GRAPHITE INTERCALATION COMPOUNDS

W. Rüdorff

University of Tübingen,
Tuebingen, Germany

I. Crystal Structure and Mode of Reaction of Graphite

Of the two modifications of elementary carbon, diamond and graphite, the latter is not only more abundant and of greater technical importance, but it is also more versatile and interesting in its reactions. In its reactions diamond depends on the removal of successive carbon atoms from the three-dimensional net and the formation of compounds of low molecular weight, as, for example, in combustion to carbon monoxide and dioxide. Graphite, on the other hand, is able, under certain conditions, to take up atoms, ions or molecules in its lattice while leaving its structure largely unchanged. The formation and constitution of these *intercalation compounds* may be explained in terms of the structure of graphite and the special bonding relationships encountered in it.

Graphite crystallizes in a layer lattice. The carbon atoms form regular sheets of linked hexagons which are displaced relative to one another. In the stable hexagonal modification (*3, 25*), which has the space group D_{6h}^4-$C\ 6/mmc$, alternate sheets are situated above one another, giving a sequence ABAB . . . , so that the identity period in the direction of the c axis embraces two carbon layers (see Fig. 1).

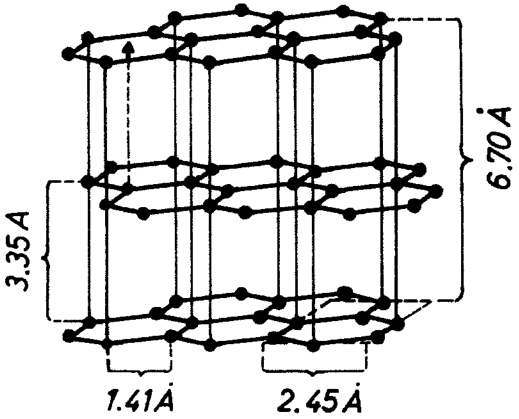


FIG. 1. The graphite crystal lattice.

In addition to the hexagonal modification, graphite has a second form (*17, 45*) which, according to Lipson and Stokes (*47*), has a rhombohedral structure with the space group D_{3d}^5-$R\ \bar{3}m$. In this, the carbon layers are displaced in such a way that each third layer is superposed, giving a sequence ABCABC. New investigations by Hofmann and Boehm (*34*) and by Laves (*46*) show that the hexagonal form may be transformed into the rhombohedral by mild mechanical treatment involving shear, for example, by grinding. In dressed natural graphite the proportion may be as high as 30%, but it is seldom encountered in artificial graphite or in single crystals. The rhombohedral reverts to the hexagonal form on heating above 1300°. The two forms have not been observed to differ in their ability to form graphite intercalation compounds. Since, moreover, the distances of the carbon atoms and the bonding relationships are the same in the two modifications, we may neglect the rhombohedral modification in what follows.

Within the layer planes each carbon atom is surrounded by three other atoms at 1.41 Å. The distance between layers is 3.355 Å and is thus substantially greater. Corresponding to these different distances there are different types of bonding. Within the layers each carbon atom is linked by a strong homopolar bond with its three neighbors. On the other hand the electrons representing the fourth valency of the carbon atoms are not localized in definite bonds but, as in the case of the π-electrons of a large aromatic molecule, are shared by the whole layer. Graphite owes its high thermal and electrical conductivity to these so-called free electrons, which form the conduction band in the graphite. A relatively energetic reaction is needed to break the homopolar bonds and remove separate carbon atoms from the layers, but a suitable reactant is often able under quite mild conditions to change the state or concentration of electrons in the conduction band and thus to become intercalated between the carbon planes. When this occurs the carbon planes remain intact and only their distance from one another increases. For this reason the formation of intercalation compounds is always linked with swelling of the graphite in a direction perpendicular to the basal planes.

The bonding of reactants in the graphite lattice may be very varied in type and, in some cases, is not yet fully understood. This will be discussed in detail when the separate compounds are described. At this stage, however, it may be said that the graphite compounds fall into two groups, according to the character of the bonding. In compounds of the first class there is homopolar bonding between the intercalated atoms and the carbon atoms. To this belong graphite oxide, carbon monofluoride, and tetracarbon monofluoride. In the second class, to which the majority of graphite compounds belong, the bonding has a more or less pronounced polar character. It is characteristic of these compounds that occupation of the lattice occurs in a series of steps or "stages." Thus the reactant may enter the space between each set of basal planes, or that between each second, third, fourth, and so on. The separate compounds or phases, which may be clearly distinguished from one another by analysis or by

X-ray examination are called the stages 1, 2, 3, ... The alkali metal-graphite compounds and the graphite salts afford an opportunity for the detailed study of this type of stepwise intercalation.

This review deals with the present position of our knowledge of these graphite compounds. This requires also that brief reference be made to compounds which have been known for a long time and repeatedly studied. In so far as this work is covered by earlier reviews (*33, 52, 53, 57*), it has been omitted here. On the other hand, research done in the last fifteen years, in so far as it has led to the discovery of new compounds or new results on the constitution and structure of graphite compounds, is discussed somewhat more fully. Numerous recent studies of physical properties of graphite compounds, such as conductivity, magnetism, and the Hall effect are mentioned here only when they are significant in elucidating the type of bond in the compounds dealt with.

II. Graphite Compounds with Homopolar Bonding

A. GRAPHITE OXIDE

1. Properties and Composition

Graphite oxide, which is also known as graphite acid, was described by Brodie (*6*) as early as 1860 and is probably the most fully studied graphite compound (for bibliography see refs. *33, 53*). In spite of this, however, its constitution is not yet fully elucidated. It is best prepared by oxidizing graphite with a mixture of potassium chlorate and concentrated sulfuric and nitric acids (*81*). Thorough washing with water yields products which vary in color from yellow to dark brown. Hofmann and his co-workers (*8*) recently were able to prepare light-colored preparations, which darkened on warming or in light, by washing in the dark with water saturated with chlorine dioxide and containing hydrochloric acid. The light-colored graphite became black at once when introduced into dilute sodium hydroxide solution. No correlation between color and composition was found, however.

Graphite oxide is thermally unstable. When rapidly heated to about 200° it deflagrates with formation of carbon monoxide, carbon dioxide, water, and soot-like carbon. This graphite oxide soot is shown by the electron microscope to be different from ordinary soot. It consists of thin plates, 20-30 Å thick and up to 10000 Å^2 in extent (*75, 37*). When warmed slowly, graphite oxide is broken down to graphite-like products, which, however, still contain oxygen. Carbon dioxide predominates in the gaseous decomposition products. Graphite oxide possesses oxidizing properties and is reduced to graphite by reducing agents, though the reaction is never quite complete.

The composition of graphite oxide is most suitably characterized by the C:O ratio, after taking into account the hydrogen found in combustion (*33*). If all four of the valencies of each carbon atom were satisfied by bonding to oxygen this ratio would be two, but this value is never reached. Values for C:O of 2.4 to 2.9 are found for well-oxidized preparations and values of 2.7 to 2.8 are particularly common. Less oxidized preparations with C:O ratios of 3.5 to 4 are, however, homogeneous phases, and show the same characteristic properties as more highly oxidized specimens.

Among the characteristic properties of graphite is the ability to undergo swelling. Water and organic liquids with polar groups may be taken into the lattice with a reversible change in the interplanar distance. This is 6.35 Å and 9 Å in preparations dried over phosphorus pentoxide and in the air, respectively, and it increases in liquid water to 11 Å. In weakly alkaline solutions (0.01 *N*) swelling is so great that the interplanar distance can no longer be measured with X-rays.

Hydrogen found by analysis to be present in graphite oxide cannot be attributed solely to water taken up in the swelling process, since it is always present in well-dried specimens. According to Thiele (*85*) and to Hofmann *et al.* (*35, 36*), graphite oxide always contains hydrogen ions capable of exchange, which are probably associated with weakly acid hydroxyl groups and more strongly acid carboxyl groups. The presence of carboxyl groups in graphite oxide is to be expected from its mode of preparation, for mellitic acid is produced in the oxidation of carbon with potassium chlorate in the presence of sulfuric and nitric acids.

In connection with the constitution of graphite oxide, the question of the number and nature of the acid groups and the point of their attachment is especially interesting. Comprehensive studies by Hofmann and his co-workers (*36, 35, 8, 74*) on the extent of base exchange and on the methylation of graphite oxide have made a substantial contribution towards solving this problem. The results of these investigations may be summarized as follows.

In well-oxidized specimens the fraction of —OH groups, as calculated from measurements of sodium ion exchange from sodium ethylate solution, is found to be about 1100 meq per 100 gm of graphite oxide (dried over phosphorus pentoxide). Roughly the same value is obtained by eluting from a well-dried specimen all the water left from swelling by means of dioxane, and attributing the remaining hydrogen to —OH or —COOH groups.

Only a part of the —OH groups—about 700 meq per 100 gm—can be methylated with diazomethane or acetylated with acetic anhydride. That it is the —OH groups attached to the carbon planes which react in this way follows from the fact that, after methylation or acetylation, the interplanar distance in the dry graphite oxide is increased by 3-4 Å. Methylated graphite oxide preparations retain the property of base exchange with sodium methylate solution to an extent corresponding with the number of —OH groups not involved in the methylation reaction.

The number of carboxyl groups has the comparatively small value of 30-100 meq per 100 gm. These groups may be determined by methylation with methanol and hydrochloric acid. In this case the weakly acid —OH groups of the layer planes do not react. Carboxyl groups can probably be attached only at the edges of the crystal or at the edges of cavities in the layer planes, for preparations methylated with methanol show the same interplanar distance as unmethylated specimens.

2. Constitution and Structure

Neither the infrared spectrum nor X-ray analysis enables a detailed picture of the structure of graphite oxide to be obtained. According to Hadzi and Novak (*24*) the —OH stretching and bending frequencies and the C=O bond frequency occur in the infrared spectrum, but it is not possible to determine whether the C=O group is present only in carboxyl groups, or in keto groups as well. A band at 9.3μ is attributed by the authors to the C—OH bond vibration, but the assignment of further weak bands is uncertain. The position and bonding of the atoms cannot be determined with certainty by X-ray analysis since, apart from the ($00l$) reflections, from which the distance between the basal planes may be calculated, only (hk) cross lattice reflections occur.

In a structure proposed by Ruess (*74*), see Fig. 2, hydroxyl groups and oxygen atoms are bonded to the carbon layers according to a statistical distribution. The carbon layers are believed to have lost their aromatic character and are no longer planar, as they are in graphite, but puckered (see the structure of carbon monofluoride under Section IIB1b). Puckering of the rings is supported by the expansion of the carbon hexagonal network which, if tetrahedral bonding of the carbon atoms is assumed, leads to a C—C distance of 1.52 Å. Ruess assumes an ether-like bonding of oxygen atoms in the 1:3 position above and below the layer planes. The mode of bonding cannot be established experimentally. All attempts to cleave the oxygen bridges and increase the number of —OH groups have failed. If a reaction occurs as it does, for example,

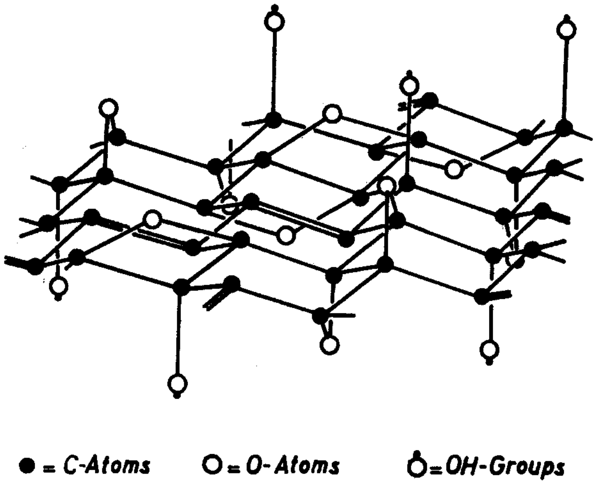


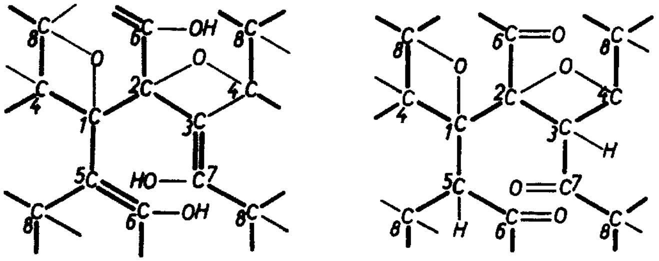
FIG. 2. Layer of graphite oxide with tertiary OH-groups (Ruess, *74*).

with hydriodic or hydrobromic acid, immediate reduction to graphite-like products ensues.

Hofmann (*8*) supposes that the layers in graphite oxide are under strain because of the oxygen bridges and that the aromatic state of the carbon planes in graphite itself is relatively more stable. This is supported by the fact that the heat of formation of graphite oxide from graphite, oxygen, and water is almost zero (*38*). On breaking the oxygen bridges, therefore, reduction is favored with the formation of C=C bonds and a gradual transition to the aromatic conditions of graphite itself. Riley (*2, 7*) suggests another mode of bonding of oxygen. He supposes that graphite oxide contains peroxide groups, —O—O—, which bind the graphite layers together. Contrary to this idea is the fact that free oxygen is never observed in the thermal decomposition of graphite oxide. Hofmann and Ruess (*33, 74*) also suggested that oxygen bridges are broken when graphite oxide swells and that the number of —OH groups increases. This, however, is not in keeping with what is found experimentally.

