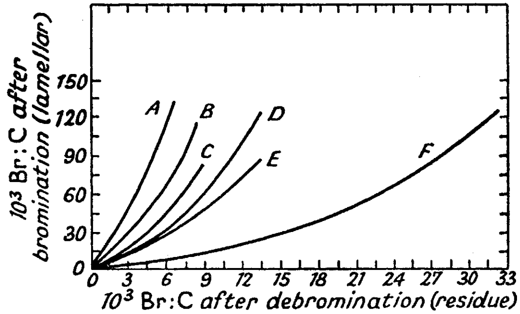

FIG. 7. *Effect of particle size on the relation between composition of the parent graphite bromide (lamellar) and that of the corresponding residue compound. Curve A refers to debromination at* 310° *and holds for a range of particle sizes; curves B, C, D, E, and F refer to particle sizes of* 25 μ, 59 μ, 74 μ, 125 μ, and 600 μ, *respectively, for debromination at* 27°.

[Reproduced with permission from Hennig, *J. Chem. Phys.*, 1952, **20**, 1438]

Graphite bifluoride. Until the discovery of this compound by Rüdorff[65,75] all known graphite salts contained ions and molecules of oxyacids. Graphite bifluoride can be prepared by anodic oxidation of graphite or by oxidation with fluorine in the presence of anhydrous hydrogen fluoride. It has the formula $C_{24}^{+}HF_2^{-},2H_2F_2$ which corresponds with $C_{24}^{+}HSO_4^{-}$,

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[75] Rüdorff, *Z. anorg. Chem.*, 1947, **254**, 319.

$2H_2SO_4$, the composition of the first stage of graphite bisulphate. Reduction of graphite bifluoride yields second, third, and fourth stages of intercalation similar to those of the bisulphate. Rüdorff has confirmed by *X*-ray examination that carbon layer planes in the bifluoride are separated to a distance of 8 Å as they are in other graphite salts. As usual with graphite salts, graphite bifluoride is only stable in anhydrous hydrogen fluoride. The original graphite can be readily obtained from it by reduction or by the action of water.

Graphite Residue Compounds.—Many of the lamellar compounds of graphite can be decomposed in a manner which leads to the recovery of the substance originally intercalated in the graphite. In such cases most of the intercalated substance is recovered, but, as Hennig[76] found, a small amount may remain in the graphite. This residue can only be removed by more drastic treatment. Decomposition products in which small amounts of the original reactant are tenaciously retained have been termed residue compounds.

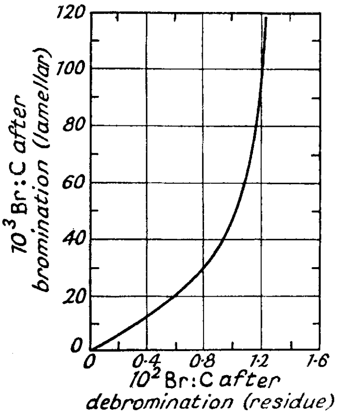

FIG. 8. *Composition of the graphite bromide residue compound as a function of that of the parent lamellar compound.*

[Reproduced with permission from Hennig, *J. Chem. Phys.*, 1952, **20**, 1438]

The amounts of impurity retained in residue compounds varies with the nature of the original graphite and the composition of the lamellar compound from which it was obtained. Herold[50] studied residue compounds of graphite bromide and found that those of Acheson graphite retained 10% of bromine whereas the amounts retained in Ceylon and Madagascar flake graphites were 5 and 7% respectively. Results of Hennig's studay on the effects of particle size and temperature of decomposition shown in Fig. 7 indicate that finely divided graphites retain considerably less bromine than do coarser graphites.[76] Fig. 8 also demonstrates that the

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[76] Hennig, *J. Chem. Phys.*, 1952, **20**, 1438.

amount of bromine retained in the residue compound increases with increasing bromine content of the lamellar compound from which it is obtained.

