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GRAPHITE INTERCALATION COMPOUNDS

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I. Introduction

Twenty years ago, Walter Rüdorff wrote a review for this series entitled "Graphite Intercalation Compounds" (*R1*). It was one of four definitive articles to come out in 1959 and 1960 (*H1, C1, U1*), a period of intense activity in graphite research. We have now again reached the "fever pitch," with not only the appearance of several new articles (*E1, H2, W1*) but also the convening of the first international conference dedicated exclusively to graphite compounds (*H3*). In the following, we shall concentrate on work performed between 1974 and the present,

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with particular emphasis on advances in the chemistry of graphite–acceptor compounds.

A glance at the structure of graphite, illustrated in Fig. 1, reveals the presence of voids between the planar, sp^2-hybridized, carbon sheets. Intercalation is the insertion of ions, atoms, or molecules into this space without the destruction of the host's layered, bonding network. Stacking order, bond distances, and, possibly, bond direction may be altered, but the characteristic, lamellar identity of the host must in some sense be preserved.

The interlayer voids are frequently attacked, to yield a periodic sequence of filled and empty spaces. The stage of a compound is defined as the ratio of host layers to guest layers, so that a first-stage compound, in which every interlayer void is filled, is the most concentrated. There is evidence that the staging concept may be, to some extent, an idealization, as is illustrated in Fig. 2.

Historically, compounds of graphite have been placed in three categories, depending on the strength of interaction between reacting species and graphite:

(*1*) Covalent compounds, arising from the attack of strong oxidizing systems, such as fluorine or Mn(VII), on graphite. The aromatic planarity of the graphite sheet is destroyed, and a buckled, sp^3-hybridized sheet is created.

(*2*) Lamellar compounds, arising from the attack of moderately strong reductants (such as potassium metal) or oxidants (such as AsF_5)

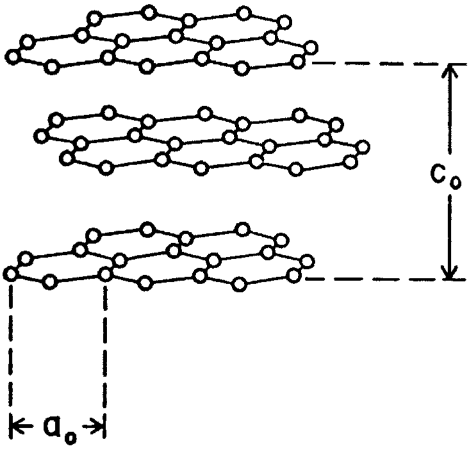

FIG. 1. The hexagonal modification of graphite. Typically, a_0 = 2.46 and c_0 = 6.7 Å, so that the spacing between adjacent, carbon planes is 3.35 Å.

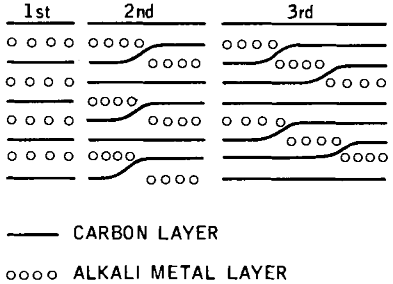

FIG. 2. A nonclassical view of staging proposed by Herold and co-workers (*H3*). From left to right are first-, second-, and third-stage compounds. (—, Carbon layer; oooo, alkali-metal layer.)

on graphite. The aromaticity of the graphite sheet is largely preserved, and the conductivity of the sheets (i.e., σ_a) increases dramatically.

(*3*) Residue compounds, arising from the decomposition of lamellar compounds by thermal or *in vacuo* treatment.

II. Covalent Compounds of Graphite

A. GRAPHITE OXIDE

Although it is the oldest of graphite compounds (*B1*), graphite oxide is still among the least understood. Made by the action of such strongly oxidizing systems as nitric acid–alkali chlorate, or sulfuric acid–sodium nitrate–permanganate, on graphite (*H4*), its formula is represented as $C_8O_2(OH)_2$ (*C2*) or $C_7O_4H_2$ (*V1*). Boehm (*B2*) suggested that graphite oxide formation is preceded by oxidative intercalation of the inorganic acid to yield a graphite "acid salt" of formula $C_n^+A^-(HA)_2$.

There are two schools of thought as to the structure of graphite oxide. Ortho or meta ether linkages have been postulated to enforce a puckering of planes (*A1*), whereas a keto–enol tautomerism was suggested to keep the carbon layers planar (*C3*).

With its oxygen functionality, graphite oxide has chemical properties more akin to those of layered disulfides or sheet silicates than to those of graphite (*G1, T1, A2*). Many studies have been of an extremely applied nature: the possibility of fluorination (*L1, N1*), redox potentials in the presence of hydrogen peroxide (*V2*), the apparent density (*L2*), the adsorption isotherms with nitrogen (*L3*), and the diffusion of Cs^+ in graphite oxide (*R2*).

B. CARBON MONOFLUORIDE

As a review on poly(carbon monofluoride) has recently appeared (*K1*), our treatment here will be cursory.

Made by direct combination of graphite and fluorine in the temperature range 420–630°C, carbon monofluoride is a white, nonconducting powder, chemically more similar to Teflon than to graphite.

As with graphite oxide, there are currently two views as to the structure of carbon monofluoride. Although detailed X-ray diffraction work suggested a chair arrangement of the sp^3-hybridized, carbon sheets (*M1*), second-moment calculations of the adsorption mode of the fluorine nuclear magnetic resonance suggested that a boat arrangement is more plausible (*E2*). The structures are illustrated in Fig. 3.

It is curious that the chair–boat problem, which is most associated with small, liquid-state molecules, arises in the context of solid-state research (*B3, I1*). Although the paucity of useful experiments militates against a definitive solution here (*E3*), the frequency independence of the NMR second moment (*E2*), the absence of an observable free-induction decay ($T_2 < 25\ \mu s$) in the pulsed NMR spectrum (*E1*), and the smoothness of the absorption mode itself (*S1*), all argue against the

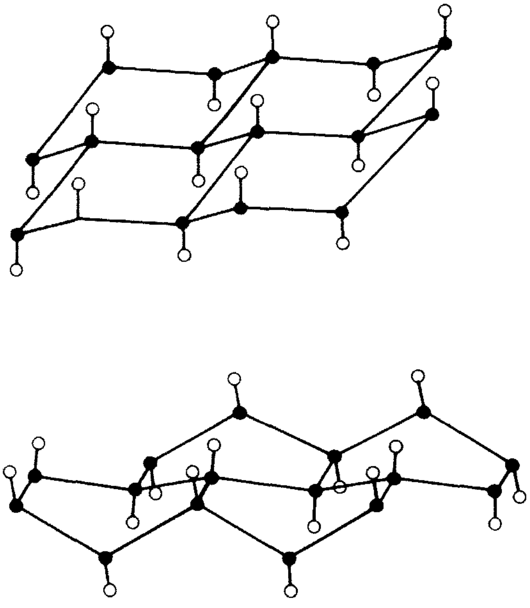

FIG. 3. The chair (top) and boat (bottom) models for the structure of poly(carbon monofluoride). (●, C; O, F.)

presence of a F_2^- species in carbon monofluoride. Additionally, there are no peculiar features in the F_{1s} and F_{2s} ESCA profiles, and the C_{1s} profile indeed suggests that the boat structure more closely fits experimental data than the chair (*C4*).

Carbon monofluoride has found use as a lubricant. Studies by Fusaro and Sliney (*F1, F2*) and Gisser (*G2*) showed that carbon monofluoride is superior to molybdenum disulfide under many conditions. Grafting of monomers can further improve lubricity (*B4*). Electrochemical applications are discussed later.

Although the covalent compounds of graphite are thus important in their own right, they represent the extreme form of oxidative intercalation. The use of fluoride compounds to achieve highly conductive materials may ultimately lead to new forms of graphite fluoride (*S1*).

III. Lamellar Compounds

A. GRAPHITE–ALKALI METALS

First reported by Fredenhagen in 1926 (*F3, F4*), the graphite–alkali-metal compounds possess a relative simplicity with respect to other intercalation compounds. To the physicist, their uncomplicated structure and well defined stoichiometry permit reasonable band-structure calculations to be made (*S2, I2*); to the chemist, their identity as solid, "infinite radical-anions" frequently allows their useful chemical substitution for such homogeneous, molecular-basis reductants as alkali metal–amines and aromatic radical anions (*N2, B5*).

A number of synthetic procedures are available (*N2*). (*1*) For precisely defined stoichiometries, the isobaric, two-bulb method of Herold is preferred (*H5, H6, H2*). (*2*) To generate compounds suitable for organic synthesis work, graphite and alkali metal may be directly combined, and heated under inert gas (*P1, L4*). (*3*) Electrolysis of fused melts has been reported to be effective (*N2*). (*4*) Although alkali metal–amine solutions will react with graphite, solvent molecules co-intercalate with the alkali metal. Utilization of alkali metal–aromatic radical anion solutions suffers the same problem.

Whereas technique (*4*) works for all alkali metals, lithium and sodium behave differently from potassium, rubidium, and cesium with respect to graphite on direct combination. The last three react facilely with graphite, to form compounds C_8M (first stage) and $C_{12n}M$ (stage $n > 1$), but lithium reacts only under more extreme conditions of temperature or pressure, or both, to form compounds of formula $C_{6n}Li$ (*G3*, *G4, Z1*). Sodium reacts to form $C_{64}Na$, although ternary systems with other alkali-metal compounds are known (*A3, B6*).

There are a number of graphite–electron-donor systems that are formally analogous to the graphite–alkali metals. Intercalation compounds of graphite with barium (*G5*), with strontium, calcium, and samarium (*G6*), and with europium and ytterbium (*G7*) may be formed by direct combination of the elements. Craven (*C5*) had prepared intercalation compounds of graphite with cerium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium by utilization of metal–ammonia solutions. In a different vein, both Besenhard (*B7*) and Simonet (*S3*) reported the electrochemical intercalation of tetraalkylammonium cations into graphite, thereby creating donor compounds without the use of metals.