The acidic character of —OH groups in graphite oxide may be explained if the —OH groups are attached to a carbon atom with a C=C double bond, that is to say, if they are enolic in character. The presence of C=C bonds in the layers would then be characteristic of graphite oxide. This would explain why, in the oxidation, a C:O ratio of 2 is never reached.

Doubly bound carbon atoms with an enolic group can only be bound to one further carbon atom. It follows that in those positions where the enolic group is attached the hexagonal network must be broken. Figure 3a shows the section of a graphite oxide basal plane according to a new proposal by Hofmann (*8*). This structure leads to an idealized formula $C_8O_2(OH)_2$ with a C:O ratio of 2.67 and 1240 meq of OH per 100 gm, which is close to the observed value.



(a) (b)

FIG. 3. Segment of a layer of graphite oxide (Hofmann, *8*). (a) Enol groups. (b) Keto groups.

In addition to this enolic form, a keto form is also structurally possible (Fig. 3b) which may predominate in the light-colored graphite oxide. The change of graphite oxide from the light to the dark color in dilute alkali could then be associated with the transition to the enolic form.

It is possible that tertiary hydroxyl groups are present in graphite oxide in addition to enolic groups. This is shown in Fig. 2. This would explain why, with aqueous alkali metal hydroxides and with diazomethane, only a fraction of the —OH groups which are present undergo reaction.

A totally different structure for graphite oxide was proposed by R. E. Franklin (*18*). He concluded from X-ray studies that there was a structural continuity between the oxygen atoms of the graphite oxide and those of water intercalated in the lattice. Both form together a negatively charged polylayer (O_xH_y) with respect to which the carbon layers are cationic. The chemical properties of graphite oxide are not, however, readily reconciled with an ionic structure and negative hydroxyl ions.

B. GRAPHITE-FLUORINE COMPOUNDS

1. *Carbon Monofluoride*

a. Conditions of Formation. Whereas soot and active carbon burn in fluorine when exposed to it at room temperature, coarse graphite is stable to fluorine up to about 400°. Between 500° and 700° reaction is for the most part explosive and above 700° the graphite burns to a mixture of fluorocarbon such as CF_4 and C_2F_6. Only in the narrow temperature range 420-460° did Ruff and Bretschneider (*77*) obtain a gray product of the composition $CF_{0.92}$ which they called carbon monofluoride. In a further investigation of carbon monofluoride W. and G. Rüdorff (*62*) obtained homogeneous preparations the composition of which was between $CF_{0.68}$ and $CF_{0.995}$. While the fluorine-poor preparations are still black, the color lightens with increasing fluorine content. The compounds with the highest fluorine content are pure white and transparent in their layers. At the same time the electrical resistance increases very much and the white preparations are practically nonconducting.

Formation of carbon monofluoride is catalyzed by gaseous hydrogen fluoride (*63*). There are characteristic differences according to the crystalline condition of the carbon. With coarse crystalline graphite in the form of flakes, formation of carbon monofluoride is determined almost entirely by the partial pressure of hydrogen fluoride and shows little dependence on temperature. At an HF partial pressure of 200 mm, reaction occurs at 250°. When, however, the carbon forms a very dense aggregate of fine crystals, which is the case with retort graphite, reactivity is determined less by hydrogen fluoride pressure and much more by temperature. Retort graphite is very resistant at 250°, even at high hydrogen fluoride concentrations, but it becomes more reactive than flake graphite above 320°.

Catalysis by hydrogen fluoride explains the formation of a carbon monofluoride layer on carbon and graphite anodes in the electrolysis of potassium fluoride—hydrogen fluoride melts, which was observed by Ruff (*76*). This unwanted reaction can lead to destruction of the anodes in the space above the electrolyte and, according to Rüdorff and Hofmann (*71*), is also responsible for the so-called aging of carbon and graphite anodes, which manifests itself by an increase in the anode voltage on prolonged electrolysis.

Carbon monofluoride is strikingly unreactive, being unwetted by water and unattacked even by concentrated acids and alkalis. No reaction occurs up to 400° on heating in hydrogen. When rapidly heated the compound deflagrates with production of a flame, reaction being more vigorous the higher the fluorine content. It gives a cloud of very finely divided soot together with carbon tetrafluoride and higher fluorocarbons.

b. Crystal Structure. The structure proposed by Ruff is based on the assumption that fluorine is present in the graphite lattice as ions. The ratio of the radii of fluoride ion and carbon does not, however, allow the fluoride ions to occupy a layer above and below each graphite plane, so that Ruff had to arrange the fluoride ions in six layers between two carbon planes. This structure is, however, very unlikely on electrostatic grounds. Quite apart from this, the great inertness of the monofluoride is not indicative of ionic bonding of the fluorine, for all graphite compounds which are ionic in type, and especially the graphite salts (compare Section IIIB), are very reactive and are decomposed by traces of water, with reversion to graphite. By contrast, carbon monofluoride is hydrophobic and cannot be changed back to graphite.

According to W. and G. Rüdorff (*62*) carbon monofluoride is a homopolar compound in which fluorine is bonded in the same way as in organic fluorides. Figure 4 shows the new structure proposed. The fluorine atoms form a layer above and below the carbon layer but, because of the sp^3 bonding, the carbon atoms no longer lie in a plane, as in graphite. Instead, the layers are puckered and the C—C distance (1.54 Å) is that for a single bond. Each composite layer is comparable with a giant hydroaromatic molecule.

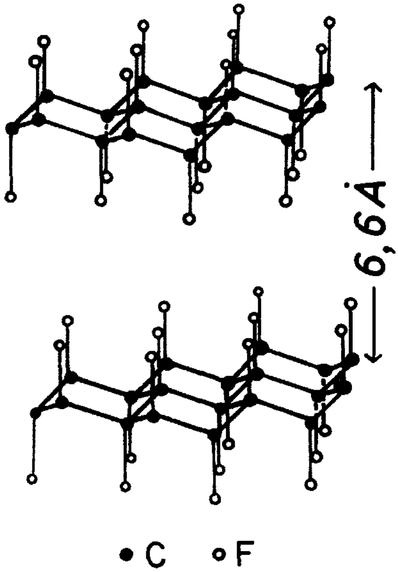


FIG. 4. Crystal lattice of carbon monofluoride (W. and G. Rüdorff, *62*).

Total absence of (*hkl*) reflections in the X-ray diagram shows that the separate CF-layers are no longer regularly arranged with respect to one another, and are only roughly at the same distance apart. This distance depends on the fluorine content: with the highest fluorine content it is 6.6 Å and it increases as the fluorine content decreases, to 8.8 Å at $CF_{0.68}$. A clear explanation for this unusual dependence of the distance on the fluorine content has not been given.

Unfortunately the X-ray powder diagram of carbon monofluoride shows only a few reflections, so that the structure suggested above cannot be based on an exact structural analysis. The increase in the C-C distance relative to that in graphite follows unambiguously from the fact that (*hk0*) reflections, which occur as cross lattice reflections, are displaced to smaller diffraction angles. These reflections in the case of a puckered layer do not give the C—C distance directly but only the projection on the basal plane. The position of the reflections gives this projection as 1.467 Å, while calculation based on a tetrahedral angle and a C-C distance of 1.54 Å leads to the value 1.453 Å. If the size of the C—C—C bond angle is increased somewhat the rather higher experimental value may be correctly reproduced.

A sure proof of the presence of a C—F bond has recently been furnished by recording the infrared spectrum of the compound (*59*). In the region 2-25μ there is a single strong broad band at 1215 cm^{-1}. The C-F frequency in perfluorinated organic compounds such as C_6F_{12} lies at 1200-1320 cm^{-1} (*86*), so that the observed band may be assigned with certainty to a C—F vibration—probably an unsymmetrical stretching vibration. The above model readily explains the low reactivity, the absence of electrical conductivity, and the formation of carbon fluorides of low molecular weight on thermal decomposition.

2. Tetracarbon Monofluoride

a. Preparation and Properties. In addition to carbon monofluoride, graphite and fluorine are able to form yet another compound which is like carbon monofluoride in many properties, but differs from it clearly in composition, color, conductivity, and structure. This is tetracarbon monofluoride, which was prepared by W. and G. Rüdorff (*64*).

The compound is readily formed by passing a fluorine-hydrogen fluoride mixture over graphite at room temperature. The rate of reaction depends on the composition of the gas mixture and drops rapidly with decreasing hydrogen fluoride partial pressure. If the graphite is held at 80-100°, the reaction does not occur, from which it follows that the temperature range in which the compound is formed is relatively closely limited. Using powdered graphite, the compound has a velvet black appearance, sometimes with a bluish tinge. The composition may vary in the range C_4F-$C_{3.6}F$ and clearly depends on the conditions of preparation.

Like carbon monofluoride, tetracarbon monofluoride is also very inert, though it is appreciably less stable thermally. It is completely stable in air, and is unattacked by dilute acids and alkalis, even in the warm. Strong reducing agents such as ferrous salts or hydriodic acid produce no change, and even chromic-sulfuric acid has no action in the cold. From the last observation it follows that graphite, in combining with fluorine, has lost its ability to form graphite bisulfate (compare Section IIIB).

When warmed above 100° tetracarbon monofluoride preparations begin to decompose and when rapidly heated they deflagrate—sometimes with flame—and leave a very finely divided soot. Decomposition also occurs when the compound is gradually heated to 200-300° in a stream of fluorine or of a fluorine-hydrogen fluoride mixture. Thus it is not possible to convert the compound to carbon monofluoride by further fluorination.

Unlike carbon monofluoride, the compound retains an electrical conductivity which, however, is about two powers of ten lower than that of the original graphite. W. and G. Rüdorff found a specific resistance of 2-4 ohm · cm at a pressure of 750 kg/cm^2. Measurements by McDonnell *et al.* (*48*) also showed a similar strong decrease in conductivity on going from graphite to C_4F.

The compound is diamagnetic, the molecular susceptibility referred to $CF_{0.25}$ being -9.03×10^{-6} (*48*). Although it may be shown that the compound contains no hydrogen fluoride, the latter plays a decisive role in the synthesis for, as already mentioned, the rate of reaction is strongly dependent on the hydrogen fluoride concentration. In this connection it is of interest that graphite when oxidized with fluorine forms a salt-like graphite bifluoride with the approximate composition $C_{24}{}^{+}HF_2{}^{-} \cdot 4HF$ (*58*). In this compound the C:F ratio is also 4:1, but it is formed only in the presence of liquid anhydrous hydrogen fluoride and has quite other properties and a different constitution from tetracarbon monofluoride. It is not impossible, however, that the bifluoride occurs as a short-lived primary product, since a skin of liquid hydrogen fluoride may form on the graphite crystals at room temperature from the gas stream. Further oxidation by fluorine would then lead from this compound to tetracarbon monofluoride. This assumption that the bifluoride occurs as an initial product would explain the observation that at 80° graphite is unchanged in a fluorine-hydrogen fluoride stream since, at this temperature, no liquid film can form.

b. Constitution and Structure. The properties mentioned above indicate clearly that in this compound, as in carbon monofluoride, a covalent C—F bond is present. Since, however, only every fourth carbon atom gives an electron for bonding fluorine, it is understandable that the compound still conducts electricity. The structure is shown in Fig. 5.

The network of carbon hexagons remains, with a practically unaltered C—C distance, as in graphite. There is, however, a difference from the graphite structure in that the carbon planes are in identical positions one above the other. Their distance apart is 5.34 Å for preparations with the composition C_4F and this increases to 5.50 Å for the composition $C_{3.6}F$.

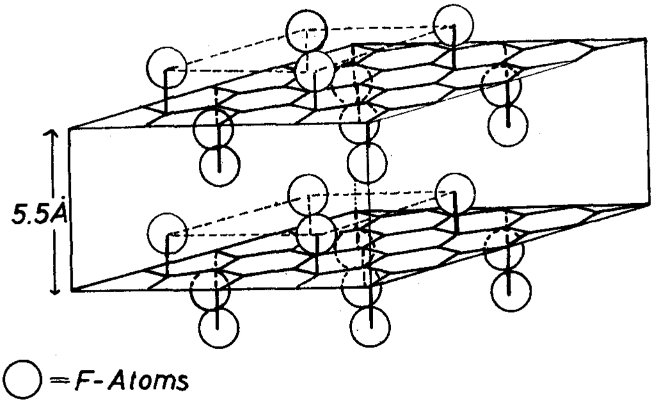


FIG. 5. Crystal lattice of tetracarbon monofluoride (W. and G. Rüdorff, *63*).