Several ways in which impurities are retained in residue compounds have been suggested. Hennig recognised two possibilities. Impurities may be trapped between carbon layer planes, as in lamellar compounds, but in much lower concentrations, or alternatively they may be trapped at imperfections in the graphite crystal lattice. Since the distance between graphite layer planes would be altered in the first case but not in the second it was possible to show by *X*-ray measurement that the amount of impurity trapped between carbon planes in residue compounds of graphite bromide and graphite bisulphate was only 1% or less of the total impurity in each case. Trapping of impurities probably occurs at crystallite boundaries since these are the only imperfections present in sufficient concentration to account for the amounts of impurity trapped. It is also probable that substantial trapping could occur at hole and claw defects in the layer planes. Such imperfections have been suggested by Ubbelohde[77] to account for observations on unpaired electron spins which have been observed[78] in partly ordered graphite. Hennig's observation that larger particles of graphite retain more impurity in the residue compound than do small particles clearly supports the latter possibility since consideration of crystallite boundaries in a simple geometrical sense would lead to the opposite conclusion. Also, the fact that high concentration of the intercalated substance in a lamellar compound favours a high proportion of impurity retained in the residue compound obtained from it, implies that graphite imperfections responsible for trappings are not easily reached and that their saturation occurs under conditions which also favour maximum intercalation during formation of the lamellar compound.

As can be seen from Fig. 7, residue compounds of graphite bromide possess substantial thermal stability at 310°. Hérold reports that these compounds are not completely decomposed by molten potassium hydroxide and that they liberate bromine and bromine derivatives of carbon only slowly at red heat.

Bromine retained in the residue compound of graphite bromide lowers the diamagnetism of the original graphite as it does in the lamellar compound. This decrease is shown in Fig. 9 as a plot of relative susceptibility against acceptor concentration, *i.e.*, bromine ion concentration determined from electrical resistance measurements. Similarities between the electrical properties of lamellar and residue compounds have also been observed. Results of measurements given in Fig. 2 illustrate this and furthermore demonstrate similarity in properties of the halogen and bisulphate compounds of each type. Since the bisulphate compound is believed to be

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[77] Ubbelohde, *Nature*, 1957, **180**, 380.

[78] McIntosh, Robertson, and Vand, *J.*, 1954, 1661.

partly ionic,[1] this agreement in properties suggests that each of the halogen compounds is partially ionic in both lamellar and residue forms.

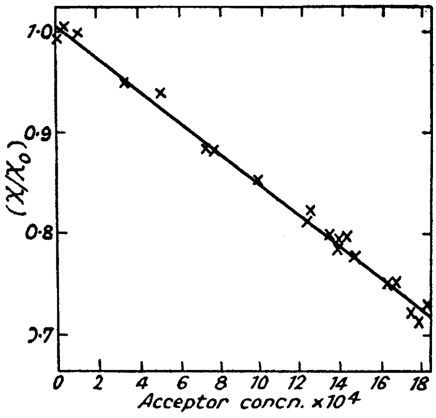

FIG. 9. *Relative susceptibility* (χ/χ_0) *of conduction electrons in graphite containing acceptors.*

[Reproduced in part with permission from Hennig and McClelland, *J. Chem. Phys.*, 1955, 23, 1431; the points are from the original paper but the curve has been redrawn by the Reviewer.]

Chemical reactions of residue compounds. Graphite bromide residue compounds react more rapidly and to a greater extent with chlorine than does graphite. Hennig[76] observed that in 30 minutes a sample of graphite suspended above boiling liquid chlorine took up only 0·3 atom % of chlorine, whereas under the same conditions the residue compound containing 1 atom % of bromine gained 3 to 4 atoms %. Similarly a residue compound containing 1·44 atoms % of bromine took up 28 times more $AlCl_3$ than graphite when heated at 200° in a vacuum with the trichloride. Reaction of graphite bromide residue compounds with iodine is of particular interest because graphite does not react at all with iodine. A residue compound containing one atom % of bromine left standing for 6 months in iodine vapour at room temperature took up enough iodine to lower the electrical resistance of the compound by 50%. These observations agree with conclusions drawn from magnetic investigations by Juza and Schmeckenbecher.[62] The latter also note that rate of intercalation of molecular chlorine in residue compounds of graphite chloride is greater than in the case of graphite.

Molecular Compounds of Graphite.—These compounds are distinguished from other compounds of graphite by the fact that the substances intercalated in them are, at the moment of penetration of graphite at least, molecular and not atomic or ionic as in other cases. The best known and most studied example of this class is graphite–ferric chloride[1,79,80] formed by the intercalation of $FeCl_3$ molecules in graphite when mixtures of these reactants are heated at temperatures generally above 250°. As in the case of C_8K and C_8Br, intercalated molecular substances can be recovered from graphite compounds, that is, formation of the latter is reversible (except for the formation of residue compounds which retain small quantities of the molecular impurity). As this similarity implies, the molecular compounds are ionic as is shown by the fact that the electrical conductivity of graphite–ferric chloride is greater than that of graphite.[80] Also, change in sign of the Hall coefficient as the result of intercalating ferric chloride in graphite[81] indicates that electrons are transferred from the graphite to the chloride. Like other ionic compounds of graphite, the molecular compounds form stages characterised by structure and composition. In the first stage corresponding with maximum intercalation they also show the iridescent blue colour typical of other ionic graphite compounds.