Historically, the C_8M graphite–alkali-metal compounds have been considered to have a hexagonal, two-dimensional network, as illustrated in Fig. 4, leading to an orthorhombic, Bravais lattice through an $A\alpha A\beta A\gamma A\delta$ stacking of respective graphite (A) and alkali metal (α) planes. The C_6M graphite–metal compounds also have sixfold, in-plane, metal coordination, but at a distance of 4.3 Å [graphite a_0 × sqr (3)], instead of the C_8M distance of 4.9 Å (graphite a_0 × 2). Through a detailed study of multiplicity factors and relative intensities of (*hk0*) and *hkl*) reflections, Lagrange (*L5*) suggested the existence of three, distinct, C_8M, orthorhombic phases, arising from a-axis displacements in the all-metal layers, to yield $A\alpha A\beta A\gamma A\delta$, $A\alpha A\gamma A\delta A\beta$, and $A\alpha A\delta A$-

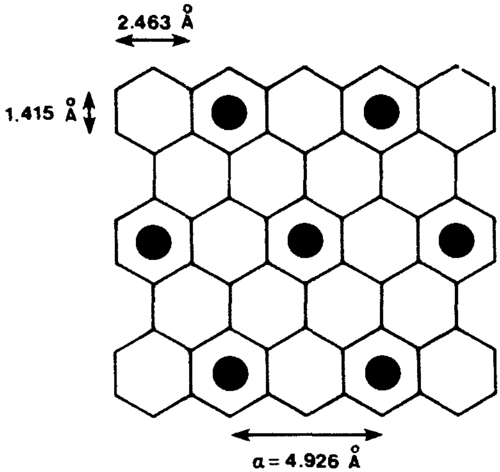

FIG. 4. The in-plane arrangement of a C_8X network typical of many donor and acceptor compounds of graphite.

$\beta A \gamma$ stackings along the *c* axis. Combining this behavior, which arises from "defects" within the *ab* plane, with the work of Thomas (*E4, T2*), which suggested stacking disorder along the *c* axis, it may be concluded that intercalation compounds of graphite may not, in the general case, be entirely well defined structurally. Consistent with this concept is the uncertainty that surrounds the in-plane structure of the second-stage, $C_{12}M$ compounds. Whereas Rüdorff and Shulze (*R3*) proposed a straightforward, in-plane, metal network, of spacing 4.9 Å (*R3*), Parry and co-workers concluded that this structure is incorrect (*P2, P3*).

Raman spectroscopy has been used as a structural probe of graphite–alkali-metal compounds (*N3, E5*). Pure graphite has a sharp reflection of E_{2g} symmetry at 1582 cm^{-1} (*T3*), but alkali-metal-intercalated graphite can reveal modes at different energies, arising from the distinction of environment of a graphite plane directly bounded by two graphite planes, by one graphite plane and one alkali-metal plane, or by two alkali-metal planes. As a given stage would have a well-defined number of each of the symmetry environments, the Raman experiment offers an alternative approach to X-ray diffraction for the determination of stage information. For molecular compounds, such as intercalated, metal amines, spectral position and polarization of the Raman modes could be used as a subtle probe of *molecular* structure, although preliminary work on the acceptor compound C_xAsF_5 (*D1, S4*) did not, in fact, reveal molecular vibrations.

With the increased structural knowledge of graphite–alkali-metal compounds have come electronic, band-structure calculations on both C_8K (*I2*) and C_6Li (*H7*). The study of the potassium compound revealed the coexistence of isotropic, three-dimensional carriers with extremely two-dimensional carriers, and suggested the possibility of charge-density waves, in analogy to established behavior in layered dichalcogenides (*T4*). The investigation of the lithium compound revealed a possible covalent contribution to interlayer bonds, consistent with the frequent observation of lithium carbide in C_6Li synthesis (*N2, G3*).

The electronic properties of graphite–alkali-metal compounds have been the subject of a review by Fischer (*F5*), so we shall not discuss them in depth. One of the most promising techniques is optical spectroscopy, first used by Hennig (*H8*), to determine the number of carriers from the position of the plasma edge (*K2*). The optical properties of $C_{24}M$ (blue in reflection) and C_8M (bronze in reflection) are those expected from the "alloying" of graphite (with an inferred plasma edge in the infrared) and alkali metal (with an edge in the ultraviolet). This "sweep" of the plasma edge across the visible spectrum [from 1.4 to

2.6 eV for $C_{36}Rb$ to C_8Rb (*G8*)] is similar to that found for the alkali-metal–tungsten bronze system M_xWO_3 (*D2*).

The color of the intercalation compound may be a useful guideline in monitoring chemistry. The bronze, first-stage C_8K reacts with hydrogen to form a blue, second-stage $C_8KH_{2/3}$, which may then be further intercalated by alkali metal to form a first-stage compound $C_{16}MK_2H_{4/3}$ (*G9*). Conversely, when such aromatic molecules as phenanthrene or perylene (*B8*), or benzene in tetrahydrofuran (*B9*), react with C_8K, radical ions are created, and the resultant solid is again blue.

Comparison of physical and chemical measurements suggested something of the true identity of compounds customarily written as C_8M. Measuring the Knight shift of ^{133}Cs in C_xCs compounds, Carver (*C6*) inferred a 55% ionization of cesium in C_8Cs, but a 100% ionization of cesium in $C_{24}Cs$ and more-dilute compounds; this was directly consistent with Hennig's previous optical data (*H8*), which had suggested 67% ionization in stage 1 graphite–alkali-metal compounds, and 100% ionization for higher stages. Later, Mössbauer measurements (*C7*) on the C_xCs system suggested a 50% ionization for the first stage and a 100% ionization for higher stages, a result qualitatively confirmed by specific-heat measurements (*M2*) and electron-spin resonance observations (*P4*).

For chemical comparison, the reaction of C_8M with water can distinguish between M^+ and M^0 (*B10, B11*). If, as an example, C_8K were entirely atomic, we should expect

$$C_8K + H_2O \rightarrow 8\,C + KOH + 0.5\,H_2. \tag{1}$$

Were the potassium entirely ionic, we should expect

$$C_8^-K^+ + H_2O \rightarrow C_8^-H^+ + KOH. \tag{2}$$

Using these two reactions as extreme cases, hydrogen evolution can be monitored to infer a value of potassium ionicity. Although initial reports (*B10*) suggested a maximum yield of hydrogen of 16% of the theoretical value of reaction (1), corresponding to 84% ionization of potassium, later reports (*E6, E7*) suggested yields as high as 40% of the theoretical (60% ionized), a value consistent with physical measurements. Thus, in going from $C_{24}^+M^-$ to "$C_8^{-0.6}M_{0.6}^+M_{0.4}^0$", a great deal of *atomic* alkali-metal character is added to the compound, and this should result in enhanced chemical activity.

The reductive capability of C_8K has been a subject of interest (*L4*). Uses for C_8K include the reductive cleavage of carbon–sulfur bonds (*S5*), the reductive alkylation of nitriles and esters (*S6*), and the reductive alkylation of aldehydes and ketones (*S7*). The activity of C_8K has been compared to that of high-surface-area, alkali-metal dispersions in the reductive alkylation of ketones (*H9*). Bergbreiter (*B11*) evaluated reaction mechanisms for the interaction of C_8K with protic acids, alkyl and aryl halides, and alkyl sulfonic esters. The potential of C_8K in inorganic reductions has also been evaluated (*U2, U3*).

B. GRAPHITE ACID SALTS

The acid salts, known since 1841 (*S8*), are among the best characterized graphite compounds. Their properties have been discussed in recent reviews (*H10, E1*). The acid salts can be prepared either by oxidation with a chemical reagent, or electrochemically. The resulting compounds are ionic in nature, with electrical charges balanced between acid anions and carbon macrocations. They usually also include neutral acid molecules. Intermediate stages are formed, and critical threshold-concentrations are needed for intercalation to occur (*U4*). The general stoichiometry is $C_m^+A^-\cdot n\mathrm{HA}$. Acid salts of the oxygen acids sulfuric, chlorosulfonic, fluorosulfonic, selenic, perchloric, and nitric acids have been known for some time (*B12, R4*), as has the salt $C_{24}^+HF_2^-\cdot 4\ HF$ (*R5*). On the other hand, layer compounds of type C_nHF ($n = 4-8$), prepared by reaction of HF with graphite without oxidation (*O1*), could not be confirmed in the authors' laboratory. Conversions of one type of salt to another can sometimes be accomplished by double decomposition (*B12*). Values close to $m = 24$ are repeatedly encountered and seem to represent a structure with relatively close packing. Because of the instability of these compounds in air or water, they are difficult to analyze; this, as well as the presence of defect sites, may account for different values reported for the number (n) of neutral molecules. For bisulfate, it has been reported as 2 (*R4*) or ~2.5 (*A4, A5, H11*), whereas, for nitric (*N4*), perchloric (*A4, F6*), and trifluoromethanesulfonic (*H11*) acids, $n = 3$, 2, and 1.64, respectively. The neutral, acid molecules are presumed to participate in hydrogen bonding between themselves and the anions (*A5*), in contrast to Hennig's theory, which suggested a role as spacers to lessen electrostatic repulsion (*H12, D3*). There are, in fact, indications that the incorporation of neutral acid molecules may be altogether unnecessary (*B13*). Simple lamellar salts of the type C_nX were obtained by anodic oxidation of solutions of $LiClO_4$, $NaBF_4$, and KPF_6 in nonaqueous, aprotic solvents (*B13*).

Thermodynamic information has been obtained in different stages of graphite bisulfate (*A5*). The results have been interpreted in terms of a model previously applied to alkali-metal–graphite compounds. Part of the bonding energy results from electrostatic attractions of bisulfate ions to positive carbon layers. It is unlikely, however, that such effects can account for long-range stacking-orders found between different intercalate layers in the low-temperature phase of graphite nitrate (*N4*). Rather, ordering has been attributed to Brillouin-zone effects and redistribution of energy surfaces associated with the latter (*N4*). Order–disorder transitions occur around −20°C (*N4*); these have been confirmed by differential thermal analysis, by a discontinuity of T_1 in proton magnetic resonance spectra (*A6, A7*), and by changes of line width in esr spectra (*K3*). A further transition at −140°C may be due to freezing of rotational moments of nitrate ions (*A6, A7*).