The fluorine atoms are arranged in two layers, one above and one below each carbon plane. The C—F distance cannot be determined by X-ray diffraction, but is assumed to be 1.4 Å, as in organic fluorine compounds. For C_4F, if the fluorine atoms are regularly distributed, they form in each layer a triangular network with an F—F distance of 4.9 Å.

c. Comparison of the Structures of C_4F *and* CF. The structure of tetracarbon monofluoride differs from that of carbon monofluoride in that the distance between layers is smaller and, especially, in that the carbon planes are not puckered. It seems unlikely that those carbon atoms to which fluorine atoms are bonded project out of the plane and that the carbon planes are buckled, for this would distort the hexagonal network and would be recognizable in the X-ray powder diagram, both in the position of and in a broadening of the (*hk0*) reflections. These reflections are, however, relatively sharp, as in graphite itself.

Structural studies made up to the present lead to the generalization that in a graphite compound all C—C distances in the carbon layers, apart from lattice imperfections, are the same and that the layers are either plane or puckered, even when some of the carbon atoms have a different type of bonding. In carbon monofluoride and tetracarbon monofluoride the two possible structures for the carbon layers are realized.

So long as the proportion of carbon atoms involved in bonds with fluorine remains small—in C_4F it is one quarter—the aromatic character of graphite with plane carbon sheets is retained. Bonding of fluorine, however, certainly produces tension within the layers and this may be the reason for the low thermal stability. The carbon planes become puckered when, as in carbon monofluoride, the majority of the carbon atoms become involved in sp^3 bonds. The fact that no further compound occurs in the region between $CF_{0.28}$ ($= C_{3.6}F$) and $CF_{0.68}$ and that there is no continuous transition from the one compound to the other is in keeping with this view. For the monofluoride the most stable preparations are those which approximate most closely to $CF_{1.0}$, as the puckered carbon planes are then free of strain. The further the composition deviates from the ideal formula the greater is the strain, as is shown by the observed increase in thermal instability with decreasing fluorine content.

III. Graphite Compounds with Polar Bonding

A. POTASSIUM- RUBIDIUM- AND CESIUM-GRAPHITE

1. *Composition and Properties*

Graphite reacts with striking readiness with the molten alkali metals potassium, rubidium, and cesium, or their vapors, to form alkali metal-graphite compounds. Fredenhagen *et al.* (*19, 20*) showed that for all three alkali metals, depending on the temperature and alkali metal vapor pressure, products were formed which differed from one another in color. The first compound has a color between bronze and copper-red and has the approximate composition C_8Me ($Me = K, Rb, Cs$). Such a compound is prepared readily by carefully distilling off in a vacuum the excess of alkali metal used in the preparation. On further heating, C_8Me loses alkali metal and passes over into a steel-blue compound. Finally, all the alkali metal may be driven off by heating strongly.

The composition of the blue product was not established with certainty in Fredenhagen's work and Schleede and Wellmann (*79*) first derived the formula $C_{16}Me$ from crystal-structure measurements. However, further analytical and X-ray investigations by Rüdorff and Schulze (*66, 67*) showed conclusively that the blue compounds contained less alkali metal and had the formula $C_{24}Me$. This conclusion is supported by Hérold's work (*32*) which showed that in the isobaric breakdown curve of C_8K the first clear break occurs at $C_{24}K$. This product gave the same X-ray powder pattern as the blue compound studied by Schleede (*31*).

Fredenhagen found calorimetrically a value of 12 kcal/mole for the heat of formation of C_8K formed by introducing graphite into an excess of molten potassium. A careful redetermination by Quartermann and Primak (*51*) led to the lower value of 7.8 kcal/mole. Hérold (*31*) calculated from vapor-pressure measurements that ΔH for the reaction $C_{24}K + 2K_{liq} = 3C_8K$ was −6.8 kcal. The corresponding ΔH values for the Rb and Cs compounds are −11.6 kcal and −20.2 kcal, respectively. With Fredenhagen's value for the heat of formation of C_8K we then obtain

$$24C + K_{liq} \rightarrow C_{24}K; \qquad \Delta H = -29.2 \text{ kcal.}$$

If Quartermann's value is taken, ΔH = −16.6 kcal.

The alkali metal-graphite compounds are extremely reactive. They ignite in air and may react explosively with water. In the controlled reaction with water or alcohol only alkali hydroxide and hydrogen result: there is no acetylene or any other hydrocarbon. Fredenhagen concluded from this that the compounds could not be carbides. Mercury dissolves the alkali metal out of the lattice. When treated with liquid ammonia, C_8Me gives up only a third of the alkali metal and takes in its place two molecules of ammonia (see Section IIIA4).

2. Structure of the Alkali Metal-Graphite Compounds

The crystal structure of these compounds was first determined by Schleede and Wellmann (*79*). In the compound C_8Me a layer of alkali metal atoms is present between each pair of carbon planes, whereas in the blue alkali-poor compound this occurs between every other pair. Introduction of the alkali metal increases the interplanar distance to 5.41 Å for potassium, 5.61 Å for rubidium, and 5.95 Å for cesium. According to the definition given in the introduction these two compounds are referred to as the first and second stage.

In the first stage the alkali metal atoms form a triangular net, the edge of which has the value $a = 4.91$ Å and is exactly twice as long as the hexagonal *a* axis of the hexagonal carbon net (Fig. 6a). When the layers are fully occupied the first stage has the composition C_8Me. The arrangement of atoms in this compound, as found by new structural determinations (*67*), is shown in Fig. 7. The new model differs from that of Schleede and Wellmann only in orientation of the carbon and alkali metal planes relative to one another. According to these authors, the carbon planes are arranged as they are in the hexagonal modification of graphite (i.e., in the sequence ABAB . . .) and the metal atoms lie between one carbon atom and the middle of a hexagonal ring of carbon atoms situated above or below it. In the new structure all the carbon planes are in identical positions (i.e., they have a sequence AAAA . . .) and the alkali metal atoms always occupy positions above or below the

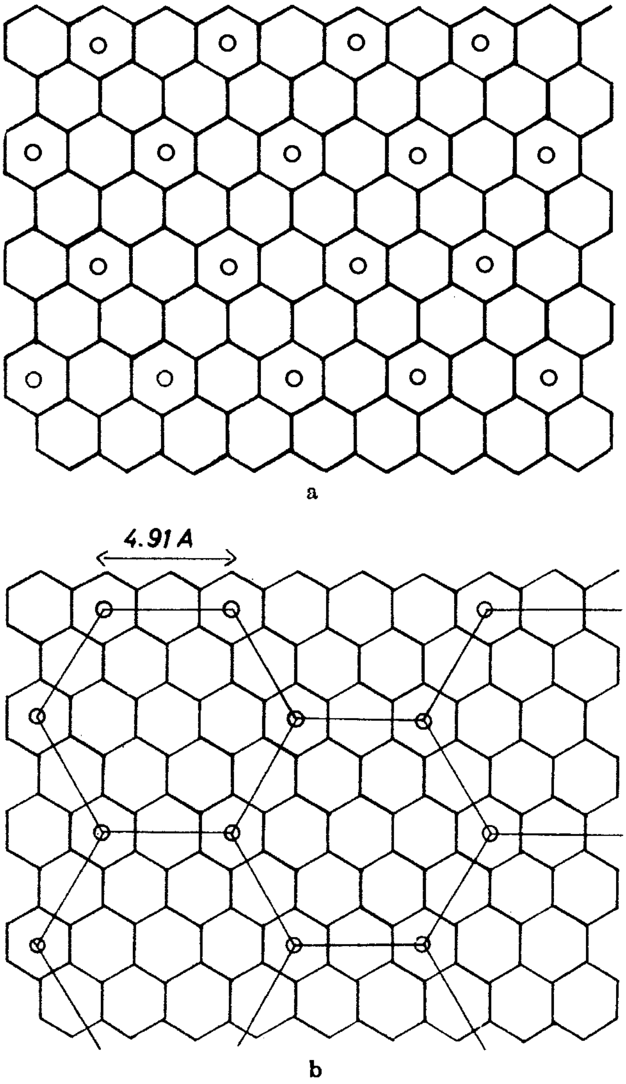


FIG. 6. (a) The triangular packing of the alkali atoms in C_8Me. (b) The hexagon net of the alkali atoms in $C_{24}Me$, $C_{36}Me$. Both (a) and (b) are shown in relation to the hexagon net of carbon atoms

middle of a hexagonal ring of carbon atoms. This arrangement seems intrinsically more likely for, in it, every metal atom has twelve carbon atoms at the same distance from it (3.07 Å for C_8K or 3.24 Å for C_8Rb), whereas in the first model each metal atom has as neighbors one carbon

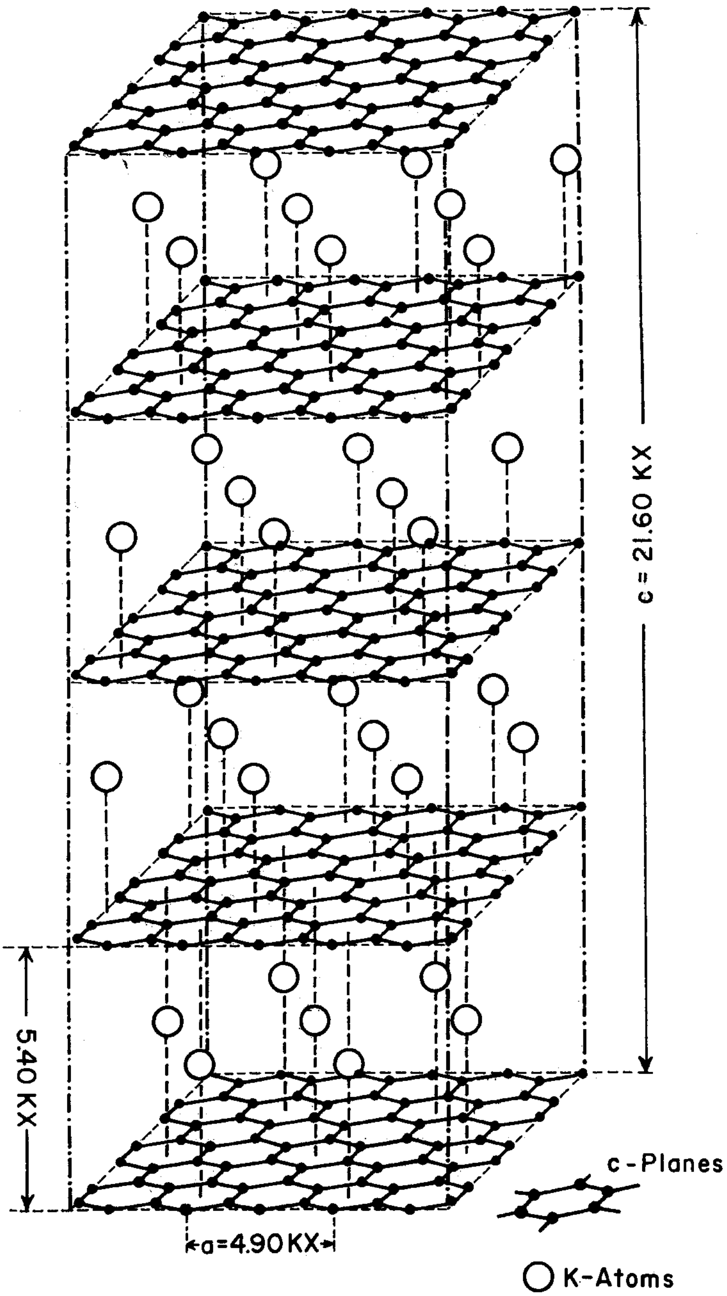


FIG. 7. Crystal lattice of potassium graphite C_8K (Rüdorff, 67).

atom belonging to the layer above, and six belonging to the layer below it, at different distances.

Since a metal layer in stage 2 is separated from the next by two carbon planes, the Me:C ratio should be half as big as in stage 1 if the alkali metal layers were populated equally in the two stages. On this assumption Schleede arrived at the formula $C_{16}Me$. Since, however, the composition is actually $C_{24}Me$, the metal atoms must be less densely packed in the second stage. Such a result is obtained if every third Me atom is removed from the triangular network as it exists in stage 1. The resulting hexagonal network fits the carbon network with the same Me-Me distance as does the triangular network (Fig. 6b). This arrangement gives the exact composition $C_{24}Me$ for stage 2.

The arrangement of metal atoms in a hexagonal network cannot be rigidly proved by X-ray methods, since no further superstructure reflections which require a greater identity period than the carbon network possesses can be recognized for stage 2. Presumably the metal atoms in the wide-meshed net are much more mobile in the direction of the layer plane than at right angles to it, so that the (*h0l*) and (*hkl*) reflections are more disturbed than the (*00l*).

In addition to these two stages there are other alkali-poor stages to which the author drew attention in 1944 (*57*). A systematic study of the systems graphite-potassium and graphite-rubidium (*67*) showed that in all, five stages occur in the range between C_8Me and $C_{60}Me$. Their compositions are shown in Table I. The formulae of stages 2 to 5 are whole number multiples of 12:1 from which it follows that the same hexagonal network of metal atoms is present in all these stages as has already been described above for stage 2.

TABLE I

Composition	Lattice constants, *c* for potassium graphite (Å)*
1st stage C_8Me	$5.41 = 5.41$
2nd stage $C_{24}Me$	$8.76 = 5.41 + 1 \times 3.35_5$
3rd stage $C_{36}Me$	$12.12 = 5.41 + 2 \times 3.35_5$
4th stage $C_{48}Me$	$15.48 = 5.41 + 3 \times 3.35_5$
5th stage $C_{60}Me$	$18.83 = 5.41 + 4 \times 3.35_5$

* The published values in kX have been converted into Å.