The molecular compounds are more stable than the other ionic compounds of graphite. Consistently with their relatively high temperatures of formation they are reasonably stable to heat. Admittedly graphite–ferric chloride loses $FeCl_3$ when heated, say, at 320°, but the $FeCl_3$ content of the compound only falls from 56 to 32%. In the main, solvents and mineral acids (except concentrated sulphuric and concentrated nitric) do not react with or remove noticeable quantities of the intercalated substance.

Advances in experimental techniques are largely responsible for several of the more recent investigations of graphite discussed here. The exchange of ferric ions between graphite–ferric chloride ($C_{12},FeCl_3$) and solutions of radioactive[59] $FeCl_3$ in various solvents was studied by Lazo and Hooley.[82] No exchange was observed. In further experiments, $C_{12},FeCl_3$ was irradiated for 48 hr. in a neutron flux of 4×10^{12} cm.$^{-2}$ sec.$^{-1}$. Examination of acid extracts of the irradiated compound showed that only 1% of the total number of iron atoms had been extracted. Since activation of the iron atoms with neutrons at this density would break the bonds linking them with chlorine atoms, the fact that such a small proportion of the iron atoms could be extracted indicates two possibilities. Either the remaining 99% of the iron atoms recombined with the lattice on dissipation of the radiation energy, or these atoms were inaccessible to the extracting acid. Although these experiments did not succeed in their object of elucidating the nature of bonds between graphite and ferric chloride intercalated in it, the results indicate that the strength of these bonds is reasonably high. Possibly steric hindrance accounts for the results, but this does not seem likely as Rüdorff and Schulze[80] noted that ammonia

[79] Thiele, *Z. anorg. Chem.*, 1932, **207**, 340.
[80] Rüdorff and Schulze, *Z. anorg. Chem.*, 1940, **245**, 121.
[81] Hennig, Proceedings of the Carbon Conference Symposium, Buffalo, 1955, 103.
[82] Lazo and Hooley, *Canad. J. Chem.*, 1956, **34**, 1574.

can enter the lattice of graphite–ferric chloride and fully co-ordinate the ferric ions.

In the first detailed examination of graphite–ferric chloride Rüdorff and Schulze[80] claimed the existence of two complexes: the first, obtained by heating an excess of anhydrous ferric chloride and graphite at 180—300°, contained 60—72% of ferric chloride; and the second, obtained at 325—400°, contained 31—37%. A small fraction of the ferric chloride could be removed by digestion with dilute acids, leaving residues which were stable to further treatment with boiling dilute acids, alkalis, and reducing agents. *X*-Ray diffraction studies of the stable complexes showed that, in the first complex, layers of hexagonally spaced carbon atoms alternate with layers of ferric chloride, whereas in the second complex three carbon layers separate each layer of ferric chloride.

The existence and stability of the ferric chloride complexes described above has been confirmed by the Reviewer[83] using a natural graphite of Australian origin. It was found, however, that the second complex described by Rüdorff and Schulze is a decomposition product of the first. Thus the complex containing 60—72% of ferric chloride is formed at all temperatures in the range 180—400°. This complex can be freed from excess of ferric chloride by sublimation up to 309°. Above that temperature, however, it decomposes to yield the 31—37% complex. If unchanged ferric chloride and the graphite–ferric chloride complex prepared above 325° are separated by washing with dilute hydrochloric acid instead of by the sublimation method employed by Rüdorff and Schulze, the washed complex contains 56—57% of ferric chloride. This composition is the same for acid-washed complexes prepared in the range 180—325°.