The salts most studied are the graphite nitrates. These occur in several stages that have been formulated as $C_{8n}HNO_3$ ($n = 1, 2, 3$) with a repeat distance $I_c = 7.8 + 3.35\ (n - 1)$ Å (*F7*). A general formulation of $C_{(8+2x)n}\ N_2O_5 \cdot x\ H_2O$ ($n = 1, 2, 3$; $0 \leq x \leq 3$) has been proposed, leading to two series $C_{5n}HNO_3$ with $I_c = 7.80$ Å and $C_{6n}HNO_3$ with $I_c = 6.55$ Å, which are interconvertible (*F8*). The final composition appears to depend on the nitric acid concentration, but, probably, all contain at least some nitrate ions. Graphite nitrates and other acid salts display metallic behavior, as shown by measurements of various electrical properties, such as resistivity and the thermoelectric power (*U5*), magnetoresistance, and the Hall effect (*U6, U7*). The thermal expansion, specific heat, and magnetic properties of second-stage graphite nitrate confirm metallic properties (*I3*). Similar results were obtained from optical-reflectance studies (*F7*), which were compared with dc transport properties, although not being consistent with a simple Drude model.

Changes in electrical resistivity (*V3*) and mechanical properties (*V3, V4*) of graphite fibers upon nitration have been studied. Increases in elastic modulus, and decreases in tensile strengths, have been related to removal of boundary dislocations by the intercalation process proposed elsewhere (*N4*).

NMR studies on graphite–phosphoric acid showed simultaneous, motional narrowing of both ^1H and ^{31}P resonances above 225 K, indicating high mobility of phosphoric acid in the compound (*E8*). Chlorosulfonic acid is inserted alone into graphite in the presence of many inorganic chlorides. The reaction temperature and stage seem to be related to the redox potential of the M^{n+}–M couple (*M3*).

Graphite acid salts have been considered in terms of possible practical applications. Their potential as useful electrodes in high-energy-density batteries has been reviewed (*A8*), as well as their potential usefulness as chemical reagents (*B14*).

C. HALOGEN GRAPHITE COMPOUNDS

Reactions of graphite with the halogens are of such a variegated nature that they are best discussed element by element. The reaction of fluorine is rather different in nature from those with the other halogens, and, in the limit, leads to compounds in which the aromatic graphite layer-structure is totally destroyed, leading to a perfluorocyclohexane net. Regarding the other halogens, a comparison of their interatomic distances [Cl_2 (1.99), Br_2 (2.28), I_2 (2.66), ICl (2.33), and IBr (2.47 Å)] with the distance separating centers of adjacent hexagons in the graphite layers (2.46 Å) suggested that epitaxy may play an important role in compound formation (*H13, H14*). Thus, iodine does not intercalate with graphite at all. The existence of graphite–chlorine is moot; and if such compounds exist at all, they are relatively unstable, and exist only at low temperatures.

On the other hand, bromine compounds are well known, and their formation and properties have been most thoroughly studied. Epitaxy is not the only factor affecting intercalation, however (*H14*); it does not explain why some compounds (ICl) form first stages, whereas others (IBr, Br_2) form only second stages. Other factors suggesting a role in compound formation are the relative electronegativities of the halogens and the graphite (*D4*), as well as polarizabilities of the former (*R6*). The amount of charge transfer to or from an atom directly over the carbon undoubtedly plays a role as well (*H13*).

Chlorine–Graphite.—According to Hennig (*H15*), graphite reacts slowly with chlorine at low temperatures accompanied by a drastic diminution in the resistance of the graphite. Similar conclusions were reached by Juza *et al.* (*J1*), who reported that the reaction of chlorine at −78°C removes the anomalous diamagnetism of the graphite. The reaction rate is strongly dependent on particle size and temperature, reaching a maximum at −12°C. Above 0°C, no chlorine uptake was noted (*J1, J2*). A limiting stoichiometry C_8Cl is supposedly attained (*H15, J1*). X-Ray evidence for chlorine–graphite was adduced by Juza and Seidel (*J3*). They suggested a second-stage compound, having $a = 2.45$ Å and $c = 10.09$ Å, indicating a 50.5% expansion of the lattice constant c over graphite. Their starting material was, however, $C_{104}Br$ rather than virgin graphite. The composition determined at −57.7°C by isothermal tensimetry was $C_{8.5}Cl$, the deviation from ideal C_8Cl being attributed to lattice imperfections. Others have been unable to duplicate these results (*T5*), although they may have encountered difficulties in compound transfer. According to Herold (*H6*), the chlorine uptake by graphite at low temperature is due to adsorption only, no intercalation taking place. Hooley (*H16*) has come to similar conclusions based on adsorption-isotherm measurements over a wide temperature-range. He also pointed out that changes in susceptibility do not necessarily prove intercalation. Although the existence of chlorine–graphite is debatable, there seems to be agreement that chlorine –graphite residues are formed. Moreover, it appears that the reaction can be catalyzed by the presence of HCl or by using residue compounds as starting materials (*J4*).

Iodine–graphite.—In contrast to the situation with chlorine, there is general agreement that iodine is not intercalated into graphite (*H6, H15*). However, reaction of iodine with a bromine residue led to a marked decrease in its diamagnetic susceptibility (*J4*). *Bromine–graphite.*—As early as 1933, the uptake of bromine by graphite was shown to lead to a compound of stoichiometry C_8Br (*F9*). X-Ray investigations by Rüdorff showed (*R7*) that C_8Br has one bromine layer for every two graphite layers, the expanded layer-spacing becoming 7.05 Å. The existence of this second-stage compound, as well as stages poorer in bromine, namely, $C_{12}Br$ and $C_{16}Br$, was confirmed by Herold (*H6, B15*). Single crystals of natural graphite treated with bromine vapor were examined by electron and X-ray diffraction (*E9, E10*). The saturated compound is, indeed, second-stage, with I_c = 10.3 Å (*E9*). Upon desorption, a relatively stable fourth stage, $C_{28}Br$, is formed, having a repeat distance I_c = 17.0 Å. The bromine layers are well-defined, two-dimensional structures with a_0 = 8.5 Å (along $[10\bar{1}0]$) and b_0 = 17.25 Å (along $[1\bar{2}10]$). The interatomic distances in the bromine layers are virtually identical with those of molecular bromine, indicating that van der Waals forces play no less a role than charge transfer in determining the configurations between layers (*E10*). Although the bromine molecules have precise orientations with respect to adjacent, graphite layers, relative positions could not be uniquely determined. The formation of a $C_{14}Br$ phase was also reported in which bromine layers are intercalated into every second layer-spacing of graphite. As the compound C_8Br is formed from the latter without alteration of layer sequences, additional bromine appears to enter already existing bromine layers.

In a subsequent study (*S9*), isotherms of bromine on pyrolytic graphite showed the presence of several phases $C_{4n}Br$ (n = 2 to 5). X-ray studies confirmed these to be stages 2 to 5, respectively. At intermediate concentrations, X-ray patterns showed mixtures of higher and lower stages. The density and configuration of intercalated bromine molecules were believed to be the same in all stages. Other structural types of lower density reported by Eeles and Turnball (*E10*) were believed to be metastable states.

An electron-microscope study (*H17*) showed the existence in bromine–graphite of isolated dislocations bounding intercalated reactant layers. Such migrating loops of occluded reactant are believed to account for residues retained upon decomposition. The existence of crystallites having grain boundaries within larger graphite flakes has also been postulated to account for isotopic exchange-rate of bromine with bromine–graphite (*S10*).

An electron-diffraction study showed reversible changes in pattern as a function of temperature (*C8, C10*). These were interpreted as order–disorder transitions for the intralayer structure, occurring for bromine–graphite at 108°C. The intralayer intercalate structure was found to be independent of intercalate concentration. Therefore, a concentration increase changes the number of intercalate layers without changing the arrangement within an intercalate layer. Evidence for ordering persists up to the fifth stage, which contradicts the well-known concept (*H18*) that, in residues, the intercalant resides at the structural defects (*C9*). Another reversible transition at 194°C, having a large hysteresis effect, was identified with charge-density waves (*C8*).

Simultaneous weight-change and diamagnetic-anisotropy measurements upon adsorption and desorption of bromine in PG have been carried out (*M4*). They showed that final susceptibility values are reached well before full bromine saturations, and remain until 80% desorption is attained.

Many attempts have been made to elucidate the intercalation mechanism. No clear picture has yet emerged, but it is obvious that the nature of the graphite, as well as the manner in which the intercalation process is carried out, strongly influence the experimental results. Saunders, Ubbelohde, and Young (*S11*) postulated that the absorption process involves the withdrawal of electron charge from all layers by bromine adsorbed by carbon edge atoms. This "unpins" the layers, allowing the penetration of more bromine molecules. They used conductivity measurements to show that the threshold pressure is lower for more perfect graphite. Confirmation of threshold lowering was obtained on even more perfect graphite specimens (*U8*). The rate of intercalation of natural graphite by bromine was measured over a large range of crystal areas and thicknesses (*H19*). Results indicated that diffusion is independent of thickness over a factor of two, and all layers are attacked randomly. Further experiments (*H20*) on marked-off

HOPG cylinders showed that intercalation starts close to the basal planes and proceeds thence to the central layers. Cylinders capped at both ends with glass caps and grease are not intercalated. The layer system is split into a number of discs at a rate that increases with the degree of alignment of layer planes. For non-heat-treated PG, the threshold pressure increases with the number of layer planes in the sample. Similar results confirming this mechanism have been obtained with metal halides (*H13*). A mechanism of intercalation based on these results has been discussed by Hooley (*H22*).