The formulae correspond to idealized compositions, though each stage has a definite homogeneity range within which the characteristic sequence of carbon and metal layers remains undisturbed. When there are large deviations from the ideal formula two stages are obtained together as, for example, when, in attempting to make preparations with the composition $C_{16}Me$, stages 1 and 2 result. The transition of the separate phases into one another thus occurs discontinuously.

Introduction of the metal layer leads, for all the stages, to the same increase in the distance between the adjacent carbon planes, as may be seen from the identity periods for potassium-graphite (see Table I). In addition the carbon planes next to the metal layers always have identical positions. Thus entry of the alkali metal into the lattice is linked not only with an expansion lattice but also with a lateral displacement of the carbon planes. Metal atoms are then able to arrange themselves so that they lie over and under the carbon hexagons and are surrounded symmetrically by twelve carbon atoms. Figure 8 shows the sequence of carbon and metal layers and the orientation of the carbon planes to one another for stages 1 to 5.

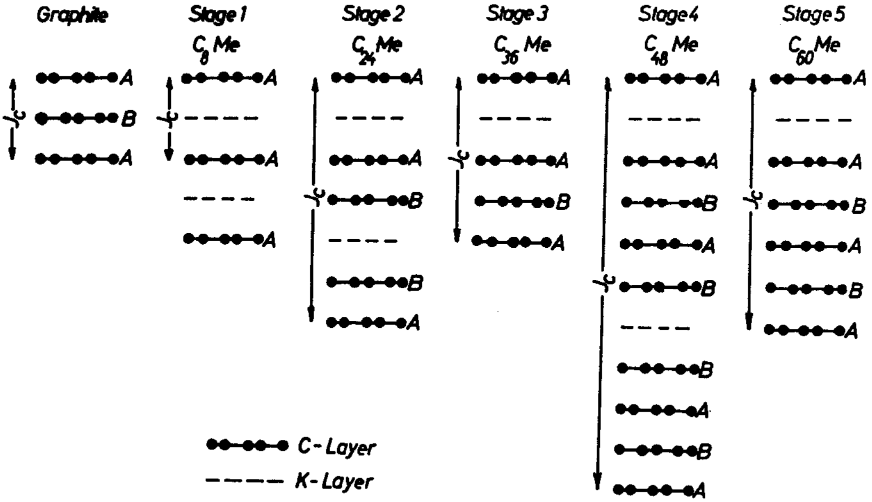


FIG. 8. Layer-plane sequence in stages 1-5 of alkali graphite (section perpendicular to the layer planes).

3. *Intercalation of Sodium and Lithium*

While potassium, rubidium, and cesium enter the graphite lattice very readily, sodium and lithium are much less reactive towards graphite and do not appear to form the corresponding compounds. Fredenhagen (*19, 20*) found that sodium reacts with soot but not with graphite. Tammann and Sworykin (*82*) observed that little rods of retort carbon are attacked by sodium vapor between 500° and 900° and disintegrate, giving products which ignite in air. They concluded that sodium, like potassium, is able to form a solid solution in carbon at higher temperatures. In spite of this, attempts to prepare definite compounds were at first unsuccessful (*31*). Hérold (*31*) was then able to intercalate sodium and cesium together by allowing a sodium-cesium alloy to react with graphite, but the Na:Cs ratio in the product was only 0.12.

In recently published work Asher and Wilson (*1*) report that when graphite is heated with about 3% of sodium to 400° a deep violet product results; the X-ray powder diagram differs characteristically from that of graphite. Quantitative X-ray analysis gave values for the composition between $C_{60}Na$ and $C_{68}Na$. The authors believed that a stage 8 compound had been formed, but, in spite of wide variations in the experimental conditions, they were unable to obtain any further compounds. It follows that there are certain differences in behavior towards graphite for sodium on the one hand and the heavy alkali metals potassium, rubidium, and cesium on the other.

The reaction between lithium and graphite has been studied by Hérold (*31*). At 500° and above, after long periods of reaction only the carbide Li_2C_2 results, but at intermediate stages products occur which differ distinctly in their properties from the carbide. With an over-all composition C_4Li a product was obtained which was harder than graphite and gave a homogeneous golden-yellow powder when broken up. On increasing the Li:C ratio first black, then grey and finally white substances result. The graphite compounds containing lithium are, according to Hérold, stable in dry air. Hydrogen and acetylene are produced when they are decomposed with water, the proportion of acetylene increasing with the Li:C ratio in the sample and reaching 100% for $Li:C = 0.5$. No X-ray study has yet been made of these striking compounds which differ in properties and composition from the other graphite compounds.

4. Ammonia and Amine Derivatives of Alkali Metal- and Alkaline Earth Metal-Graphite Compounds

These compounds resemble alkali metal-graphite compounds both in their structure and in their properties. The method used in their preparation was the result of a chance observation in the author's laboratory (*80*). During an investigation of electrolytic reactions in liquid ammonia a solution of sodium amide in liquid ammonia was electrolyzed with graphite electrodes, and it was found that the cathode swelled and disintegrated. Since the electrodes were not attacked in the solution when there was no electrolysis it was clear that the change could only have been brought about by a reaction of sodium separated at the cathode in the presence of ammonia.

Rüdorff *et al.* (*66, 72, 54*) obtained the ammoniates in a pure state by the action of the blue solution of the alkali or alkaline earth metals on graphite. If the metal is in excess a deep blue graphite compound with the structure of stage 1 results. The strontium and barium compounds are violet at low temperatures. After washing with liquid ammonia and removal of the absorbed ammonia in a vacuum at 0°, the composition corresponds approximately to the formula $C_{12}Me(NH_3)_2$. The potassium, rubidium, and cesium compounds may also be obtained by treating C_8Me with liquid ammonia.

$$3C_8K + 4NH_3 \rightarrow 2C_{12}K(NH_3)_2 + K.$$

If the graphite is in excess, the ammonia solution is completely decolorized and one obtains black or blue-black preparations which are less rich in metal. At a ratio of about 1Me:28C only stage 2 occurs.

TABLE II

AMMONIATES OF ALKALI AND ALKALINE-EARTH COMPOUNDS

First stage		Second stage	
Composition	I_c (Å)	Composition	I_c (Å)
$C_{10.6}\,Li(NH_3)_{1.6}$	6.6_2	$C_{28.8}\,Li(NH_3)_{1.7}$	9.9_3
$C_{13.4}\,Na(NH_3)_{2.0}$	6.6_3	$C_{26.7}\,Na(NH_3)_{2.3}$	9.9_7
$C_{12.5}\,K(NH_3)_{2.1}$	6.5_6	$C_{28.7}\,K(NH_3)_{2.8}$	9.9_4
$C_{11.9}\,Rb(NH_3)_{2.0}$	6.5_8	—	—
$C_{13.8}\,Cs(NH_3)_{3.2}$	6.5_8	—	—
$C_{12.1}\,Ca(NH_3)_{2.2}$	6.6_2	$C_{26.5}\,Ca(NH_3)_{4.1}$	9.9_5
$C_{11.3}\,Sr(NH_3)_{2.4}$	6.3_6	$C_{29.5}\,Sr(NH_3)_{3.4}$	9.8_7
$C_{10.9}\,Ba(NH_3)_{2.5}$	6.3_6	$C_{28.3}\,Ba(NH_3)_{3.9}$	9.7_9

In Table II analytical data are given for preparations which appear, on X-ray examination, to be single substances. Deviations from the ideal formulae may be caused by some phases occurring over a certain range of composition. It is, however, clear from the data that on passing from stage 1 to stage 2 the ratio Me:C decreases by more than half, as in the case of the ammonia-free compounds. In stage 2 of the alkaline earth metal compounds it seems that up to four molecules of ammonia may be bound per metal atom.

All these compounds are exceedingly sensitive to air and moisture, but they are no longer spontaneously inflammable as the alkali metal-graphite compounds are. They are decomposed by water with vigorous evolution of hydrogen and formation of metal hydroxide solutions. In the absence of air the cesium, rubidium, and potassium compounds may be kept unchanged for years in a sealed tube at room temperature, but they decompose at elevated temperatures with evolution of hydrogen and the formation of metal amide. The lithium and alkaline earth metal compounds are much less stable and decompose even at ordinary temperatures in the course of a few days.

By the simultaneous intercalation of the metal and ammonia the graphite lattice is expanded more than for pure alkali metal-graphite compounds. The distance between the carbon planes is 6.6 Å for the ammonia derivatives of all the alkali metals and of calcium: for those of strontium and barium a value of 6.4 Å has been found.

The approximately constant expansion of the graphite lattice, which is practically independent of the size of the intercalated metal atom, appears at first sight unusual for, in the ammonia-free compounds, the distance between the layer planes increases, as expected, with increasing size of the alkali metal atom from potassium to cesium. The constancy of the expansion for the ammoniates is perhaps attributable to the effect of the positions of the ammonia molecules in the lattice in determining the increase in the interplanar distance. If this were so, metal atoms or ions could perhaps find sufficient room in holes in the ammonia lattice. In support of this view it may be added that the expansion becomes greater if, in place of ammonia, a layer of amine such as methylamine or ethylamine is intercalated.

In the deep blue first stage of the lithium-methylamine compound, $C_{12}Li(CH_3NH_2)_2$, which may be prepared in the same way as the ammonia compound, the distance between the carbon planes is 6.9 Å. The corresponding potassium compound, which contains only one molecule of methylamine per atom of potassium and which is prepared by prolonged treatment of C_8K with methylamine, has exactly the same interplanar distance. Graphite reacts with lithium and ethylene diamine to form a stage 2 compound $C_{28}Li(en)$, in which the interplanar distance has increased even to 8.5 Å (*54*).

Tetramethyl- and tetraethyl-ammonium or -phosphonium can take the place of an alkali metal (*54*). These compounds are formed at graphite anodes on electrolyzing solutions of the corresponding salts in liquid ammonia. The tetraethyl ammonium compound is best prepared by allowing the blue solution obtained by electrolysis of the azide in liquid ammonia to react with finely powdered graphite. In this case intercalation leads only to stage 2, as may be seen from the ratio $1(C_2H_5)_4N{:}25C$ determined by analysis. Whereas the blue solution starts to decompose at −60°, the graphite compound may be kept unchanged under liquid ammonia at −40° for several hours. Apparently ammonium is also able to enter the graphite lattice. Dzurus and Hennig (*14*) have electrolyzed solutions of ammonium nitrate in liquid ammonia with carbon cathodes and have found that the resistance of the latter decreases. Similar results were obtained with solutions of methylamine hydrochloride in methylamine.

5. Magnetic Properties of Alkali Metal-Graphite Compounds[1]

Unpublished measurements by Klemm and Abitz (*44*) have shown that the compound C_8K possesses a weak temperature-independent paramagnetism ($\chi_{\text{mole}} = +9.7 \times 10^{-6}$), which corresponds to the order of magnitude of the paramagnetism of the electron gas in a metal. Ubbelohde (*48*) found a somewhat higher value ($\chi_{\text{mole}} = +16.2 \times 10^{-6}$) for the compound $C_{7.78}K$ and this was also independent of temperature. Rüdorff and Schulze (*67*) have made measurements on stages 1 to 5 of the potassium and rubidium compounds. Surprisingly, the difference in magnetic properties for the various stages was quite small. Down to stage 5 all compounds are weakly paramagnetic. The values for stages 1 to 5 of potassium graphite at room temperature are: +10.0, +8.7, +8.5, +5.7 and +4.0 (all $\times 10^{-6}$). Values for rubidium graphite were between $+5.0 \times 10^{-6}$ (stage 1) and $+3.7 \times 10^{-6}$ (stage 5). It is seen that the paramagnetism of the alkali-poor stages is not made up additively of the paramagnetism of stage 1 and the diamagnetism of pure graphite. It follows that introduction of alkali metal atoms influences the special state of the electrons in the graphite lattice which is responsible for the anomalous diamagnetism of pure graphite, and that this effect extends throughout the lattice even when the metal atoms occupy more widely spaced planes, as in stage 5.

Measurements made in the author's laboratory by W. Sprissler on stage 1 of the ammoniates of potassium and rubidium graphite and on stage 1 of the lithium-methylamine compound gave susceptibilities of the same order of magnitude as those of pure alkali metal-graphite compounds. Values of the susceptibilities, corrected for the diamagnetism of ammonia or methylamine, are: $C_{13.9}K(NH_3)_2$, +5.68; $C_{13.2}Rb(NH_3)_{1.9}$, +8.0; $C_{12.0}Li(CH_3NH_2)_{1.9}$, +8.35 (all $\times 10^{-6}$). The approximately equal values for paramagnetism of the alkali metal-graphite compounds and their ammoniates leads to the conclusion that their constitutions are similar.

---

[1] All susceptibility values given in this section refer to 1 gm-atom of carbon.

6. Bonding in the Alkali Metal-Graphite Compounds

These may be considered as intermetallic compounds. However, they possess a certain polar character, as Zintl (*90*) has shown to be always the case for intermetallic compounds between a noble and a very base metal. The alkali metals are base and show a transition in favor of cation formation whereas for graphite, which ranks as a noble metal, the transition is to an anion: in other words, the bond has a limiting structure Me^+ $Graphite^-$.