Ibers and Cowley[84] have re-examined the structure of graphite–ferric chloride by high-resolution electron-diffraction techniques and by *X*-ray powder photography. They found that the so-called first-stage compound containing 55·5% of $FeCl_3$ consists of about 17% of free graphite and about 83% of a graphite–ferric chloride compound. Detailed analysis of the structure of the latter by the above methods revealed that the intercalated chlorine ions attempt to occupy preferred positions relative to the carbon lattice as in Fig. 10. This tendency is demonstrated by the 30° angle between the *a* axis of the $FeCl_3$ and graphite and also by variations in Cl–Cl distances which range from 3·15 Å to 4·2 Å compared with normal distances of 3·40, 3·49, and 3·75 Å in ferric chloride. The possibility of excessive distortion prevents more than approximately half of the chlorine ions from occupying these preferred positions. Those which do are distributed randomly in the chlorine planes. Further observations indicate that graphite–ferric chloride exists in a single phase of variable composition at high temperatures, but at room temperature the stable phases are free graphite and a graphite compound richer in ferric chloride. This is also

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[83] Croft, *J. Appl. Chem.*, 1952, **2**, 557.

[84] Ibers and Cowley, *Acta Cryst.*, 1956, **9**, 421.

true for graphite–ferric chloride compounds prepared by thermal decomposition of the compound containing 55·5% of $FeCl_3$. During thermal decomposition, therefore, the $FeCl_3$ content is reduced partly by loss of ferric chloride contained in each layer and partly by increase in the amount of free graphite. Ibers and Cowley confirmed that the presence of free graphite in all cases was not due to inadequate reaction between graphite and ferric chloride. They showed, as had Boehm and Hofmann,[85] that the rhombohedral form of graphite present in the starting material was absent from graphite recovered after intercalation. These observations are inconsistent with the ordered structure of layers proposed by Rüdorff and Schulze,[80] and Ibers and Cowley were unable to confirm the types II and III graphite–ferric chloride claimed by these authors.

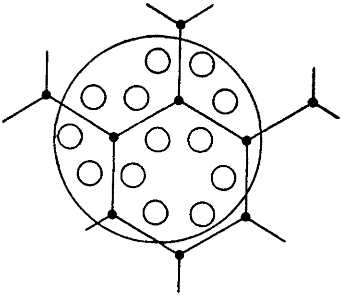

FIG. 10. *Preferred position of chlorine atoms (circles) relative to a carbon layer lattice.* [Reproduced from Ibers and Cowley, *Acta Cryst.*, 1956, **9**, 421]

Since the discovery of graphite–ferric chloride by Thiele,[79] many new molecular compounds of graphite have been found. Croft and Thomas[86] observed that graphite reacts readily with chromyl chloride both in the pure state and in solution in carbon tetrachloride to give a compound containing up to 43% of CrO_2Cl_2. The reaction with chromyl fluoride in which some 40% of the fluoride is intercalated in graphite was found to be very rapid. Croft[64] examined the reactivity of a large number of chlorides towards graphite and reported the results given briefly in Table 7.

The new compounds listed above resemble graphite–ferric chloride in appearance and as regards expansion of the original graphite in the direction of the *c*-axis. In most cases, intercalated substances can be recovered unchanged by reversal of the formation process. The compounds formed by graphite with chlorides of Group III elements and yttrium and zirconium differ from the remaining compounds in that these chlorides are capable of hydrolysis while intercalated in graphite. However, in view of their resemblance to graphite–ferric chloride which has been shown to be an ionic compound[80,87] it appears that all the new compounds

[85] Boehm and Hofmann, *Z. anorg. Chem.*, 1955, **278**, 58.

[86] Croft and Thomas, *Nature*, 1951, **168**, 32.

[87] Dzurus and Hennig, *J. Amer. Chem. Soc.*, 1957, **79**, 1051.

are ionic and that their formation involves transfer of electrons from graphite as demonstrated[54,55] for other ionic graphite compounds.

Table 7 shows that graphite is remarkably specific in its reactions with chlorides. The latter are either intercalated in substantial quantities (15—83% w/w in a compound) or, if unreactive, in amounts not detectable by normal analytical procedures. Also with few exceptions only the chlorides of transition elements and elements of Group III (boron, aluminium, etc.) react with graphite. Furthermore, only those chlorides in which the cations normally exhibit multivalency and are in their highest valency states are intercalated. The reason underlying the specificity of graphite reactions with chlorides does not appear to be connected with polarity or molecular size of the latter. Covalent character of a chloride is not a necessary condition for intercalation either. This is apparent from the difference in behaviour of titanic and stannic chloride from that of chromyl chloride and cupric and chromic chlorides.