One of the cardinal problems regarding bromine–graphite (as well as other intercalates) has been the extent to which intercalate molecules are ionized. Hennig (*H15*) found that the presence of bromine in graphite drastically lowers the resistance and magnetoresistance, the Hall effect being similar for graphite bisulfate of the same resistivity. He concluded that the compound should be formulated $C_n^+Br^-\cdot 3\ Br_2$, i.e., only one out of seven bromine atoms is ionized. The fact that only part of the molecules is ionized was explained by mutual electrostatic repulsion of negative ions requiring uncharged "spacers" between them. The electrical conductivity has been reinvestigated many times, and it depends on the manner of intercalation and the type of graphite (*U8, U9, B16, T6, S12*). Although the results differ in detail, there appears to be general agreement that some intercalate ionization occurs. Blackman *et al.* (*B16*) concluded that, at high dilutions, the bromine is fully ionized, but, as the concentration increases, the total charge-transfer continues, but fractional charge transfer per bromine falls below unity. Others (*D5*) reinterpreted Hennig's Hall-effect data (*H15*) according to the rigid-band model, and concluded that the fraction of ionized, molecular intercalate is $\nu = 0.025$, consistent with infrared magnetoreflection results (*P5*). Raman-scattering experiments (*S13, D1*) showed that the molecular vibration attributed to intercalated bromine molecules is shifted to 242 from 323 cm^{-1} in the free molecule. The low frequency is attributed to coupling with the E_{2g_2} mode for carbon atoms in the adjacent plane. Weak fine-structure observed at 77 K was attributed to ionized, intercalate species. A summary of all experimental evidence related to halogen ionization showed it to be consistent with low intercalate ionization ($\nu = 0.02$) and preservation of molecular identity of the halogen intercalates (*D6*). Hennig's considerably higher value ($\nu = 0.29$) can be reconciled with this if charged, molecular, bisulfate ions are screened in the graphite layers bounding the intercalate layers, i.e., only a fraction of the charge associated with intercalate layers will contribute to delocalized charge-density in the graphite layers.

Graphite Intercalation Compounds with Interhalogens

Given the proper conditions, all known halogen fluorides that can be isolated in stable form at room temperature will form layer compounds with graphite. Iodine pentafluoride was first reported to form an intercalate of composition $C_{18}IF_5$ (*O2*). Later work appeared to confirm this, suggesting a first-stage compound, $C_{8.7}IF_5$, as well (*S14*). It has now been shown that IF_5 intercalation is catalyzed by HF (*S15*) and such Lewis acids as BF_3 (*S16*). Both thermogravimetric and mass-spectrometric studies showed that IF_5 is evolved as a function of temperature, in stages (*S15*). Broad-line, ^{19}F-NMR spectra showed a resonance that could not be identified with any known, pentavalent iodine fluoride species.

The reaction of iodine heptafluoride is accompanied by reduction to the pentavalent state (*S15*). The intercalation process can thus be described in terms of the reaction

$$x\,C + y\,IF_7 \rightarrow C_x(IF_5)F_{2y} + (y - 1)\,IF_5.$$

Infrared spectra and ^{19}F-NMR spectroscopy showed the presence of IF_5 and covalently bonded fluorine. Grafoil turns white upon intercalation with IF_7; this is reminiscent of graphite fluoride, $CF_{1.12}$ (*L6*). The IF_7 intercalate also evolves IF_5 upon heating, but at much higher temperatures than C/IF_5; this has been attributed to the lowered mobility of IF_5 in the fluorinated matrix, which may no longer be planar. At 450°C, considerable amounts of fluorocarbons are evolved.

A layer compound, $C_{8.9}BrF_3$, stable up to 179°C, has been reported (*O2*). Fluorine NMR and infrared spectra have been interpreted as indicating that the BrF_3 is present in molecular form. In another study (*S15*), a stoichiometry $C_{8.9}BrF_3$ was observed on the basis of weight increase of the original graphite, but considerable bromine evolution was observed, and chemical analyses confirmed that the graphite was partially fluorinated. Thermal stabilities and ^{19}F-NMR shifts also differed sharply from those reported earlier. It is evident that experimental conditions, including types of graphite used, play a decisive role in the intercalation process.

A study of the intercalation of BrF_5 led to inconclusive results (*S15*). The difficulty may result from reduction of BrF_5 to BrF_3, which itself intercalates.

Of the chlorine fluorides, only the monofluoride does not intercalate in the neat state. It does, however, intercalate in the presence of HF (*S15*), BF_3, or PF_5 (*S16*). Chlorine trifluoride intercalates into graphite with simultaneous fluorination of the graphite lattice (*S15*), releasing

ClF in the process. Upon heating, only chlorine and fluorocarbons are emitted. In the presence of HF, a different product is obtained (*O3*). The green-colored compound formed, with liberation of ClF, has the composition $C_{14}F \cdot ClF_3 \cdot 3\ HF$. Infrared spectra have been interpreted in terms of the structure $C_{14}^+H_2F_3^-ClF_2^+HF_2^-$. However, some of the infrared bands ascribed to $H_2F_3^-$ and HF_2^- ions could be assigned to covalent C–F bonds in the intercalate. Reactions of $C_{14}F \cdot ClF_3 \cdot 3HF$ with the acids CF_3COOH, CH_3COOH, $HClO_4$, and HNO_3 gave products in which the three HF molecules were replaced by one molecule of the respective acid (*N5*). Reaction of graphite with solutions of cesium fluoride in ClF_3 gives a compound of stoichiometry $C_4F \cdot ClF_3$ (*N6*). Interaction of graphite with solutions of antimony pentafluoride in ClF_3 leads to a product of composition $C_8F \cdot SbF_5 \cdot ClF_3$ (*O4*). On the basis of infrared spectroscopy, the structure $C_8^+SbF_6^- \cdot ClF_3$ has been proposed.

Although iodine does not intercalate, and the situation regarding chlorine is controversial, ICl does intercalate, to form C_8ICl and higher-stage compounds (*R6, H15, T5*); this has been attributed to the importance of polarizability of the molecule, combined with its high electron-affinity (*R6*). The threshold for ICl intercalation is even considerably lower than that for Br_2 (*U8*). Upon intercalation, the graphite resistance decreases markedly (*H15*). A theory relating the a-axis conductivity, σ_a, to intercalate concentrations, X, has been developed by Fischer (*F10*) using some simplifying assumptions. The predicted behavior that σ_a is proportional to $X^{1/2}$ seems to hold approximately only for ICl, however; this has been attributed to the unusually large layer-spacings and correspondingly weak interactions between layers (*F10*). The identity period, $I_c = 21.15$ Å, emcompasses two carbon planes (*R6*). The ICl layers become disordered above the transition temperature of 43°C (*C10*).

Iodine monobromide forms an intercalate with limiting composition $C_8I_xBr_{1-x}$ (*C9*) when natural graphite is used. Higher stages $C_9I_xBr_{1-x}$ and $C_{12}I_xBr_{1-x}$ have also been shown to exist (*C9*). An order–disorder transition within IBr layers occurs at ~60°C (*C10*).

Ternary compounds $C_8Br_xCl_{1-x}$ have been synthesized. The configuration having $x = 0.55$ seems to be especially stable, and the limiting value in the bromine-poor regime is $x = 0.33$ (*F11*).

D. NOBLE-GAS FLUORIDES–GRAPHITE

It has been pointed out on a number of occasions that the chemistry of the noble gases resembles in many respects that of its neighboring elements, namely, the halogens. Reasoning based on this analogy led to the synthesis of the first intercalate with xenon oxide tetrafluoride (*S14*). Since then, intercalates have been prepared with all known binary fluorides of the noble gases, xenon and krypton (*S1, S18, S19, N7, R8*). These are listed in Table I.

The identification of the valence state of the intercalated xenon species has been facilitated by ^{19}F-NMR spectroscopy (*E11*). It has been shown (*F12*) that both the fluorine chemical-shift and the $^{129}Xe-^{19}F$ spin–spin coupling-constant are strongly dependent on the oxidation state of the central xenon atom (see Fig. 5). By using this technique, it has been determined that, upon intercalation, some of the noble-gas fluorides are reduced to the next lower oxidation state (XeF_4 and XeF_6), whereas others (XeF_2 and $XeOF_4$) are intercalated without attendant reduction. However, the proviso must be added that, in the case of XeF_2, reports from different laboratories conflict as to the nature of the intercalation process. Nikolaev *et al.* (*N7*) reported that graphite intercalates with solutions of XeF_2 in anhydrous hydrogen fluoride (AHF) leading to a product of composition $C_{17}XeF_2 \cdot 1.3\ HF$, with no oxidation of graphite taking place. This material was reported to undergo oxidation at 155°, with formation of a mixture of graphite and a new product, $C_9F \cdot XeF_2 \cdot 3\ HF$. The latter decomposes at 470°, liberating, *inter alia,* xenon and fluorocarbons. The presence of XeF_2 and HF in the product was shown by infrared spectroscopy.

In another study (*R8*), it was found that graphite does not intercalate with neat XeF_2 or with solutions of XeF_2 in acetonitrile. However, reaction with solutions of XeF_2 in AHF led to copious xenon evolution, indicating that oxidation does take place, even at room temperature. Broad-line, ^{19}F- and ^{1}H-NMR spectra (*E11*) showed the presence of both XeF_2 and HF in the product, but no definite stoichiometry could be as-

TABLE I

INTERCALATES OF GRAPHITE WITH NOBLE-GAS FLUORIDES

Formula	Stage	Color[a]	Ref.
$C_{8.7}XeOF_4$	1		*S14*
$C_{19}XeF_6$			*S18*
$C_{28}XeF_4$	2		*S19*
$C_{40}XeF_4$	3		*S19*
$C_9F \cdot XeF_2 \cdot 3\ HF$		Brown	*N7*
$C_{17}XeF_2 \cdot 1 \cdot 3\ HF$			*N7*
C_mKrF_n ($n > 2$)			*S1*
$C_xF(HF)_y(XeF_2)_z$		Blue in the presence of HF	*R8*

[a] Where not otherwise indicated, no color change occurred upon intercalation.