The stereochemical interpretation[2] of the alkali-graphite compounds may also be explained in this way (*57*). If the volume of graphite is deducted from the molecular value of the compound C_8Me, the alkali metal increments shown in Table III, column 2, are obtained. Comparisons with the corresponding atom and ion volumes show that the increments approximate to the values for the Me^+ ions, as they are found in salts. Formation of the compound C_8Me is therefore associated with an appreciable contraction which is greatest for cesium, probably because in that case the polar character is most pronounced.

TABLE III

COMPARISON OF SPACE INCREMENTS OF THE ALKALI METALS IN THE ALKALI-GRAPHITE COMPOUNDS WITH ATOMIC AND IONIC VOLUMES

Compound	Increment of alkali metal in the graphite compounds	Atomic volume Me in metals	Ionic volume Me^+ in salts
C_8K	25.7	43.4	16
C_8Rb	30.3	53.1	20
C_8Cs	33.6	66.0	26

Ubbelohde and his co-workers[3] have made an experimental contribu-

---

[2] The alkali increments were first calculated by K. Meisel (see ref. *4*), but the incorrect formula $C_{16}Me$ was used for stage 2. The values can, however, as is done here, be referred to only the first stage, C_8Me, since the alkali atoms in stage 2 are less densely packed. Meisel comes to almost the same values as are given here because he assumed the same density of occupation of the alkali layers.

[3] Ubbelohde puts forward the view that in C_8K a "pseudometallic" bond is present between the potassium atoms and certain carbon atoms. He uses as a basis the structure proposed by Schleede and Wellmann. On the new structure localized K—C bonds are very unlikely. The distance of the carbon planes is erroneously given in this work as 7.76 Å instead of 5.41 Å. Arguments on the nature of the bonding, based on the higher value, are therefore weakened.

tion to the question of the bonding in these compounds by measuring the electrical conductivity of potassium graphite of various compositions (*48*). The values in Table IV, which were obtained with polycrystalline material at a pressure of 20 kg/cm², are taken from Ubbelohde's work. The intake of potassium thus brings about a considerable increase in the conductivity. The temperature coefficient of conductivity is also negative, as it is for a true metal. This signifies that the alkali metals give up electrons to the conduction band of graphite, thus increasing the number of charge carriers.

TABLE IV

ELECTRICAL CONDUCTIVITY OF POTASSIUM GRAPHITE

Composition	Conductance (ohm^{-1} cm^{-1}) 90°K	Conductance (ohm^{-1} cm^{-1}) 298°K
Kish	110	128
Graphite	26.5	35.2
$KC_{8.46}$	1302	980
$KC_{12.3}$	1073	870
$KC_{27.8}$	—	565

The polar character of the alkali-graphite compounds also explains readily why the regular sequence of Me and C layers is maintained, even in the alkali-poor stage, for the electropositive alkali layers will always tend, because of mutual repulsion, to distribute themselves as uniformly as possible over the whole graphite lattice.

Similar bonding relationships should also exist in the ammoniates and amine derivatives of the alkali graphite compounds. This is indicated by Hennig's discovery (*14*), which has already been mentioned, that the conductivity of carbon electrodes increases in the electrolysis of ammonium salts in liquid ammonia. Moreover, the ammoniates have practically the same temperature-independent paramagnetism as the ammonia-free alkali graphite compounds (see Section IIIA5). It remains, however, to be explained why sodium and the alkaline earth metals, which are taken up very incompletely or not at all in the molten or vapor state, react as readily as do potassium, rubidium, and cesium if the metals are dissolved in liquid ammonia. This is certainly related to the fact that the state of all these metals in the blue solutions is very similar. They are extensively or completely ionized, while the dissociated electrons are loosely bound in solvate complexes. Uptake of electrons by graphite and the associated absorption of the metal can occur much more readily from these solutions than in a reaction with the metals in the fused or vaporized state. In the latter case the ionization energy of the metal is involved (*48, 29*) and this increases from cesium to lithium and the alkaline earth metals. The ammonia molecules taken up with the metal in stoichiometric proportions presumably form complexes and stabilize the interstitial compound. It is relevant in this connection to think of Zintl's polyanionic compounds, such as Na_4Pb_9 and others (*91*), which are stable only in the form of ammoniates and decompose when the ammonia is removed.

The decrease in stability of the ammoniates from cesium to lithium and the alkaline earth compounds does, however, make it less probable that in these compounds a true ionic bond, corresponding with the formula $C_{12}^{-}K^{+} \cdot 2NH_3$, is present. If this were so the stability of the ammonia complex would increase with decreasing radius and increasing charge, as it does for a saltlike compound. For the ammoniates, therefore, the ionic formula represents only a limiting case.

B. GRAPHITE SALTS

In the presence of concentrated acids, graphite may be oxidized by strong oxidizing agents or by anodic oxidation to the so-called graphite salts (*22, 83*). In these compounds, according to Hofmann *et al.* (*22, 60, 58, 68*), anions such as HSO_4^-, NO_3^-, ClO_4^-, HF_2^-, and CF_3COO^- are incorporated in the graphite lattice together with molecules of acid. The separate graphite salts may be transformed reversibly into one another by treatment with other concentrated acids. Thus, the bisulfate may be produced from the nitrate by treatment with concentrated sulfuric acid, and this in turn made into the perchlorate with perchloric acid (*60*). These changes may also be reversed.

The name "graphite salt" is justified by the fact that in the production of these compounds graphite behaves as a true metal. The oxidizing agent takes electrons from the graphite, leaving the carbon layers positively charged and able to bind anions,

$$\text{Graphite} + \frac{n}{2}\,O + nH_2SO_4 \rightarrow \text{Graphite}^{n+}\,(HSO_4)^{n-} + \frac{n}{2}\,H_2O.$$

Oxidation and the associated incorporation of the anions occurs stepwise. The first stage for the bisulfate, which is deep blue in color, like the first stage of all other graphite salts ("blue graphite") (*5, 78*) has the approximate composition $C_{24}^{+}HSO_4^{-} \cdot 2H_2SO_4$. Each anion takes two molecules of acid with it into the lattice. With this relationship a close and regular packing of anions and acid molecules is obtained which fits the hexagonal network of carbon atoms well (*60, 55*).

The second, third, and following stages, which are no longer blue but black, result on incomplete oxidation or by reduction of the first stage. In stages 2 and 3 the ratios anion:C atoms are 1:54 and 1:81, respectively, from which it follows that the anion net in the second and following stages is less dense than in the first stage (compare the similar relationships for the alkali graphite compounds in Section IIIA).

The stage to which the graphite is oxidized in the presence of a particular acid depends not only on the strength and quantity of the oxidizing agent but also on the acid concentration. As an example of the influence of acid concentration it may be mentioned that in 83% sulfuric acid and with excess of oxidizing agent, the formation of the first stage of the bisulfate does not occur and only the second stage is obtained. In 63% sulfuric acid oxidation goes to the third stage and at concentrations below 50% uptake of bisulfate can no longer be detected by X-ray examination.

The nature of the acid is also important. With sulfuric, nitric, perchloric, and selenic acids the corresponding first stage is readily obtained. Phosphoric and arsenic acids lead only to stages corresponding to a low degree of oxidation and organic acids such as acetic acid give no graphite salts. The incidence of reaction is apparently related to the strength or self-dissociation of the acid. This is especially well seen by comparing the behavior of graphite anodes on electrolyzing concentrated or anhydrous acetic, dichloroacetic, trichloroacetic, and trifluoroacetic acids. Unlike acetic acid, the halogenated acids attack graphite increasingly in the order given above, which corresponds to that of increasing acid strengths. In trifluoroacetic acid and also in the strongly acidic boron trifluoride-diacetic acid compound graphite electrodes swell so much as a result of graphite salt formation that they disintegrate in a short time (*68*).

Graphite salts are instantly decomposed by water and by polar organic solvents. Consequently the isolation of these compounds is extraordinarily difficult and attempts to remove adhering acid by washing with other liquids almost always leads to decomposition of the graphite compound. They may be reduced to graphite under certain conditions by such reducing agents as ferrous or stannous salts or by cathodic reduction, and these reactions may be used in evaluating the degree of oxidation.

TABLE V

DISTANCE (Å) BETWEEN CARBON PLANES IN FIRST-STAGE GRAPHITE SALTS

NO_3^-	ClO_4^-	HSO_4^-	HF_2^-	CF_3COO^-	$HSeO_4^-$
7.85	7.95	7.99	8.06	8.19	8.26

The graphite salts were the first case in which the stepwise uptake and the associated change of the graphite lattice was followed exactly by X-ray methods up to the fifth stage (*55*). Discussion of details may be dispensed with as the structure, including the arrangement of the carbon planes, is the same as in the alkali metal-graphite compounds. A picture of the graphite salt structure may be obtained from Fig. 8 by replacing the alkali metal layers by anion and acid layers. The distance between the carbon layers when acid layers are incorporated in the lattice is naturally greater than with alkali layers. It amounts to about 8 Å. From the values given in Table V it may be deduced that the degree of lattice expansion increases somewhat with the size of the acid residue from nitrate to biselenate.

The regular distribution of the anionic layers and the discontinuous transition from one stage to another, which is associated with a completely new distribution of the anion layers in the lattice, as well as the ready anion exchange, may be explained readily in terms of the ionic character of the compound. Finally, this ionic structure may be recognized most clearly from the fact that the transformation of graphite into a graphite salt may be carried out reversibly by electrochemical means. The emf of the first stage of the bisulfate has been determined as 0.6 volt against graphite and 0.49 volt against a platinum-hydrogen electrode (*60*).

The work of Hennig (*27*) on the change of electrical properties of graphite on forming graphite bisulfate is consistent with the constitution of graphite salts. It must be mentioned at the outset that the investigation was limited to compounds with a very low degree of oxidation (the maximum was 4 meq/gm-atom of C as opposed to 47 meq/gm-atom in stage 1). The bisulfate compounds were prepared by anodic oxidation in concentrated sulfuric acid. Resistance measurements during the oxidation showed that a decrease of resistance of the graphite was associated with the uptake of bisulfate ions. The Hall coefficient also acquires a positive sign.

These results may be interpreted on the basis of the band model for graphite (*49, 88*). Because of the loss of electrons during the oxidation, "holes" are produced in the lower almost completely occupied band of graphite and as a result the number of charge carriers increases. Since this occurs predominantly in the lower band, the Hall constant is positive. Graphite bisulfate is thus a conductor of the *p*-type.

When the bisulfate compound is reduced cathodically, the conductivity sinks once more, though the initial value for the graphite taken is not reached again. When about two-thirds of the compound is reduced, the conductivity does not change further even when further current is passed. Hennig concluded from this that reduction was not completely reversible and explained this by the occurrence of stable "residue compounds" (compare Section IV).

C. HALOGEN-GRAPHITE COMPOUNDS

The halogens show characteristic differences in their behavior towards graphite. Investigations up to the present have failed to show a reaction of iodine with graphite. Bromine and chlorine give unstable graphite compounds with the limiting composition C_8X, which are stable only under the saturation pressure of the halogen. On the other hand fluorine forms the two compounds C_4F and CF which are very inert chemically and are homopolar in character. Iodine monochloride behaves towards graphite similarly to bromine.

1. *Graphite Bromide*

Graphite bromide is formed by the action on graphite of gaseous or liquid bromine or of bromine dissolved in organic solvents. About 0.8 gm of bromine per gram of graphite is taken up from an atmosphere saturated with bromine vapor at room temperature, corresponding with an atomic ratio of 1Br:8C (*21, 56*). This value, which is calculated from the weight increase, is found for natural graphites of very different particle size and has been verified by Hérold (*31*) from tensimetric measurements. The same author finds the somewhat lower value of 1Br:10C for Acheson graphite.

The bromine which has been taken up is for the most part rapidly given up on diminishing the external pressure of bromine vapor. However, a residue, which can amount to 3-10% according to the crystal size of the graphite and the rate of decomposition, remains behind in the graphite. Even at a red heat it is not possible to get graphite completely free of bromine. These bromine-poor products, which are called "residue compounds," have been more closely investigated by Hennig (*28*) (compare Section IV).

From X-ray investigations, pyknometric measurements under liquid bromine, and from microscopic measurements of the volume increase of graphite crystals it is found that, for the composition C_8Br (or $C_{16}Br_2$) alternate interplanar spacings of the graphite lattice are widened to 7.05 Å by the entry of bromine. Intensity calculations for the (00*l*) interferences agree best with the assumption that the bromine forms a layer between two carbon layers (*56*). In addition to this second stage there probably exists a third stage poorer in bromine (*89, 31*).

The constitution of graphite bromide has been discussed many times. An indication of a partly ionic structure is derived from the fact that the spacing of the carbon planes (7.05 Å) is greater than the sum of the effective cross section of a graphite and a bromine layer. In accordance with this one obtains in a calculation of the spatial requirement of bromine too high a value (23.5), which approximates to the value for bromide ions in salts (25.0) and is considerably above the atomic volume of bromine (19.2).