TABLE 7.

Substances intercalated in graphite			*Substances not intercalated in graphite*			
$CuCl_2$	$SbCl_5$	$RbCl_3$	$CuCl$	$SiCl_4$	$AsCl_3$	$PdCl_2$
$CuBr_2$	$TaCl_5$	$PdCl_4$*	$BeCl_2$	$CeCl_4$	$SbCl_3$	$PtCl_2$
$AuCl_3$	$FeCl_3$†	$PtCl_4$	$MgCl_2$	$TiCl_4$	$BiCl_3$	$LaCl_3$
BCl_3	$CrCl_3$	ICl†	$CaCl_2$	$FeCl_2$	VCl_4	$CeCl_3$
$AlCl_3$†	CrO_2Cl_2†	ICl_3	$BaCl_2$	$SnCl_2$	SO_2Cl_2	$PrCl_3$
$AlBr_3$	CrO_2F_2†	YCl_3	$ZnCl_2$	$SnCl_4$	$SOCl_2$	$NdCl_3$
$GaCl_3$	$MoCl_5$	$SmCl_3$	$CdCl_2$	$PbCl_2$	$SeOCl_2$	$ErCl_3$
$InCl_3$	WCl_6	$GdCl_3$	CdI_2	$PbCl_4$	$TeCl_4$	$ScCl_3$
$TlCl_3$	UCl_4	$YbCl_3$	Hg_2Cl_2	$ThCl_4$	$MnCl_2$	
$ZrCl_4$	UO_2Cl_2	$DyCl_3$	$HgCl_2$	ThI_4	$CoCl_2$	
$HfCl_4$	$ReCl_4$	$EuCl_3$	CCl_4	PCl_3	$NiCl_2$	
	$CoCl_3$*			PCl_5		
	$RuCl_3$					

*Normally unstable, but stable when intercalated in graphite.
†Previously known to react.

Croft[88] observed that intercalation of chlorides can be correlated with the positions of their cations in the Periodic Table and is therefore probably related to the outer electronic configurations of the cations concerned. Cations of successfully intercalated chlorides (excepting those of Group IIIA elements) all have incomplete penultimate electron shells in which electrons from the upper conducting band of graphite might be accommodated. This interpretation would require that these molecular

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[88] Croft, *Austral. J. Chem.*, 1956, 9, 194.

compounds of graphite owe their existence to the transfer of π electrons of graphite to incompletely filled electron shells of intercalated metal cations. The physical requirements of intercalation would readily be met by expansion of the graphite host structure normal to the carbon layers.

That high electron affinities of intercalated cations would assist electron transfer from graphite is confirmed by the experimental observation that only higher chlorides or transition-metal chlorides are intercalated.

Croft suggests therefore that two conditions are necessary for intercalation. First, electronic interaction between a cation and graphite must be possible; secondly, the electron affinity of the cation must be sufficient to promote such interaction. These conditions, which account for the specificity shown by graphite towards chlorides, are the same as those proposed by Mulliken[89] and can be conveniently represented by the spectrographic expression[90] for the energy required to effect charge transfer:

$$W = E_A - I_D + \Delta$$

where E_A is the electron affinity of the acceptor, I_D the ionisation potential of the donor, and Δ the difference in energy of the reacting system, including environment, before and after transfer, should be applicable to the intercalation phenomena shown by graphite. Interpretation of the experimental results along these lines suggests that intercalation occurs by reason of the low ionisation potential of π electrons of graphite and maximum electron affinities of cations which the latter show in their higher valency states.

Elucidation of the manner in which charge is transferred from graphite to (n—1) d orbitals of transition-metal cations awaits full investigation. At present, however, transfer appears to occur *via* associated anions. This suggestion is consistent with the lack of correlation between intercalation and spatial configurations of chloride molecules. Observations on paramagnetic resonance, particularly those of Hennig[91] and Owen and Stephens,[92] and also Zener's[93] and Zener and Heikes's[94] interpretation of charge transfer in the solid state, provide a reasonable basis for these views. The probability, voiced by Weyl[95] and Hennig, that high polarisability facilitates charge transfer over considerable distances also supports the above interpretation.

The foregoing explanation of intercalation is inapplicable to the Group III chlorides. For these Croft suggests that cations of these chlorides can only interact with graphite by means of vacant valency orbitals which may accept paired but not single electrons from $2p\pi$ orbitals of graphite.