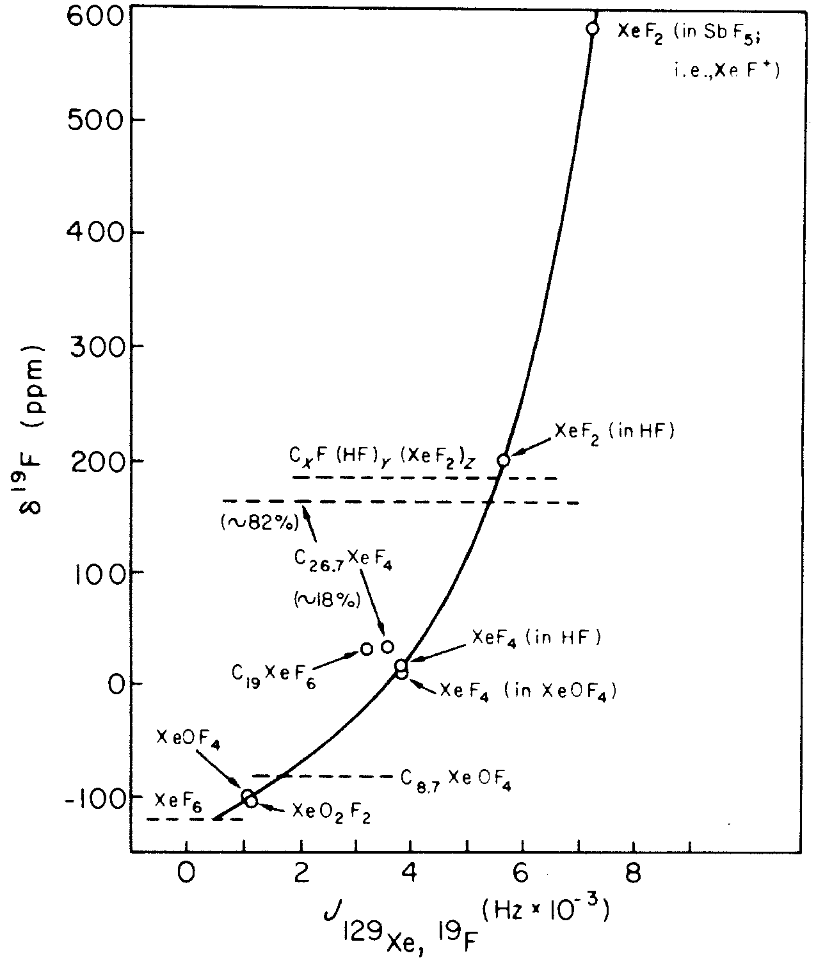

FIG. 5. Dependence of the spin–spin coupling-constant and the ^{19}F chemical shift on the oxidation state of the central xenon atom.

signed, because of the variability of the products. It is interesting that, in the presence of liquid HF, the solid product has a blue color reminiscent of that of such graphite acid salts as $C_{24}^{+}HF_2^{-}\cdot(HF)_4$. The origin of the discrepancy is unknown, although it may be related to the different types of graphite used.

Xenon tetrafluoride forms intercalates with graphite at room temperature (*S19*). Powder and Grafoil have both been used, and products have been isolated having stoichiometries $C_{28}XeF_4$ and $C_{40}XeF_4$ that apparently correspond to the second- and third-stage compounds, respectively. Analysis of the oxidation power of these intercalates showed only two equivalents of iodine liberated per mole of intercalate (*S19*); this is consistent with ^{19}F-NMR measurements that showed that the major species in the intercalate is XeF_2, although some XeF_4 is present as well (*S19*). Both thermogravimetric measurements (*S19*) and mass spectra (*S20*) showed that, at room temperature, the second-stage compound liberates slight amounts of xenon difluoride as well as traces of XeF_4. Xenon difluoride evolution ceases at ~100°. The rest of the xenon is held very tenaciously, and xenon evolution becomes appreciable only above 350°. At this temperature, fluorocarbon emission also becomes appreciable, reaching a maximum at ~380°. This feature is common to many of the inorganic fluoride intercalates, and apparently corresponds to the decomposition of covalent, carbon–fluoride bonds formed either during the initial intercalation or subsequent fluorination of the graphite matrix (*S20*). Preliminary investigations showed that the intercalate may be useful as a moderate fluorinating agent in organic chemistry.

Xenon hexafluoride forms with graphite an intercalate of nominal stoichiometry, $C_{19}XeF_6$ (*S18*). Both the ^{19}F chemical-shift and the ^{129}Xe–^{19}F coupling-constant showed that the intercalated species is XeF_4. This conclusion was confirmed by ^{129}Xe Mössbauer measurements (*P6*), which showed little or no XeF_6 present, but, instead, a signal corresponding to XeF_4 or XeF_2, based on its quadrupole splitting and absence of isomer shifts. XeF_2, can however, be excluded, on the basis of NMR spectra. Because the compound exhibits an oxidation power corresponding to hexavalent xenon, it has been tentatively proposed that it has the formula $(C^{+}_{9.5}F^{-})_2XeF_4$ (*R8*). In analogy to the behavior of graphite–antimony pentafluoride intercalation-compounds (*E12*), the fluorine line-widths of "$C_{19}XeF_6$" are narrow (0.1–0.2 G) to relatively low temperatures (*E11, R8*), suggesting the possibility of translational motion of the inserted species. The intercalate appears to be relatively stable thermally. Thermogravimetric analysis indicated that substantial weight-loss occurs only above 400°C (*R8*). Mass spectrometry showed that the minor weight-loss at lower temperatures is accompanied by evolution of XeF_4 up to ~150° (*S20*). At higher temperatures, only xenon and fluorocarbons are evolved, probably as a result of fluorination of the graphite lattice by xenon fluoride, and subsequent decomposition of the graphite fluoride formed (*S20*). The XeF_6 intercalate has been used as a conveniently handled, moderate, fluorinating agent in organic chemistry (*S18, R8*). It has been shown to be particularly useful as a mild, selective, fluorinating agent of carcinogenic, polycyclic, aromatic hydrocarbons (*A9*).

The intercalate of graphite with xenon oxide tetrafluoride was the first one isolated for this series (*S14*), based on the analogy of the latter with iodine pentafluoride. Xenon oxide tetrafluoride forms a compound with stoichiometry $C_{8.7}XeOF_4$. The compound is stable at 0°, but decomposes slowly above room temperature, presumably to a higher-stage compound (*R8*). Because variable amounts of compounds other than $XeOF_4$ are released at higher temperatures, the second-stage stoichiometry could not be clearly defined. Appreciable amounts of $XeOF_4$ can be recovered from the graphite up to 80° (*S20*). Above this temperature, substantial amounts of molecular oxygen are liberated in addition to minor amounts of XeO_2F_2 and XeF_2. Above 200°, mass spectra showed that decomposition proceeds with the emission of xenon, fluorocarbons, and carbonyl fluorides (*S20*), as well as some CO_2. As COF_2 emission proceeds well beyond that of xenon, the formation of graphite oxyfluoride is indicated, a product of this type having been described previously (*L6*). Broad-line, fluorine-NMR measurements showed that the chemical shift of the intercalated species corresponds to that of neat $XeOF_4$ (*E11*), this being in harmony with the mass-spectral measurements. C_9XeOF_4 has also been shown to be a potentially useful fluorinating agent of organic compounds (*R8*). In addition, it reacts with anthracene to form substantial yields of anthraquinone (*R8*).

In contrast to xenon difluoride, krypton difluoride reacts directly with graphite to form intercalates of variable composition, having the general formula C_mKrF_n ($n > 2$) (*S1*). The krypton difluoride both intercalates into, and partially fluorinates, the graphite lattice. X-Ray powder photographs showed the absence of the graphite line at 3.35 Å and the presence of new lines having a *c*-axis, repeat-distance of $4.22n$ Å (n = an integer) distinct from that of either CF or C_4F. Also, wide-line ^{19}F-NMR measurements showed a spectrum different from those of these species, although it was not possible to distinguish between the presence of either KrF^+ or KrF_2 as the intercalated species. It is unlikely, however, that the trapped, krypton species is present as atomic krypton, because of the relatively high temperature at which decomposition occurs.

E. GRAPHITE–METAL HALIDES

The graphite–metal halides constitute the most populous group of intercalation compounds. Most of the investigative efforts have been directed towards the metal chlorides, particularly $FeCl_3$, whereas considerably less is known about the metal bromides (*S21*). Compounds with metal iodides are unknown. Metal fluoride compounds, unknown prior to 1972, have since sprung into prominence, because some of them (AsF_5, SbF_5) display theoretical and practical interest owing to their unusually high metal-like conductivities (F13). Nevertheless, the group as a whole appears to be among the least understood in terms of chemical bonding.

A number of general, synthetic techniques have been developed for preparing graphite compounds.

(1) Direct combination of graphite with the metal halide in a sealed tube in the presence of chlorine or bromine at temperatures giving reasonable reaction rates. As a corollary to this method, compounds may be prepared by heating graphite and metal, or graphite and metal oxide, together in the presence of halogen.

(2) In order to define more precisely the conditions for compound formation, the two-temperature method has been used (*H6*). Here, the graphite is maintained at a higher temperature than the intercalant, in order to avoid condensation of an excess on the graphite. Holding either the graphite or the intercalant at constant temperature while varying the temperature differential allows the determination of intercalation or deintercalation isotherms or isobars, giving information on stage formation and hysteresis effects (*H13, H23*).

(3) Intercalation from solutions in nonaqueous solvents (*S21*). This method may suffer from the drawback that final stoichiometries may not correspond to equilibrium conditions, because of partial leaching out of metal halide. For this reason, some chlorides can be intercalated only from solvents in which they have limited solubility (*L8*). It has often been the practice to wash intercalates with solvents to remove the excess of intercalant; this may lead to stoichiometries lower than the original ones. The two-ampoule method may, therefore, be preferable (*H24*).