Magnetic measurements have not made any substantial contribution to the question of the bonding of bromine. A weak diamagnetism has been found by several authors (*41, 23, 48, 30*). Ubbelohde finds for $C_{9.98}Br$, $\chi_{gm} = -0.40 \times 10^{-6}$. It follows from all the measurements that the anomalous diamagnetism of graphite is lowered by the uptake of bromine and is almost lost at high bromine concentrations.

Conductivity measurements carried out on preparations with high and low bromine contents show that the conductivity of graphite increases considerably with the incorporation of bromine (*48, 28*). Hennig (*28*) finds that the Hall constants of graphite bromide and bisulfate, after treating the graphite so as to produce the same fractional decrease in the resistance, are approximately of the same magnitude and he concludes that the two compounds are very similar in constitution. From these measurements Hennig calculates the relationship of the ionized to the un-ionized fraction in graphite bromide as $1Br^-$ to $3Br_2$. The ideal formula of stage two is then $C_{56}{}^+Br^- \cdot 3Br_2$. According to this view the compound is a graphite bromide and belongs to the saltlike graphite compounds. It is, however, characteristic of these that they may be changed reversibly into one another by ion exchange. One would therefore expect that, under concentrated sulfuric acid, graphite would be transformed into the second stage of the bisulfate. This reaction does not, however, occur at room temperature even after weeks. The bisulfate is first formed at 80-100°C and then only the third stage results with a ratio $1HSO_4{}^-:81C$. It thus appears that there are certain differences between graphite bromide and graphite bisulfate.

Graphite bromide is of interest in relation to the carbon-catalyzed formation of hydrogen bromide from the elements. This synthesis occurs without a catalyst as a homogeneous reaction at 500° but has a measurable rate at 120° if carbon is used as a catalyst. It is not very likely that under the reaction conditions (higher temperature, low partial pressure of bromine) bromine molecules can be introduced between the carbon planes. A much more likely assumption is that bromine is absorbed on the basal faces of the graphite crystals and is bound there in the same way as it is bound between the planes in graphite bromide. This view is supported by measurements of the catalytic behavior of graphite oxide soot in the synthesis of hydrogen bromide (*75*). This soot, the surface of which is predominantly made up of basal faces (compare Section IIA1), shows so high a catalytic activity that it seems impossible to attribute this effect to the small surface of the prismatic faces.

The activation of halogens by carbon may probably be thought of in the same way as the activation of molecular oxygen by semiconductors (see summaries under refs. *16, 26*). According to this view, chemisorption of bromine on the basal faces of the graphite crystal is linked with an electron displacement or transfer of the free electrons of the graphite to bromine. We may then expect that when the electron concentration in the carbon planes is lowered, as it is by the incorporation of metallic halides (see Section IIID3), the catalytic properties of the graphite will deteriorate. This has been fully substantiated in the author's laboratory by a comparison of the rate of formation of hydrogen bromide with graphite or indium trichloride-graphite as catalyst.

2. Graphite Chloride

Whereas graphite bromide has been known for a long time, the lower rate of reaction of chlorine with graphite delayed the discovery of graphite chloride, the existence of which has been proved only recently. In the course of an investigation of the conductivity of graphite under liquid chlorine at −33° Hennig (*28*) observed that the resistance decreased in the course of three days to one-tenth of its initial value. He concluded that chlorine, like bromine, is able to enter the graphite lattice. Juza and Schmidt (*42, 40*) came to the same conclusion when, in studying the sorption of chlorine and bromine on active carbon, they noticed a fall in the anomalous diamagnetism of the carbon. Juza and his coworkers (*43, 39*), in a detailed investigation, used the change of susceptibility as a criterion for interstitial compound formation. The rate of reaction between chlorine and graphite proved to be very dependent on particle size. With particles of diameter 0.5-1 mm at −78° the anomalous diamagnetism disappeared in about 500 days whereas, for a diameter of 0.03 mm, it did so in about 100 days. The rate of entry of chlorine into the graphite lattice increased with rising temperature and was a maximum at −12°. At 0° and above a reaction could no longer be detected by the magnetic method.

In order to determine the composition of the saturated graphite chloride a susceptibility-concentration diagram was drawn, from which it was found that 0.10-0.136 gm-atoms of chlorine per gram atom of carbon sufficed to destroy the anomalous diamagnetism completely. These values are consistent with the formula C_8Cl, which is analogous to the formula of graphite bromide. Isobaric degradation of the graphite chloride at low temperatures yields results which also support this formula.

Graphite chloride prepared at low temperatures is stable at 0°, above which temperature it decomposes, even under the saturation pressure of chlorine. Juza refers to the fact that graphite bromide also decomposes at increased temperatures under the saturation pressure of bromine.

Uptake of chlorine may be substantially increased if the decomposition product of graphite bromide, i.e., the residue compound, is used in place of pure graphite, and the amount of chloride absorbed rises with the bromine content of the graphite. On thermal decomposition, specimens which contain bromine retain more chlorine than does bromine-free graphite. An increased uptake of chlorine may also be obtained by using graphite made by decomposing the bisulfate in the presence of hydrogen chloride. Summarizing, it may be said that the behavior of chlorine and bromine is similar. The reaction rate is lower for chlorine, which must be related to the fact that the chloride is stable only at much lower temperatures.

3. Iodine and Graphite

No change in the conductivity or susceptibility of graphite can be observed when it is allowed to react with iodine at −78° to 183° (*28, 39*). Hérold (*31*) was also unable to detect any reaction up to 500°. On the other hand Juza (*39*), using graphite containing bromine, observed a pronounced lowering of the susceptibility. The amount of iodine was about three times as great as the bromine content of the graphite so that it could not have been taken up only as iodine monobromide.

4. Iodine Monochloride and Graphite

Absorption of iodine monochloride by graphite has been detected both by the conductivity change and from X-ray observations (*28*). Rüdorff and Sils (*73*) found that graphite increases in weight by about 250% in iodine monochloride vapor at 30°, while in single crystals saturated with the monochloride there was more than a threefold increase in volume. The identity period, I_c, was calculated to be 21.2 Å and embraced two carbon planes. It was not, however, clear if a first or second stage was present. Croft (*11a*) found that in the reaction of iodine trichloride with graphite, the product prepared at 90° swells when heated strongly. After washing with hydrochloric acid it retains 30% of trichloride.

D. INTERCALATION OF METAL CHLORIDES IN GRAPHITE

1. Preparation and Properties

These compounds, which have become known in large numbers only in recent years, form a specially interesting class of graphite compounds because of problems associated with their constitution. Their investigation probably cannot yet be regarded as complete, for a number of experimental observations still await an explanation. The compounds result when graphite is heated with the anhydrous metal chloride. The intercalated chloride is given off again at a sufficiently high temperature. Up to the present only metal chlorides have been observed to form these compounds, but compounds with other halides should also be formed.

The first compound of this sort was ferric chloride graphite (*21, 84*). Rüdorff and Schulz (*65*) obtained from graphite and ferric chloride at 200-300° a stage 1 compound with 60-70% of ferric chloride. In this compound separate layers of ferric chloride, as they occur in the lattice of the pure $FeCl_3$, were intercalated between the carbon planes, which were unchanged, though the distance between them was increased to 9.4 Å.

In attempts to separate ferric chloride and aluminum chloride by intercalation in graphite, Croft (*10*) found that aluminum chloride could be intercalated either alone or together with ferric chloride. Further work (*11, 11a*) led to the surprising result that numerous metal chlorides are able to react with graphite. The compounds studied are set out in Table VI, which is taken from Croft's work. It includes thirty chlorides and two oxychlorides for which intercalation was detected.

TABLE VI

SUMMARY OF INTERCALATION TEST RESULTS (CROFT, *11a*)

Substances intercalated in graphite			Substances not intercalated in graphite			
$CuCl_2$	$TaCl_5$	$RhCl_3$	$CuCl$	$SiCl_4$	$AsCl_3$	$PdCl_2$
$CuBr_2$	$FeCl_3$	$PdCl_4$	$BeCl_2$	$GeCl_4$	$SbCl_3$	$PtCl_2$
$AuCl_3$	$CrCl_3$	$PtCl_4$	$MgCl_2$	$TiCl_4$	$BiCl_3$	$LaCl_3$
BCl_3	CrO_2Cl_2	ICl	$CaCl_2$	$SnCl_2$	VCl_4	$CeCl_3$
$AlCl_3$	CrO_2F_2	ICl_3	$BaCl_2$	$SnCl_4$	SO_2Cl_2	$PrCl_3$
$AlBr_3$	$MoCl_5$	YCl_3	$ZnCl_2$	$PbCl_2$	$SOCl_2$	$NdCl_3$
$GaCl_3$	WCl_6	$SmCl_3$	$CdCl_2$	$PbCl_4$	$SeOCl_2$	$ErCl_3$
$InCl_3$	UCl_4	$GdCl_3$	CdI_2	$ThCl_4$	$TeCl_4$	$ScCl_3$
$TlCl_3$	UO_2Cl_2	$YbCl_3$	Hg_2Cl_2	ThI_4	$MnCl_2$	
$ZrCl_4$	$ReCl_4$	$DyCl_3$	$HgCl_2$	PCl_3	$CoCl_2$	
$HfCl_4$	$CoCl_3$	$EuCl_3$	CCl_4	PCl_5	$NiCl_2$	
$SbCl_5$	$RuCl_3$					

In general, reactions were carried out at temperatures near to the melting or sublimation point of the particular halide. After heating the graphite and halide together for several hours, the graphite was washed with hydrochloric acid to remove excess halide. Intercalation was recognized in most cases by swelling of the graphite when it was heated rapidly to 700°. The quantity of halide taken up was determined by evaporating to fuming with concentrated sulfuric acid and weighing the residue after burning off the graphite. Alternatively, readily volatile halides were determined by thermal decomposition of the graphite compound. The results are scattered over a wide range of compositions. Thus Croft finds for $CuCl_2$, 4%; for $AlCl_3$ and $MoCl_5$, 25%; for $TaCl_5$, 44%; and for $TlCl_3$, 70%. Two things are noteworthy in Croft's work: first, intercalation is not restricted to readily volatile chlorides of low melting point and, second, cobalt trichloride and palladium tetrachloride, which do not exist in the free state, are stabilized by intercalation.[4]

Croft refers to the use of the different behavior of metal chlorides towards graphite as a means for effecting their separation. Experiments of this sort have been made by Vickery and Campbell (*87*) for the rare-earth halides. Croft's results on the reactivity of the halides are not fully borne out. In an independent study of the action of aluminum chloride on graphite it was found that intercalation occurs only if free chlorine is present during reaction. This condition appears to have been satisfied in Croft's experiments, since the halides were prepared by chlorinating the metal and were sublimed directly onto the graphite. Rüdorff and Zeller (*70*) were able, by carefully subliming off the excess halide, to prepare homogeneous aluminum chloride-graphite preparations corresponding to stages 1, 2, and 4, among which stage 1, with 52-55% $AlCl_3$ ($1AlCl_3{:}9C$) was remarkable because of its deep blue color. The same color was shown by stage 1 of the gallium chloride graphite with 60% of $GaCl_3$. On the other hand, only the second stage for indium trichloride could be prepared, with 53% $InCl_3$ (*61*). These two halides also react only in the presence of free chlorine. The same observation was made in the reaction of graphite with uranium pentachloride, cadmium chloride, and mercuric chloride. The last two examples show that chlorides for which Croft's experiments gave negative results are able to become intercalated if the reaction is carried out in a chlorine atmosphere.

According to Dzurus and Hennig (*15*) the free chlorine necessary for the occurrence of reaction between graphite and aluminum trichloride does not act catalytically, as Rüdorff and Zeller first assumed, but is partly taken up in the lattice. Rüdorff and Landel (*61*) found this to be true of the gallium trichloride-graphite compound also. For both compounds the ratio Me:Cl is between 1:3.2 and 1:3.4 and the compounds therefore oxidize potassium iodide solution and cause iodine to separate.

---

[4] These intercalation compounds were obtained by prolonged heating of graphite with the lower chlorides $CoCl_2$ or $PdCl_2$ in a stream of chlorine.

By contrast the quantity of "active" halogen is extremely small for the compounds of graphite with indium chloride, mercuric chloride, and cadmium chloride, and lies at the limit of analytical detection.

The compounds show striking differences in their behavior to water, acids, and organic solvents. Whereas the blue aluminum chloride- and gallium chloride-graphite compounds are extremely sensitive to water and are largely decomposed by it, it seems that indium chloride- and ferric chloride-graphite are stable for, even after boiling with concentrated hydrochloric acid, one finds high values for the halogen content ($InCl_3$, 50%; $FeCl_3$, 55%). New investigations by Rüdorff and Landel show, however, that these compounds are also decomposed by water and organic solvents. This follows unambiguously from the dependence of the $MeCl_3$ content on the size of the graphite crystals, the nature of the solvent, density determinations, and X-ray investigations. Probably all metal halide-graphite compounds, as well as the other polar graphite compounds, are decomposed by water, though there are great differences in the extent of decomposition for the separate compounds.[5]

These differences may be explained as follows: the solvent undoubtedly attacks the edges of the layer planes of the graphite crystal. When the halide is leached out from the edge, the *c* interplanar distance of about 9.4 Å can no longer be maintained in this region. Before the solvent can penetrate further into the crystal or the halide can diffuse from the interior, the interplanar distance at the crystal edges reverts to about the value in graphite itself. Leached preparations are thus not homogeneous, but the crystal consists of a nucleus of undecomposed compound which is protected from further decomposition by a more or less thick skin of graphite. Analysis shows that the smaller the crystals, the greater the weight of the halide-free zone. The more rapidly the leaching agent acts (e.g., water > acetone) the more extensively does decomposition penetrate into the crystal.