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[89] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

[90] Orgel, *Quart. Rev.*, 1954, **8**, 422.

[91] Hennig, *Phys. Rev.*, 1954, **95**, 1088.

[92] Owen and Stevens, *Nature*, 1953, **171**, 836.

[93] Zener, *Phys. Rev.*, 1951, **82**, 403.

[94] Zener and Heikes, *Rev. Mod. Phys.*, 1953, **25**, 191.

[95] Weyl, *J. Phys. Chem.*, 1951, **55**, 507.

Interaction in this manner required graphite to behave as an "onium"-type donor as described by Mulliken and for convenience is referred to as "co-ordination". Taking the intercalation of aluminium chloride as typical for the Group IIIA chlorides, he further suggests that reaction of aluminium chloride in the vapour state involves dissociation of the dimeric chloride molecules with the result that one of the four sp^3 hybrid bonds originally maintaining the dimeric form becomes available for electronic interaction with the graphite. The experimentally confirmed possibility of hydrolysing intercalated aluminium chloride appears to be due to the ability of water molecules to usurp the co-ordinating rôle of graphite.

Dzurus and Hennig[87] examined the formation of graphite–aluminium chloride and concluded that the presence of some easily reducible substance, *e.g.*, Cl, Br, I, or $FeCl_3$, was necessary to permit the intercalation of $AlCl_3$ in graphite. They also found that the ions of one of these substances was always intercalated together with the chloride, approximately in the ratio of one ion to three molecules of the latter. When gaseous chlorine was used as a catalysing substance, it was found that the amount of aluminium chloride intercalated depended quantitatively on the amount of chlorine available, and that intercalation ceased when the supply of the latter became exhausted. Electrical measurements showed that electrons were removed from graphite in these compounds and that the acceptor concentrations thus determined corresponded with the amount of ionising species, other than $AlCl_3$, present. Dzurus and Hennig therefore suggested that only the substance which promotes the occlusion of aluminium chloride and is intercalated with it is ionised as a result of electron transfer from graphite. The rôle of $AlCl_3$ molecules is to stabilise the resulting graphite compound by separating and screening the charges on the ions of the catalysing substance. In other words, $AlCl_3$ molecules act as "spacers" and do not themselves interact with the graphite. In many respects, the results and interpretation given by Dzurus and Hennig are similar to those relating to residue compounds, discussed earlier, particularly as the presence of an ionising species occluded as a residue impurity permits the intercalation of substances, *e.g.*, iodine, which are not capable of penetrating graphite alone. This similarity is of interest, because, in the case of residue compounds, the residue substance is trapped at graphite lattice imperfections and is not interlamellar;[76] hence intercalated molecules of the normally unreactive substance cannot behave as "spacers".

One difficulty in regarding $AlCl_3$ as an inert "spacer" is that other chlorides do not behave in the same way. For example, heating graphite and arsenic trichloride together in chlorine does not yield a graphite–$AsCl_3$ compound. Furthermore, if $AlCl_3$ is regarded as inert it is difficult to see how it catalyses the intercalation of reasonable quantities of chlorine which is difficult at lower temperature and according to observations of Juza, Jönck, and Schmeckenbecher[61] and Hennig[60] not possible in the region of 200°.

Rüdorff and Zeller[96] have made a thorough investigation of the reaction of aluminium chloride with graphite in the presence of nitrogen, oxygen, and chlorine. They found that reaction occurs only in the presence of chlorine and that, depending on the temperature, it is possible to obtain intercalation of the chloride in adjacent, every second, or every fourth interlayer space of the graphite lattice. The first of these stages is stable up to 280° and contains 52—55% of $AlCl_3$ ($C_{9-10},AlCl_3$). The second is formed between 280° and 372° and contains 36—39% of $AlCl_3$ ($C_{18},AlCl_3$), and the fourth stage containing 18—26% of $AlCl_3$ is formed between 372° and 470°. The increase in interlayer spacing resulting from intercalation was found to be from 3·35 to 9·5 Å. In all cases Rüdorff and Zeller found the Al:Cl ratio to be exactly 1:3. Subsequent investigations[97] showed, however, that the intercalation of aluminium chloride and of gallium trichloride is accompanied by the simultaneous inclusion of small quantities of additional chlorine in the graphite lattice. The metal:chlorine ratio of 1:3 was found to be preserved in intercalated $InCl_3$. Rüdorff and Landel[97] confirmed that both gallium trichloride and indium trichloride react with graphite only in the presence of chlorine. Like aluminium chloride, gallium trichloride forms first, second, and fourth stages and the interlayer spacing of the graphite lattice is again evident to 9·5 Å. The first stage contains 60% of $GaCl_3$ and is stable up to 270°. The second stage containing 45% of $GaCl_3$ can be prepared by heating the first stage at 280°. At 400° the $GaCl_3$ content falls from 45 to 25% and marks the appearance of the fourth stage. Because of the high sublimation point of indium trichloride (489°), Rüdorff and Landel conducted reactions of this chloride with graphite between 400° and 500°. As a result only the second-stage compound containing 53% of $InCl_3$ was obtained. Rüdorff and Landel confirmed that all three chlorides are accessible to water and solvents in the intercalated state.