(4) Intercalation via complexation in the vapor phase (*S21*). Thus, for example, the nonvolatile $CoCl_2$ can be intercalated in the presence of $AlCl_3$ at 500°C, because of the enhanced volatility of the former. Graphite–$CoCl_2$ containing only traces of $AlCl_3$ is obtained.

At this time, no all-inclusive rule can be given that will predict whether a given compound will intercalate or not. Most of the information available seems to have been obtained empirically. Such analogies as similar chemical properties have been helpful. The many factors that influence the intercalation process have been surveyed by Herold (*H14*). In Tables II–VI are listed metal halides considered to intercalate into graphite, together with some structural information (*S21, R9*). Several general characteristics have been ascribed to intercalat-

TABLE II

Chlorides Claimed to Intercalate Graphite

Chloride	Composition	State	I_c (Å)	Ref.
Group Ib				
$CuCl_2$	$C_{4.9}CuCl_2$	1	9.40	*R9*
$AuCl_3$	$C_{12.6}AuCl_3$	1	6.80	*V10*
	$C_{2.52}AuCl_3$	2	10.15	*V10*
	$C_{37.8}AuCl_3$	3	13.50	*V10*
	$C_{50.4}AuCl_3$	4	16.85	*V10*
Group IIb				
$MgCl_2$	$C_{12.18}MgCl_2$	1(+2)	9.50	*S28*
	$C_{26-27}MgCl_2$	2(+3)	12.85	*S28*
	$C_{40}MgCl_2$	3	16.26	*S28*
$ZnCl_2$	$C_{16.6}ZnCl_2$	3	16.29	*S22*
$CdCl_2$	$C_{11.1}CdCl_2$	1	9.51	*R9, S28*
	$C_{6.6}CdCl_2$	1	9.63	*C13*
$HgCl_2$	$C_{21-26}HgCl_{2.1}$	3	16.45	*R9*
Group IIIa				
$AlCl_3$	$C_9AlCl_{3.3}$	1	9.54	*R10*
	$C_{18}AlCl_{3.3}$	2	12.83	*R10*
	$C_{31-50}AlCl_3$	4	19.67	*R10*
$GaCl_3$	$C_9GaCl_{3.2}$	1	9.56	*R11*
	$C_{18}GaCl_{3.5}$	4	19.69	*R11*
$InCl_3$	$C_{16-20}InCl_3$	2	12.83	*R11*
	$C_{25-31}InCl_3$	3	16.23	*R11*
	$C_{32-45}InCl_3$	4	19.69	*R11*
$TlCl_3$	$C_{8.5}TlCl_{3.3}$	1	9.77	*S21*
	$C_{18.5}TlCl_{3.2}$	2	13.12	*S21*
Group IVb				
$ZrCl_4$	$C_{23.6}ZrCl_{4.15}$	3	16.32	*S21*
$HfCl_4$	$C_{45.7}HfCl_{4.77}$	3	15.87	*S21*
Group Va&b				
$SbCl_5$	$C_{12}SbCl_5$	1	9.42	*M6, M9, F14*
	$C_{24}SbCl_5$	2	12.72	*M6, M9, F14*
	$C_{36}SbCl_5$	3	16.07	*M6, M9, F14*
	$C_{48}SbCl_5$	4	19.42	*M6, M9, F14*
	$C_{12}SbCl_{3.9}$	1	9.50	*S21*
$NbCl_5$	$C_{40}NbCl_{5.2}$	3	16.21	*S21*
$TaCl_5$	$C_{27}TaCl_5$	3	16.19	*S21*
$CrCl_3$	$C_{21}CrCl_3$	2	12.80	*V6*
	$C_{22-29}CrCl_3$	3	16.15	*V11*
$MoCl_5$	$C_{18.5}MoCl_5$	2	12.54	*N8*
	$C_{27}MoCl_5$	3	16.02	*N8*
WCl_6	$C_{70}WCl_6$	5	23.02	*R9*
UCl_5	$C_{37}UCl_5$	2	12.87	*R9, B17*
		1	9.62	*B17*

TABLE II (*Continued*)

Chloride	Composition	Stage	I_c (Å)	Ref.
GROUP VIIb				
$MnCl_2$	$C_{6.4}MnCl_{2.06}$	1	9.51	*S22*
	$C_{12}MnCl_{2.07}$	2	12.88	*S22*
$ReCl_4$	$C_{13}ReCl_{4.3}$	1	11.78	*S21*
GROUP VIII				
$FeCl_2$	$C_{4.7}FeCl_2$	1	9.56	*P7*
	C_9FeCl_2	1	9.51	*N9*
	$C_{15.8}FeCl_2$	2	12.85	*N9*
$FeCl_3$	$C_{5.9}FeCl_3$	1	9.37	*R12*
	$C_{20}FeCl_3$	2	12.80	*R12*
		2	12.73	*H31*
	$C_{23-29}FeCl_3$	3	16.21	*R12*
		3	16.08	*H31*
	C_7FeCl_3	1		*H23*
	$C_{12}FeCl_3$	2		*H23*
	$C_{31}FeCl_3$	4	19.45	*F13b*
$CoCl_2$	$C_{5.5}CoCl_{2.07}$	1	9.50	*R9*
	$C_{15}CoCl_{2.07}$	2	12.85	*R9*
$NiCl_2$	$C_{13}NiCl_{2.04}$	2	12.71	*S22*
$RuCl_3$		2	12.60	*S21*
$OsCl_3$	$C_{12.2}OsCl_3$	2	12.70	*S21*
$PdCl_3$	$C_{14.8}PdCl_2$	3	16.70	*S21*
$PtCl_4$	$C_{42-51}PtCl_{4.5}$	3	16.06	*B20*

ing materials: (*1*) The metal is generally in a high oxidation state. (*2*) For a metal in a given oxidation state, intercalation is promoted by increasing electronegativity of the ligand. (*3*) The crystal structure of the intercalant does not possess oriented bonds in all three dimensions (*C1, E1*).

The presumed nonintercalation of a given compound may, however, be due to the fact that appropriate experimental conditions for intercalation have not yet been found. Thus, some of the rare-earth chlorides originally considered not to intercalate (*C11, V5*), do, in fact, do so in the presence of a complexing agent (*S21*). In addition, the role of chlorine in compound formation has been the subject of controversy. Whereas Croft (*C1*) considered the presence of an excess of chlorine to be nonessential, it has since been shown to be a *sine qua non* for compound formation (*D3, R10, H13, R11, S22, B17, H25*). Moreover, contrary to earlier assumptions (*R10*), chlorine does not act as a catalyst, but is incorporated into the graphite to a greater or lesser extent (*R11, D3*). In cases where the presence of chlorine is *apparently* not required

TABLE III

BROMIDES

Bromide	Composition	Stage	I_c (Å)	Ref.
$AlBr_3$	$C_9AlBr_3 \cdot Br_2$	1	10.24	*S12*
	$C_{19}AlBr_3$	2	13.40	*B21*
	$C_{24}AlBr_{3.3}$	2	13.35	*S12*
	$C_{33}AlBr_3$	4	20.10	*B21*
$GaBr_3$	$C_{13-16.5}GaBr_3 \cdot Br_{2.5}$	2	13.38	*B21*
$AuBr_3$		1	6.90	*B21*
$TlBr_3$	$C_{18.6}TlBr_{3.4}$	2	13.40	*S21*
$CdBr_2$	$C_{15}CdBr_{2.06}$	2	13.30	*S21*
	$C_{28.6}CdBr_{2.1}$	3	16.62	*S21*
$HgBr_2$	$C_{23.8}HgBr_{2.1}$	3	16.62	*S21*
UBr_5	$C_{38}UBr_{5.1}$	2(+3)	13.28	*S21, S29*
UBr_5	$C_{58}UBr_{4.7}$			*S29*
$FeBr_2$	$C_{14.2}FeBr_{2.1}$	1	9.90	*S26*
		2	13.25	
		5	22.8	
$FeBr_3$	$C_{23}FeBr_3$	2	12.90	*S26*

(WCl_6, $SbCl_5$, $FeCl_3$, $CoCl_2$), the intercalants themselves supply chlorine, due to decomposition under the reaction conditions (*H13*). Where intercalation is carried out from a solvent, chlorine may be supplied by decomposition of the latter, e.g., its presence in $SOCl_2$ has been detected spectroscopically (*B17*). However, certain solvents, such as nitromethane, appear to take the place of chlorine in promoting intercalation (*H25*).

TABLE IV

RARE EARTH CHLORIDES (*S21*)

Chloride	Composition	Stage	I_c (Å)
$SmCl_3$	$C_{56.6}SmCl_{3.2}$		
$EuCl_3$	$C_{37.1}EuCl_3$	3	16.30
$GdCl_3$	$C_{23.3}GdCl_{3.1}$	3	16.42
$TbCl_3$	$C_{18.7}TbCl_{3.2}$	2	16.01
$DyCl_3$	$C_{19}DyCl_3$	2	12.90
$HoCl_3$	$C_{20.3}HoCl_{3.1}$	2	12.91
$ErCl_3$	$C_{23.3}ErCl_{3.1}$	3	16.35
$TmCl_3$	$C_{23.7}TmCl_3$	3 + 2	16.47 (13.10)
$YbCl_3$	$C_{25.4}YbCl_{3.1}$	3	16.29
$LuCl_3$	$C_{34.8}LuCl_3$	4	19.48
YCl_3	$C_{28.6}YCl_3$	3 + 2	16.54 (12.98)

TABLE V

FLUORIDES

Fluoride	Composition	Stage	I_c (Å)	Ref.
TiF_4	$C_{19-24}TiF_4$	2	15.10	*B18*
NbF_5	$C_{16.6-17.2}NbF_5$	2	11.76	*M5*
TaF_5	$C_{17.6}TaF_5$	2	11.76	*M5*
	$C_{22.4}TaF_5$	3	15.14	*M5*
AsF_5	$C_{10}AsF_5$	(1 + 2)		*H32*
	C_8AsF_5	1	8.10	*F15*
	$C_{16}AsF_5$	2	11.45	*F15*
	$C_{24}AsF_5$	3	14.80	*F15*
	$C_{32}AsF_5$	4	18.15	*F15*
	$C_8^+AsF_6^-$	1	8.06	*B22*
SbF_5	$C_{6-6.5}SbF_5$	1	8.46	*M5, T10*
	$C_{12}SbF_5$	2	11.76	*M5, T10*
	$C_{18}SbF_5$	3	15.11	*M5, T10*
	$C_{24}SbF_5$	4	18.45	*M5, T10*
WF_6	$C_{14\pm1}WF_6(HF)_x$	2	11.70	*H33*
MoF_6	$C_{11\pm1}MoF_6$	1	8.42	*H33*
UF_6	$C_{9.1}UF_6$			*B23*
	$C_{13\pm3}UF_6$	2	11.90	*E14*
OsF_6	$C_8^+OsF_6^-$	1	8.06	*B22*

The nonintercalation of $AlCl_3$, except in the presence of Cl_2, as well as its low intercalation threshold have been used as a basis for determining the extent of intercalation and distinguishing it from amounts added by other mechanisms, such as adsorption (*H26*).