There is only a difference in degree between graphite compounds of aluminum trichloride or gallium trichloride on the one hand and indium trichloride or ferric chloride on the other as regards their behavior in water; for the first two, the rate of decomposition of the graphite compound, or the mobility of the halide within the crystal, is so big that, for sufficiently small crystals, decomposition extends over the whole crystal. The lack of homogeneity in leached ferric chloride-graphite preparations has also been detected by Cowley and Ibers (*9*) by X-ray and electron diffraction. It was found that a preparation containing

---

[5] Croft's analytical results therefore probably are not valid for the composition of the pure compounds, since all samples were treated with hydrochloric acid before analysis.

55% of ferric chloride contained 18% of graphite and 82% of a ferric chloride-graphite compound with 66.9% of the halide.[6]

2. Structure

An exact structure determination has up to the present been made only for ferric chloride-graphite (*9*). The separate ferric chloride layers, which lie between two carbon layers, are only 92% occupied. The arrangement of the ferric ions and their distance from one another is the same as in ferric chloride, the hexagonal *a* axis of the network of ferric ions forming an angle of 30° with the *a* axis of the graphite. The arrangement of chloride ions and their distances, on the other hand, are different from those in free ferric chloride. They have preferred sites, which reveals a certain relationship to the carbon atoms of the neighboring graphite layers. In indium trichloride graphite certain additional lines in the powder diagram indicate that the trichloride is also intercalated as layers with almost the same In-In distance as in free indium trichloride. From the composition an approximately 80% occupation of the indium trichloride layers is deduced (*61*).

For other compounds only the lattice expansion has hitherto been determined by the X-ray method by calculating the identity period from the $(00l)$ reflections. The distance apart of the carbon planes is approximately the same for the various halides and equal to 9.5 Å.

3. Bonding in the Metal Halide-Graphite Compounds

The bonding has been discussed in detail by Croft (*11b*) and Dzurus and Hennig (*15*). These authors concluded that the compounds were ionic. Croft supported this view by considering the differences which he found in the reactivity of the halides. He points out that, except for elements of Group IIIA, the intercalated compounds belong to the transition elements, and that, for polyvalent elements, only the chloride of the higher oxidation state is intercalated. Thus cupric and ferric chlorides react whereas cuprous and ferrous chlorides do not. Intercalation occurs only when two criteria are satisfied: it must be possible to transfer electrons to the cation from the conduction band of the graphite, and the cation must have a correspondingly high electron affinity. Croft considers the presence of unoccupied orbitals in the cation to be necessary. For aluminum chloride-graphite and the homologous compounds in which the cation cannot change its charge, free valency orbitals of the cation

---

[6] The lack of homogeneity was attributed by the authors to decomposition of the ferric chloride-graphite compound formed initially into graphite and a phase richer in ferric chloride as it cooled.

are occupied by electrons from the $2p$ π-orbitals of graphite, when a bond like that in "outer orbital" complexes is thought to result.

Dzurus and Hennig have put forward a modified and more detailed theory. Measurements of the electrical conductivity and Hall effect on halide-poor $FeCl_3$-graphite and $AlCl_3$-graphite compounds with a ratio $1MeCl_3$:200-500 C atoms show that these substances belong to the acceptor or *p*-type compounds. Since the changes in electrical properties are the same as in graphite bisulfate and graphite bromide, Dzurus and Hennig conclude that the metal halide compounds are similarly constituted and adopt such formulae as, for example, $C_m{}^+Cl^- \cdot FeCl_2 \cdot 3FeCl_3$ for ferric chloride-graphite. Only a quarter of the ferric ions are thought to act as electron acceptors. Earlier magnetic measurements made on ferric chloride graphite (*65*) are consistent with this view. For other metal halides capable of existing in several oxidation states, corresponding formulae were proposed. Calculations of free energy made on Hennig's electrostatic model (*29*) give the differences in reactivity of the separate halides in roughly the correct order.

In the case of aluminum chloride-graphite the halogen which is simultaneously intercalated in the lattice acts as an acceptor: $C_m{}^+Cl^- \cdot 3AlCl_3$. Strong support for this view comes from the fact that the quantity of aluminum chloride intercalated is proportional to the concentration of acceptor. In this the acceptor may be—in addition to chlorine—bromine, iodine, or a halide of one of the transition elements. Thus aluminum chloride is intercalated in the absence of free halogen if ferric chloride is added as acceptor. For very low concentrations the ratio of intercalated aluminum chloride to ferric chloride lies between 2 and 3, so that the formula $C_m{}^+Cl^- \cdot FeCl_2 \cdot 3AlCl_3$ suggests itself for this compound. Whether, and to what extent, this view still remains to be amended can be shown only by further experiments. Magnetic measurements on suitable compounds might be particularly revealing.

E. OTHER INTERCALATION COMPOUNDS

In the view of the constitution of metal chloride-graphite compounds put forward by Croft and Hennig (see Section IIID), the controlling factor in intercalation is the electron affinity and electron configuration of the cation, while the nature of the anion is of secondary significance. Croft considers this theory to be supported by the fact that oxides and sulfides of polyvalent elements in higher oxidation states are also able to react with graphite (compare ref. *12*). In a further publication, Croft (*13*) generalizes the information gained on graphite compounds and comes to the conclusion that other crystal lattices, and particularly layer lattices, should be able to take up suitable compounds, provided an electronic interaction can occur between the host lattice and the intercalated partner, and that the host lattice has room to take up the latter. Croft has attempted to verify this prediction experimentally in the case of boron nitride, which is discussed in a later section.

1. *Intercalation of Metal Oxides and Sulfides in Graphite* (*12*)

The investigation embraces the oxides Sb_2O_4, CrO_3, and MoO_3 and the sulfides Sb_2S_5, Tl_2S, CuS_x, FeS_2, Cr_2S_3, V_2S_3, MoS_2, WS_2, and PdS. The compounds were heated in quartz ampoules with graphite in molecular ratios between 1:1 and 2:1. The temperatures were between 200° (Tl_2S or CrO_3) and 570°C (WS_2). In reactions with the sulfides, free sulfur was also added. Reaction products from sulfides were extracted with carbon disulfide to remove free sulfur, separated from finely divided metal sulfide which had not reacted by sieving and sorting under the microscope, and washed with nitric acid. Excess of molybdenum or chromium trioxide could be removed by sublimation or by washing with acid.

Analysis gave the values in Table VII for the oxide or sulfide contained in the graphite. Croft left open the question as to whether the quantities found represented the greatest possible amounts which could be intercalated. Some of these products showed properties similar to those which are characteristic of the metal chloride compounds, e.g., swelling when strongly heated. It was possible to sublime out intercalated molybdenum trioxide unchanged by heating the graphite compound. The iron sulfide and copper sulfide compounds decomposed when treated with dilute acids. X-ray powder photographs for the sulfidic products were very complicated but were different from those of the lower sulfides. Interplanar distances of 11-12 Å were measured for the compounds of the oxides with graphite. Croft interprets these experiments as showing that metals whose chlorides are intercalated in graphite

TABLE VII

PERCENTAGE OF OXIDE OR SULFIDE IN GRAPHITE

Oxide	Percentage	Sulfide	Percentage	Sulfide	Percentage
Sb_2O_4	1.6	$Sb_2S_{4.8}$	9.4	$Cr_2S_{3.5}$	4.0
CrO_3	55.0	TlS_2	27.0	$V_2S_{3.5}$	3.7
MoO_3	10.75	$CuS_{1.3}$	16.2	$WS_{2.4}$	14.1
		FeS_2	12.2	$PdS_{2.2}$	8.8

are also able to react as oxides or sulfides provided the metal is in a high oxidation state.

2. Molecular Compounds of Boron Nitride

The crystal structure of boron nitride resembles that of graphite. The boron and nitrogen atoms form plane regular hexagonal nets which are arranged parallel to one another at a distance of 3.33 Å. An essential difference between graphite and boron nitride is that in the latter there are no free electrons. Pure boron nitride is white and does not conduct electricity.

The similarity of the two structures led Croft (*13*) to attempt the preparation of boron nitride intercalation compounds. He used the metal halides $SbCl_3$, $SbCl_5$, $AsCl_3$, CuCl, $CuCl_2$, $FeCl_3$, $AlCl_3$, and also BF_3, BCl_3, Br_2, ICl, liquid ammonia, and N_2H_4. The same procedure was used as in the preparation of metal chloride-graphite compounds.

Croft concluded from the weight increase of the boron nitride as well as from analysis of the products after washing with dilute hydrochloric acid that, of the compounds studied, $SbCl_3$, $AsCl_3$, CuCl, $FeCl_3$, $AlCl_3$, and N_2H_4 were intercalated in boron nitride in amounts between 2% ($SbCl_3$ and N_2H_4) and 13% ($AlCl_3$). As in the case of graphite compounds, these products swell considerably when heated. The photographs published by Croft are very striking. They show that boron nitride single crystals containing 2% of hydrazine swell similarly to ferric chloride graphite containing 56% of ferric chloride.

Croft explains the results in terms of the acceptor property of the boron atoms. They tend to take an electron pair from a donor molecule to form sp^3 bonds. This is why only halides in lower oxidation states react with boron nitride (e.g., CuCl and $SbCl_3$ but not $CuCl_2$ or $SbCl_5$). This is different from the case of graphite in which the carbon planes are a source of electrons. The intercalation of aluminum and ferric chlorides is attributed by Croft to bonding by the electron pairs of the nitrogen atoms of boron nitride. It is surprising, however, that boron trifluoride and trichloride, which are particularly good electron acceptors, appear unable to become intercalated.

A closer investigation and characterization of these interesting reaction products seems called for, since some of Croft's results are contrary to investigations made in the author's laboratory on the behavior toward boron nitride of $FeCl_3$, $CoCl_2$, $NiCl_2$, $NiBr_2$, $AlCl_3$, and other compounds (*69*). No change in the boron nitride could be observed and, especially, there was no expansion of the boron nitride lattice, which would be expected as the result of intercalation. An explanation for the discrepancy can probably be sought only in a difference between the starting materials. In the experiments made in the Tübingen laboratory, two pure white finely divided preparations were available which had been prepared in different ways at 800°. Determinations of boron and nitrogen gave 98-99% of BN. The specimens used by Croft were obtained from an amorphous product by heating to 2000°. He described the crystalline and partly laminar product as black and lustrous. This description is not, however, consistent with the properties of boron nitride, so that Croft's results probably do not refer to the pure compound.

IV. Residue Compounds

Analytical investigations of graphite compounds have repeatedly shown that when the pure compound is decomposed or reduced, a small proportion of the intercalated substance is obstinately held in the lattice, and is often recovered only after complete destruction of the graphite. According to Hennig (*27*) decomposition always leads to "residue compounds" which differ from the actual graphite compounds in various properties, e.g., conductivity and Hall effect. Residue compounds may be reconverted into the same lamellar compounds from which they were produced. The residue compounds from graphite bisulfate and graphite bromide have been studied in detail (*27, 27a, 28, 44a, 50*).

The quantity of intercalated material retained depends on the composition of the corresponding lamellar compound and increases with the original concentration in the host lattice. Differences between the two compounds are associated with the ionized part of the intercalated component. Hennig has calculated from the conductivity of the residue compound of graphite bromide a ratio of $1Br^-:2.2Br_2$ and for graphite bisulfate $1HSO_4^-:4H_2SO_4$, whereas in the saturated lamellar compounds the ratios are $1Br^-:3Br_2$ and $1HSO_4^-:2H_2SO_4$. It is difficult to find an explanation for the increase of the fraction ionized for graphite bromide and for the decrease in the case of the bisulfate.

The two compounds differ structurally in the way in which the reaction partner is distributed in the graphite lattice. Whereas in the lamellar compounds the intercalated layers have a periodic distribution—i.e., are interspersed stepwise—between the carbon planes, distribution in the residue compounds is irregular. Precision measurements of the lattice constants for the residue compounds of graphite bromide and bisulfate gave only a trifling increase in the *c* axis of the graphite, most of the deviations being within the limits of error. Hennig concluded that impurities in residue compounds were situated mainly in holes and imperfections in the graphite lattice, the fraction remaining intercalated between the carbon planes being under 1%.

Chemically, the residue compounds are of interest because they possess a greater chemical reactivity than pure graphite. Thus Hennig was able to show that the residue compound from graphite bromide (1.4Br: 100C) was able to react to a small extent with iodine or aluminum chloride ($2AlCl_3$:100C), whereas there is no reaction for pure graphite. For the influence of the residue compound of graphite bromide on the intercalation of chlorine in graphite see Section IIIC2.