Other molecular compounds of graphite which have been examined in detail recently include those formed with iodine monochloride and chromyl chloride. Rüdorff, Sils, and Zeller[59] showed that 1 g. of graphite absorbs 2·5 g. of ICl from a saturated vapour of the latter. The expansion of the graphite lattice in the direction of the *c*-axis as a result of absorption of this amount of ICl is 3·21. Graphite also reacts readily with liquid CrO_2Cl_2 absorbing 1·05 g. of the latter per g. of graphite. In this case the graphite lattice expands 2·18 times in the *c* direction. Rüdorff states that the graphite–chromyl chloride compound is decomposed by washing with various solvents (H_2O, CCl_4, etc.). This is true as regards removal of excess of chromyl chloride used in the preparation of the graphite compound. It is noteworthy however that the Reviewer recently examined a sample of graphite–chromyl chloride which has been kept in carbon tetrachloride in a glass-stoppered vessel for seven years. No chrom-

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[96] Rüdorff and Zeller, *Z. anorg. Chem.*, 1955, **279**, 182.
[97] Rüdorff and Landel, *Z. anorg. Chem.*, 1958, **293**, 327.

ium compounds were detected in the liquid carbon tetrachloride. Although the explanations advanced by Croft[88] to account for the specificity shown by graphite in its reactions with metal chlorides are essentially theoretical, they have been useful in directing attention to two important aspects of molecular compound formation. First, they indicate that intercalation of chlorides in graphite is entirely dependent on electronic configuration of the cation and, secondly, that substances, other than graphite, possessing accessible intracrystalline space and the capacity for electronic interaction should exhibit the intercalation phenomenon.

TABLE 8. *Intercalation of sulphides and oxides in graphite.*

Test compound	*Composition of reaction mixture*	*Heated*		*Composition of graphite after reaction and washing (%)*			*Empirical formula of intercalated metal sulphide*
		At (°C)	*For* (*hr.*)	*Metal*	S	C	
S	Reactants mixed in ratio S:graphite 1:1	510	16	—	0·00	99·87	—
Sb_2S_5	B.D.H. ex-stock mixed with equal weight of graphite	510	17	5·80	3·60	90·60*	$Sb_2S_{4\cdot8}$
Tl_2S	Mixture of Tl_2S, S, and graphite in ratio 1:1:1·7 heated together	200	17	20·60	6·45	72·95*	TlS_2
Cu+S	Cu powder, S, and graphite mixed in ratio 2:3:1 ..	520	17	9·75	6·45	83·80*	$CuS_{1\cdot3}$
Fe+S	Fe powder, S, and graphite mixed in ratio 2:4:1 ..	480	48	5·70	6·54	87·76*	FeS_2
Cr_2S_3	Cr_2S_3, S, and graphite mixed in ratio 1:2:1	560	120	1·93	2·08	95·99	$Cr_2S_{3\cdot5}$
V_2S_3	Reactants mixed in equal proportions	570	137	1·77	1·95	96·28*	$V_2S_{3\cdot5}$
MoS_2	MoS_2, S, and graphite in ratio 5:3:3 ..	570	48	0·32	0·23	99·45	—
WS_2	Reactants mixed in equal proportions	570	137	10·02	4·09	85·89*	$WS_{2\cdot4}$
PdS	PdS, S, and graphite mixed in ratio 1:2:1	570	137	5·30	3·50	91·20*	$PdS_{2\cdot2}$
Sb_2O_4	Four parts of Sb_2O_4 mixed with one of graphite	520	17	1·08	0·28* (oxygen)	98·64	Sb_2O_4
CrO_3	Oxide and graphite mixed in ratio 2:1	198	48	28·60	26·4* (oxygen)	45·00	CrO_3
MoO_3	Same as for CrO_3 ..	520	17	7·18	3·57* (oxygen)	89·25	MoO_3

*Determined by difference.