Whereas most fluorides intercalate directly, some of the less reactive ones (TiF_4, TaF_5, NbF_5) also require the presence of free chlorine (*B18, M5*).

Structural information on graphite–metal halides is mostly limited to the determination of stage and repeat distances along the *c*-axis. Detailed electron and X-ray diffraction studies have been carried out only on graphite compounds with $FeCl_3$ (*C12, E4, T2*), $CrCl_3$ (*V6*), $MoCl_5$ (*J5*), and $SbCl_5$ (*M6*). Several generalizations can be made. The orientation of the graphite layers remains that of the hexagonal modification ABAB, in contrast to alkali-metal–graphites and graphite salts, where lateral displacements are observed. The structures of the free chlorides are largely preserved upon intercalation. In fact, for many metal chlorides, the *c*-axis expansion remains relatively constant between 9.4 and 9.78 Å (*R9*). This follows from the close packing of the two hexagonal arrays of chlorides facing the graphite layers that dictate the volume requirements. As in the free metal chlorides, the metal

TABLE VI

INTERCALATION OF METAL CHLORIDES FROM NONAQUEOUS SOLVENTS

Solvent	Chloride	Reaction time	Metal chloride (%)	State	Ref.
CH_3NO_2	$FeCl_3$	6 h (50°C)	36.8	2	*G11*
	$FeCl_3$	24 h (25°C)	64.6		*H25*
	$FeCl_3$	3 h (80°C)	36.3	2 + 3	*S21*
$C_2H_5NO_2$	$FeCl_3$	24 h (50°C)	20.4		*G11*
$SOCl_2$	UCl_5	3 d	61.7	1	*B17*
	From UO_3	3 d	48.3	2	*B17*
	$AlCl_3$	8 h	39.6	2	*B17*
	$NbCl_5$	12 h	34.1	3	*B17*
	$TaCl_5$	12 h	43.5	3	*B17*
	$MoOCl_4$	6 h	23.6	3	*B17*
	$ZrCl_4$	17 h	31.0	3	*S21*
	$HfCl_4$	4 d	38.8	3	*S21*
	$PtCl_4$	2 d	38.0	3	*S21*
	$AuCl_3$	6 d	46.4	2	*S21*
SO_2Cl_2	$FeCl_3$	2 d	35.2	3	*S21*
	$AlCl_3$	12 h	45.8	1	*S21*
	$AuCl_3$	3 d	47.6	2	*S21*
CCl_4	$SbCl_5$	64 h	64.4	1	*S21*
$CCl_4 + Cl_2$	$SbCl_3$	48 h	50.8	2	*S21*
	$FeCl_3$	2 d	35.8	3	*S21*
	$AuCl_3$	3 d	38.2	2	*S21*
	$AlCl_3$	3 h	40	2	*L8*
	$FeCl_3$	24 h	20		*L8*
	$NiCl_2$	72 h	24.5		*L8*
	$PtCl_4$	24 h	15		*L8*
	$CuCl_2$	48 h	22		*L8*
	UCl_4	72 h	10		*L8*
HSO_3Cl	$AuCl_3$	15 d		2	*M3*
	BCl_3		$BCl_3 + HSO_3Cl$	3	*M3*
	$SbCl_5$		$SbCl_5 + HSO_3Cl$	2	*M3*

fits into the octahedral sites created by the chlorides. There exists considerable stacking disorder, strict ordering proving to be more the exception than the rule (*S21*, *M7*, *M8*). An apparent exception is graphite–$SbCl_5$ (*M6*), in which intercalated layers are in epitaxy with the carbon layers, leading to a crystallographic, ideal formula $C_{98}\cdot 8\ SbCl_5$. The presence of certain impurities can lead to almost completely ordered, higher stages without affecting the $FeCl_3$ content (*M14*). Metz and co-workers (*S23*) developed a domain theory according to which a number of ordered structures transform into one another. The whole gamut of single stages is traversed, but with preference for certain stages. The mechanism has been detected up to stage nine, and accounts for hysteresis effects in the isotherms.

Attempts to elucidate the bonding have concentrated mainly on graphite–$FeCl_3$. This intercalate is especially suitable as a model compound, because the magnetic and Mössbauer properties of the iron nucleus constitute excellent probes for electronic structure and environment of the latter.

The role of chlorine in intercalation has been discussed. Earlier theories that the chlorine intercalates, and thus opens the layer spaces for penetration of metal halides, are untenable, because chlorine itself does not intercalate. Dzurus and Hennig (*D3*) found that chlorine (or Br_2 or I_2) is, nevertheless, indispensable for intercalation. Hall coefficient data showed that $FeCl_3$ and $AlCl_3$ give acceptor types of compounds. Electrical properties being similar to those of graphite bisulfate or graphite–bromine, these authors adopted such formulas as $C_n^+Cl^-FeCl_2 \cdot 3\ FeCl_3$ or $C_n^+Cl^- \cdot x\ AlCl_3$ $(30 < n < \infty)$. Rüdorff and Landel (*R11*) preferred the formulations $C_n^+[FeCl_3]^- \cdot x\ FeCl_3$ or $C_n^+[AlCl_4^-] \cdot x\ AlCl_3$.[1] On the basis of the electrostatic nature of these compounds, Hennig (*H1*) proposed a model to predict free energies of formation of intercalates, using a modified Born–Haber cycle. The method is not easily applicable to the complex halides, too many parameters being unknown (*E1*). According to Metz and co-workers, (*S23*), a hitherto-neglected, thermodynamic parameter that should be included is the mechanical-stress energy required for deforming domains of different stages into one another.

One of the problems in applying thermodynamic cycles is knowing the species involved. The original formulation by Hennig, which presupposes the presence of 25% of $FeCl_2$ in graphite–$FeCl_3$, is unacceptable in light of subsequent Mössbauer measurements. Most of these exhibited only a single resonance at room temperature, characteristic of trivalent iron in an octahedral environment, as in $FeCl_3$ (*L9, H27, F13a, G10, T7, T8, O5, H28, J6*). A slightly higher isomer shift indicated partial transfer of π-electrons from the graphite conduction-band to the d-shell of iron. The resulting structure has been formulated as $C_n^{\delta+}(FeCl_3)^{\delta-}$, and definitely excludes such others as $C_n^+(FeCl_4)^-$ or these proposed earlier (*D3, R11*). The slight charge-transfer to iron is considered to account for the decreased thermal stability of $FeCl_3$ intercalated in graphite, compared to that of bulk $FeCl_3$ (*H28*), shifting the equilibrium $Fe_2Cl_6 \rightleftharpoons 2\ FeCl_2 + Cl_2$ to the right. Nevertheless, $FeCl_3$ intercalated in graphite is stabilized, in that it does not react with anhydrous hydrogen fluoride up to 250°C, whereas $FeCl_3$ reacts readily at room temperature (*B34*). The ternary compound

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[1] However, magnetic-susceptibility measurements on other graphite–metal chlorides indicated that electron transfer is insufficient to account for reduction of the cation (*R9*).

$C_{31}FeCl_3(N_2O_5)_{1.7}$ has the same Mössbauer spectrum as graphite–$FeCl_3$ (*F13b*).

The reduction products of graphite–metal halides have also attracted widespread interest as potential catalysts, or battery electrodes. Samples of graphite–$FeCl_3$ reduced in H_2 or N_2 at 350° show the presence of two Mössbauer, quadrupole doublets of unequal intensities (*L9, H27, G10*). The product may not be a true intercalate, as the isomer shift is identical with that of anhydrous $FeCl_2$, indicating the absence of π-electron transfer (*L9*). The presence of two doublets seems to indicate two Fe^{2+} sites. One of these doublets has been related to $FeCl_2$ in proximity to Cl_2 trapped in certain sites, changing the electric-field gradient (*H30*). Similar results were obtained by Jadhav *et al.* (*J6*), who showed that, at still higher temperatures, further reduction, to α-Fe, occurs. However, even up to 1000°C, reduction by this method is incomplete (*V7, S24*). A graphite intercalation-compound of composition $C_{4.7}FeCl_2$, close to the theoretical limit, $C_{4.22}FeCl_2$, has been obtained by reduction of $C_{7.1}FeCl_3$ by $Fe(CO)_5$ under CO pressure (*P7*). Other reducing agents, such as lithium biphenyl (*S24*) or solvated electrons (Na–liq NH_3) (*K4, K5*) lead to iron metal. In some cases, π-complexes of graphite with Fe have been reported (*S24, V8*). The completely reduced product is probably not a true intercalate. Such compounds with transition metals are considered unlikely (*B19*), because the latter have high ionization-potentials and lattice energies. The formation of two-dimensional, intercalated layers would thus be energetically unfavorable (*B19*). The structure of Fe magnetic-layers between graphite networks is inhomogeneous, and characterized by the presence of supermagnetic clusters. More-drastic treatment produced layered systems consisting of ferromagnetic α-Fe clusters separated by graphite layers (*S25*). The iron in these layers is considerably more resistant to oxidation than free iron (*K5*). Heating graphite–$FeCl_3$ with potassium at 350°C also produces mixtures of graphite–$FeCl_2$ and α-Fe (*T8*). Similar products were obtained by electrochemical reduction of first-stage graphite–$FeCl_3$ (*T9*). On the other hand, other workers found evidence only for graphite, α-Fe, and KCl in the product (*B19*). The resulting products showed little catalytic activity for ammonia production (*B19*). In fact, the purported catalytic activity of graphite–$FeCl_3$ derives from the $FeCl_2$ produced by thermal decomposition of $FeCl_3$, which diffuses to the surface, rather than from its existence as an intercalate (*P8*); this is reminiscent of the purported catalytic activity of graphite–CrO_3 (*L10*), which is really due to Cr_3O_8 (*E13*).