Many properties of residue compounds are also consistent with the assumption that the separate crystals of a graphite compound are not homogeneous after decomposition, and still contain undecomposed compound in their interiors. This is surrounded by a more or less thick outer layer of graphite which protects it from further decomposition. This idea has been discussed already in Section IIID in connection with the behavior of metal halide-graphite compounds towards water. It will be necessary to wait for further experiments in order to explain more precisely the mode of decomposition of graphite compounds.

V. Comparative Survey

The new compounds found in the last ten years, C_4F, the ammonia and amine derivatives of alkali- and alkaline earth metal-graphite compounds and the large group of metal halide intercalation compounds, constitute further examples of the surprisingly diverse reactivity of graphite. The study of physical properties of the graphite compounds, together with elucidation of structures by X-rays, has led to a deep insight into the mode of reaction of graphite and the constitution of intercalation compounds.

The formation of graphite compounds is linked in every case to a change in the electron concentration in the graphite. The elements with the highest electron affinity, i.e., fluorine and oxygen, produce the greatest change, in that they form covalent bonds with the carbon atoms. Linked with this we find a change in the structure of the carbon layers in carbon monofluoride and graphite oxide, as well as a decrease or disappearance of conductivity. Strictly speaking, these are no longer graphite compounds, for the characteristic properties of graphite, namely the presence of free electrons and the arrangement of carbon atoms in planes, have been lost.

Chemically, these homopolar compounds differ from the other graphite compounds in their stability to water and other solvents[7] and in their relatively low reactivity, which is particularly striking for the fluorine compounds. All other reactions of graphite which lead to intercalation compounds may be associated with an electron transition between the reaction partner and the carbon planes. When this occurs only the electron concentration in the conduction band is altered and the layer planes remain as they were in graphite. The compounds are therefore polar in character. They differ from the homopolar compounds in their crystal structure, their conductivity, which is greater than that of pure graphite, and also in their greater reactivity. The intercalation of the reaction partner in a series of stages is characteristic of these compounds. This is certainly to be attributed to the tendency for the layers with a charge of the same sign to distribute themselves at equal distances in the lattice.

Graphite acts as an amphoteric substance in producing these polar compounds: it is an electron acceptor towards the strongly electropositive alkali and alkaline earth metals and a donor to atoms or ions with a sufficient electron affinity. However, the number of electrons accepted or donated always remains small in relation to the total electron concentration of the individual carbon planes. In the graphite salts, for example, in which the ionic character is undoubtedly most strongly developed, there is only one positive charge to 24 carbon atoms of a carbon layer. This follows from the formula for stage 1 of the bisulfate, $C_{24}^{+}HSO_4^{-} \cdot 2H_2O$. A similar ratio is encountered for other compounds, for example, $C_{27}^{+}Cl^{-} \cdot 3AlCl_3$ or $C_{27}^{+}AlCl_4^{-} \cdot 2AlCl_3$; $C_{27}^{+}GaCl_4^{-} \cdot 2GaCl_3$.

It is interesting that apparently only small deviations from this ratio are possible in each stage, which, although it possesses a certain range of homogeneity, goes over discontinuously to other stages with greater changes in composition. These have new charge distributions in their lattices. In relation to the charge of the carbon atoms, appreciably more atoms or molecules are intercalated, i.e., the greater part are not bound ionically, and probably serve to fill in gaps, so that the intercalated partner can form coherent layers between the carbon planes. All compounds of this sort studied to the present have been found to be reactive and to be more or less completely decomposed by water.

REFERENCES

1. Asher, R. C., and Wilson, S. A., *Nature* **181,** 409 (1958).
2. Balfour, A. E., Riley, H. L., and Robinson, R. M., *J. Chem. Soc.* **1936, 456.**
3. Bernal, J. D., *Proc. Roy. Soc.* **A106,** 749 (1924).
4. Biltz, W., "Raumchemie der Festen Stoffe." L. Voss, Leipzig, 1937.

---

[7] Swelling of graphite oxide in water is reversible and does not change the degree of oxidation.

5. Brodie, B. C., *Ann. Chem. Phys.* [3] **45**, 351 (1855).
6. Brodie, B. C., *Ann. Chem.* **114**, 6 (1860).
7. Carter, A. H., De Moulds, V., and Riley, H. L., *J. Chem. Soc.* **1937**, 1305.
8. Clauss, A., Plass, R., Boehm, H. P., and Hofmann, U., *Z. anorg. u. allgem. Chem.* **291**, 205 (1957).
9. Cowley, J. M., and Ibers, J. A., *Acta Cryst.* **9**, 421 (1956).
10. Croft, R. C., *J. Appl. Chem.* **2**, 557 (1952).
11. Croft, R. C., *Nature* **172**, 725 (1953).
11a. Croft, R. C., *Australian J. Chem.* **9**, 184 (1956).
11b. Croft, R. C., *Australian J. Chem.* **9**, 194 (1956).
12. Croft, R. C., *Australian J. Chem.* **9**, 201 (1956).
13. Croft, R. C., *Australian J. Chem.* **9**, 206 (1956).
14. Dzurus, M., and Hennig, G. R., *J. Chem. Phys.* **27**, 275 (1957).
15. Dzurus, M., and Hennig, G. R., *J. Am. Chem. Soc.* **79**, 1051 (1957).
16. Fensham, P. F., *Quart. Revs.* 11, 227 (1957).
17. Finch, G. J., and Wilman, H., *Proc. Roy. Soc.* **A155**, 345 (1936).
18. Franklin, R. E., *J. chim. phys.* **50**, C 26 (1953).
19. Fredenhagen, K., and Cadenbach, G., *Z. anorg. u. allgem. Chem.* **158**, 249 (1926).
20. Fredenhagen, K., and Suck, H., *Z. anorg. u. allgem. Chem.* **178**, 353 (1929).
21. Frenzel, A., Dissertation, Berlin, Technische Hochschule, 1933
22. Frenzel, A., and Hofmann, U., *Z. Elektrochem.* **40**, 511 (1934).
23. Goldsmith, M., *J. Chem. Phys.* **18**, 523 (1950).
24. Hadzi, D., and Novak, A., *Trans. Faraday Soc.* **51**, 1614 (1955).
25. Hassel, O., and Mark, H., *Z. Physik* **25**, 317 (1924).
26. Hauffe, K., *Angew. Chem.* **67**, 189 (1955).
27. Hennig, G. R., *J. Chem. Phys.* **19**, 922 (1951).
27a. Hennig, G. R., *J. Chem. Phys.* **20**, 1438 (1952).
28. Hennig, G. R., *J. Chem. Phys.* **20**, 1443 (1952).
29. Hennig, G. R., *Proc. 1st and 2nd Conf. on Carbon, Univ. of Buffalo,* p. 103 (1956).
30. Hennig, G. R., and McClelland, J. D., *J. Chem. Phys.* **23**, 1431 (1955).
31. Hérold, A., *Bull. soc. chim. France* **1955**, 999.
32. Hérold, A., *Compt. rend.* **232**, 838 (1951).
33. Hofmann, U., *Ergeb. exakt. Naturw.* **18**, 229 (1939).
34. Hofmann, U., and Boehm, H. P., *Z. anorg. u. allgem. Chem.* **278**, 58 (1955).
35. Hofmann, U., and Holst, R., *Chem. Ber.* **72**, 754 (1939).
36. Hofmann, U., and König, E., *Z. anorg. u. allgem. Chem.* **234**, 311 (1937).
37. Hofmann, U., and Ohlerich, G., *Angew. Chem.* **62**, 16 (1950).
38. Hofmann, U., Frenzel, A., and Csalan, E., *Ann. Chem.* **510**, 1 (1934).
39. Juza, R., and Schmeckenbecher, A., *Z. anorg. u. allgem. Chem.* **292**, 46 (1957).
40. Juza, R., and Schmidt, P., *Chem. Ber.* **89**, 428 (1956).
41. Juza, R., Lübbe, H., and Heinlein, L., *Z. anorg. u. allgem. Chem.* **258**, 105 (1949).
42. Juza, R., Schmidt, P., Schmeckenbecher, A., and Jönck, P., *Naturwiss.* **42**, 124 (1955).
43. Juza, R., Jönck, P., and Schmeckenbecher, A., *Z. anorg u. allgem. Chem.* **292**, 34 (1957).
44. Klemm, W., and Abitz, ref. in *FIAT Rev. German Sci. 1939-1946* **9**, II, 14 (1948).
44a. Kmetko, E. A., *J. Chem. Phys.* **21**, 2152 (1953).
45. Laidler, D. S., and Taylor, A., *Nature* **146**, 130 (1940).
46. Laves, F., and Baskin, Y., *Z. Krist.* **107**, 338 (1956).

47. Lipson, H., and Stokes, A. R., *Proc. Roy. Soc.* **A181,** 93 (1942).
48. McDonnell, F. R. M., Pink, R. C., and Ubbelohde, A. R., *J. Chem. Soc.* **1951,** 191.
49. Mrozowski, S., *Phys. Rev.* **78,** 644 (1950).
50. Mrozowski, S., *J. Chem. Phys.* **21,** 492 (1953).
51. Quartermann, L., and Primak, W., *J. Am. Chem. Soc.* **74,** 806 (1952).
52. Riley, H. L., *Fuel* **24,** 8 (1945).
53. Riley, H. L., *Fuel* **24,** 43 (1945).
54. Rubisch, O., Dissertation, Tübingen, 1956.
55. Rüdorff, W., *Z. physik. Chem. (Leipzig)* **B45,** 42 (1938).
56. Rüdorff, W., *Z. anorg. u. allgem. Chem.* **245,** 383 (1941).
57. Rüdorff, W., *Wien. Chem. Z.* **47,** 172 (1944).
58. Rüdorff, W., *Z. anorg. u. allgem. Chem.* **254,** 319 (1947).
59. Rüdorff, W., and Brodersen, K., *Z. Naturforsch.* **12b,** 595 (1957).
60. Rüdorff, W., and Hofmann, U., *Z. anorg. u. allgem. Chem.* **238,** 1 (1938).
61. Rüdorff, W., and Landel, A., *Z. anorg. u. allgem. Chem.* **293,** 327 (1958).
62. Rüdorff, W., and Rüdorff, G., *Z. anorg. u. allgem. Chem.* **253,** 281 (1947).
63. Rüdorff, W., and Rüdorff, G., *Chem. Ber.* **80,** 413 (1947).
64. Rüdorff, W., and Rüdorff, G., *Chem. Ber.* **80,** 417 (1947).
65. Rüdorff, W., and Schulz, H., *Z. anorg. u. allgem. Chem.* **245,** 121 (1940).
66. Rüdorff, W., and Schulze, E., *Angew. Chem.* **66,** 305 (1954).
67. Rüdorff, W., and Schulze, E., *Z. anorg. u. allgem. Chem.* **277,** 156 (1954).
68. Rüdorff, W., and Siecke, W. F., *Chem. Ber.* **91,** 1348 (1958).
69. Rüdorff, W., and Stumpp, E., *Z. Naturforsch.* **13b,** 459 (1958).
70. Rüdorff, W., and Zeller, R., *Z. anorg. u. allgem. Chem.* **279,** 182 (1955).
71. Rüdorff, W., Hofmann, U., Rüdorff, G., Endell, J., and Ruess, G., *Z. anorg. u. allgem. Chem.* **256,** 125 (1948).
72. Rüdorff, W., Schulze, E., and Rubisch, O., *Z. anorg. u. allgem. Chem.* **282,** 232 (1955).
73. Rüdorff, W., Sils, V., and Zeller, R., *Z. anorg. allgem. Chem.* **283,** 299 (1956).
74. Ruess, G., *Monatsh. Chem.* **76,** 381 (1946).
75. Ruess, G., and Vogt, F., *Monatsh. Chem.* **78,** 222 (1948).
76. Ruff, O., *Chem. Ber.* **69A,** 181 (1936).
77. Ruff, O., and Bretschneider, O., *Z. anorg. u. allgem. Chem.* **217,** 1 (1934).
78. Schafheutl, *J. prakt. Chem.* **21,** 155 (1841); 76, 300 (1859).
79. Schleede, A., and Wellmann, M., *Z. physik. Chem. (Leipzig)* **B18,** 1 (1932).
80. Schulze, E., Dissertation, Tübingen, 1954.
81. Staudenmaier, L., *Chem. Ber.* **31,** 1394 (1899).
82. Tammann, G., and Sworykin, A., *Z. anorg. u. allgem. Chem.* **168,** 218 (1927).
83. Thiele, H., *Z. anorg. u. allgem. Chem.* **206,** 407 (1932); *Z. Elektrochem.* **40,** 26 (1934).
84. Thiele, H., *Z. anorg. u. allgem. Chem.* **207,** 340 (1932).
85. Thiele, H., *Kolloid-Z.* **80,** 1 (1937).
86. Thompson, H. W., and Temple, R. B., *J. Chem. Soc.* **1948,** 1432.
87. Vickery, R. C., and Campbell, N. L., *J. Am. Chem. Soc.* **79,** 5897 (1957).
88. Wallace, P. R., *Phys. Rev.* **71,** 622 (1947).
89. Zeller, R., Dissertation, Tübingen, 1954.
90. Zintl, E., *Angew. Chem.* **52,** 1 (1939).
91. Zintl, E., Goubeau, J., and Dullenkopf, W., *Z. physik. Chem. (Leipzig)* **A154,** 1 (1931).