Evidence of the reactivity of graphite towards sulphides and oxides obtained by Croft[98] and shown in Table 8 supports the first conclusion. Cations of intercalated compounds were in higher valency states as in the case when corresponding chlorides were intercalated. *X*-Ray examination confirmed that lower sulphides were absent and also showed that graphite plane spacings were as high as 11—12 Å in graphite compounds containing oxides. Sulphides were heated with graphite in the presence of free sulphur, which itself does not react with graphite, in order to maintain mobility of the former. Thus it is probable that, under these conditions, lower sulphides were in equilibrium with higher sulphides and that the latter were steadily removed by the graphite. The intercalation of normally highly reactive CrO_3 in graphite is of interest in that its intercalation is not accompanied by any detectable oxidation of the graphite.

The properties of the various lamellar compounds of graphite with sulphides and oxides, generally, resemble those observed for molecular compounds of chlorides with graphite. A number of the graphite–sulphide complexes swell on strong heating, graphite–CrO_3 showing marked exfoliation. The blue iridescence of the graphite observed on the intercalation of many chlorides is observed with most of the sulphides and with CrO_3. Similarly, the flake-like pseudomorphs of Cr_2O_3, obtained when graphite–$CrCl_3$ is ignited after fuming with concentrated sulphuric acid, are also obtained when graphite–Cr_2S_3 and graphite–CrO_3 are decomposed by the same method. Graphite–CuS and graphite–Sb_2O_4 also give pseudomorphs of CuO and Sb_2O_4 respectively. In the case of MoO_3 it is possible to recover MoO_3 from graphite–MoO_3 by sublimation. Graphite–FeS_2 and graphite–CuS are both decomposed by prolonged treatment with hot dilute acids.

Croft[99] examined the possibility that other crystalline materials beside graphite may possess the ability to intercalate foreign substances. Macrocrystalline boron nitride prepared by the high-temperature crystallisation method described by Pease[100] was heated with ferric chloride at 400° and also with aluminium chloride at 250°. In both cases an expansion of the BN crystal lattice in the *c*-direction was observed by means of *X*-rays. After removal of excess of chloride in each case by washing with acid, the reaction products were found to contain 10·6% w/w of $FeCl_3$ and 13·0% w/w of $AlCl_3$ respectively. Before washing, the BN–$AlCl_3$ compound showed the iridescent blue colour commonly seen with freshly prepared graphite compounds. Also, like the latter, both BN compounds exfoliated considerably when heated to 600°.

Since BN is the classical structural analogue of graphite it evidently can make intracrystalline space available to foreign substances in the same manner as does graphite. Also, in view of the high stability of BN–$FeCl_3$ and BN–$AlCl_3$ to heat and solvents observed by Croft, it seems that

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[98] Croft, *Austral. J. Chem.*, 1956, **9**, 201.
[99] Croft, *Austral. J. Chem.*, 1956, **9**, 206.
[100] Pease, *Acta Cryst.*, 1952, **5**, 356.

substantial bonding exists between the host structure and the intercalated chlorides. Similarities between BN–$FeCl_3$ and BN–$AlCl_3$ and corresponding molecular compounds of graphite suggest that these compounds are ionic in character. This view would require that the planes of the BN crystal lattice are capable of participating in electron transfer. If boron favours some measure of tetrahedral bonding in boron nitride, B–N bonds might be expected to show some double-bond character associated with the system B^- and N^+. Studies on the band structure of BN by Taylor and Coulson[101] support this view. The results of Becher and Gubeau[102] provide more definite confirmation of this conjugation of unshared electron pairs of the nitrogen in the BN planes. This structure would involve partial occupation of the boron *sp* orbitals normal to the planes, this arrangement being analogous to that of graphite. Therefore, as in the case of graphite, these normally disposed boron 2*p* orbitals would be expected to play an important part in the electronic mechanisms of intercalation.

[101] Taylor and Coulson, *Proc. Phys. Soc.*, 1952, *A*, **65**, 834.
[102] Becher and Gubeau, *Z. anorg. Chem.*, 1952, **268**, 131.