The graphite–bromine–iron system has also been studied. No stoichiometric compounds are formed, and the ratios Fe:Br:C can be varied independently (*S26*). The ^{57}Fe Mössbauer spectra of these systems have been studied (*S27*). In contrast to graphite–metal halides, graphite–$AuCl_3$ is readily reduced to metallic gold (*V7, V9*). No intercalation compounds with AuCl or Au are formed. Lamellar compounds of a number of other transition metals with graphite have been reported (*V8*). The reduction product of graphite–$MoCl_5$ is said to be a sandwich type of π-complex similar to dibenzene–chromium. Catalytic properties were ascribed to the nickel compound (*V8*).

1. Graphite Compounds with Group V Pentafluorides

Lalancette and LaFontaine (*L11*) were the first to report the intercalation of SbF_5 into a graphite lattice to give a first-stage compound, C_6SbF_5, as well as higher-stage compounds. They reported a new X-ray line at 11.10 Å, evidently for the second-stage compound. The use of these compounds as mild reagents for exchange of halogen in organic chlorides was proposed. This lessened activity of intercalated SbF_5 may be ascribed to the role of graphite as an inert solvent, as suggested by Ebert *et al.* (*E12*), who reported wide-line, ^{19}F-NMR spectra showing line-narrowing well below the freezing point of pure SbF_5. This behavior was ascribed to translational motion of the SbF_5 species, rotational motion being restricted by the presumed polymeric nature of the intercalated SbF_5. Other workers have also reported compounds of the type $C_{6n}SbF_5$ to $C_{6.5n}SbF_5$ (n = stage), with periodicities $I_c = 8.41 + 3.35 (n - 1)$ (*M5, T10*); this differs from earlier periodicity values (*L11*), as well as from others reported in the literature (*O4, S30, E12*). The discrepancies in periodicity values may arise from the methods of sample preparation, the types of graphite, and the purity of the SbF_5 used. However, the presence of HF, the most common impurity in SbF_5, seems to have little effect on the nature of the intercalated product, other than affecting the rates of intercalation (*T10*). Whereas pure SbF_5 intercalates in the vapor state, no intercalation takes place in the presence of HF; this may however, be due, to suppression of SbF_5 concentration by the high vapor-pressure of HF. Contact with liquid SbF_5–HF accelerates the intercalation process (*T10*).

The HF–SbF_5 system is known to be a superacid (*H34*). The possible relevance of this to the intercalation process was pointed out by Vogel (*V12*), who first reported on the extremely high electrical conductivity of graphite–SbF_5 measured normal to the crystallographic c-axis. The measured conductivity was approximately 40 times that of pristine graphite, and 50% greater than that of pure copper. Other workers disputed this high conductivity value, claiming it to be only about one-third that of copper (*T10, F14*). The metallic behavior was also confirmed by measurements of the temperature coefficient of the resistivity of graphite–SbF_5 (*F14*). The discrepancies in reported conductivities are apparently attributable to deficiencies in the original experimental method (*V12, V13*). In fact, the original high value was later discounted by the same workers (*F16*), who pointed out that, for quasi-two-dimensional materials of high anisotropy, such as graphite and some of its compounds, such standard techniques as the classical, 4-point-bridge method lead to serious errors in measured electrical conductivities, and should be replaced by r.f. techniques (*F16, Z2*). Various methods for conductivity measurements have been critically compared (*Z2*). Nevertheless, graphite–SbF_5 does indeed exhibit, in the *a*-plane, very high electrical conductivity, which may have important technological implications. Composite wires containing graphite–SbF_5, when drawn down, show a strong tendency for the *c*-axis of the intercalation compound to orient itself normal to the wire axis (*S30*). Optical-reflectance measurements (*H35*) also confirmed the metallic character of these compounds, showing high reflectances below a plasma edge and definite minima above it.

Another point of contention has been the extent to which, if any, SbF_5 is reduced to SbF_3 upon intercalation. Although chemical analyses have shown an F:Sb ratio of 5:1 (*L11, M5*), ^{121}Sb Mössbauer measurements (*B24*) indicated partial reduction of Sb(V) to Sb(III). On the other hand, mass-spectral measurements as a function of temperature (*S15*) showed only SbF_5, evolved in stages, with no fluorocarbons emitted at any time. The latter are usually an indication of partial reduction of the intercalant and fluorination of the graphite host. Wide-line, ^{19}F-NMR chemical-shifts are consistent with either SbF_5 or SbF_6^-, but not with SbF_3, but the occurrence of fluorine exchange could produce minor amounts of trivalent species (*E11*); this point is thus still controversial, and will be alluded to again.

The formation of intercalation compounds of AsF_5 with Grafoil and graphite powder was first reported by Selig and co-workers (*H32*). The blue compounds obtained by prolonged pumping at room temperature had a stoichiometry $C_{10}AsF_5$. Later work (*F15*) with HOPG showed that AsF_5 intercalates spontaneously, to yield compounds of stoichiometry $C_{8n}AsF_5$ (n = stage) with repeat distances, $I_c = 4.75 + 3.35\,n$ (Å), the lattice expansion being consistent with the size of an AsF_5 molecule calculated from covalent radii. In fact, the *c*-axis repeat-distance is shorter than the comparable one for graphite–SbF_5 by the approximate difference between the covalent radii of Sb and As. On leaving the first-stage compound exposed to dry nitrogen, a composition $C_{10}AsF_5$ is attained, indicating that the earlier reported stoichiometry (*H32*) corresponds to mixtures of first- and second-stage compounds. AsF_5 intercalation is unique, in that it exhibits spontaneous staging under isothermal conditions. Studies of the physical properties of $C_{8n}AsF_5$ are considerably facilitated by this property, as well as by the fact that, in contrast to SbF_5, no edge fraying or exfoliation occurs. Higher-stage compounds are more stable, and more easily handled, and milder reaction-conditions (lower temperature, shorter reaction times) may be used. Unusually well defined correlations exist between increases in *c*-axis thickness-expansion, the *c*-axis repeat-distances, and the electrical conductivity up to stage 3. Higher stages are nonhomogeneous (*F15*).

As in the case of SbF_5 intercalation, there are differences of opinion as to whether AsF_5 is reduced upon intercalation. According to Falardeau *et al.* (*F15*), direct correlations between weight loss and tensimetric measurements of gases evolved upon deintercalation indicated that AsF_5 is unaltered in the intercalation process. It should be pointed out, however, that their criterion for AsF_5 purity (molecular weight determinations ± 1% of the theoretical) is still consistent with the presence of up to 5% of AsF_3. More-direct impurity-determinations by infrared spectroscopy (*H32*) showed that small proportions (<5%) of AsF_3 are formed upon intercalation. Bartlett and co-workers (*B22*) even claimed a high degree of ionization, and a formula of $C_8^+AsF_6^-$ for the intercalate. Although their product was obtained by oxidation of graphite single-crystals by $O_2^+AsF_6^-$, several experimental results appeared to indicate similarities to graphite intercalated directly with AsF_5. The unit-cell parameters are not significantly different, and K-shell, absorption-edge spectra showed the presence of identical peaks, characteristic of As(V), for $C_{10}AsF_5$, $C_8^+AsF_6^-$, and other AsF_6^- salts. In addition, $C_{10}AsF_5$ showed an absorption-edge peak consistent with As(III). They concluded that the following reaction takes place upon intercalation:

$$3\ AsF_5 + 2\ e^- \rightarrow 2\ AsF_6^- + AsF_3.$$

There are, however, differences of opinion regarding the justification of using these K-shell, absorption-edge spectra for assignments to specific oxidation-states (*H36*). Both symmetry and ligands can affect absorptions by as much as 10 eV, and the absence or presence of a center of symmetry can determine whether a given transition is forbidden or allowed. However, a direct comparison of $C_{10}AsF_5$ with pure AsF_5 has now been made, and it suggested that these problems are minimal (*B35*).

Perhaps the most convincing argument in favor of intercalant ionization derives from the analogous reaction of graphite with OsF_6 (*B22*). The product, formulated as $C_8^+OsF_6^-$, obeys the Curie–Weiss law, and has a magnetic moment characteristic of OsF_6^-(V) salts.

Arguments against substantial AsF_5 reduction were based on the small proportion of AsF_3 released upon intercalation (*H32, F15*), and ^{19}F-NMR measurements that showed the absence of AsF_3, although not distinguishing between AsF_5 and AsF_6^-(*E11*). Moreover, optical-reflectance measurements (*H29*) indicated fractional ionization of only ~5% in the first-stage compound. These conflicting results have been discussed by Fischer (*F17*), who argued that the strong metallic character of these compounds may not be dominated by charge-transfer effects, but, rather, by structural variables.

Electrical-conductivity measurements (*F16, F18, V13*) confirmed the metallic character of graphite–AsF_5. The second stage has a peak, *a*-axis conductivity of $6.3 \times 10^5\ \Omega^{-1}\ \mathrm{cm}^{-1}$, i.e., marginally higher than that of copper ($5.8 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$); this value is considered to be conservative, as sample imperfections tend to decrease the conductivity. The *c*-axis conductivity decrease monotonically with progressive intercalation (*F16*), a feature shared with other acceptor compounds. The resulting anisotropy is $\sigma_a/\sigma_c > 10^6$, compared to 2×10^3 for pristine graphite.

Because, on balance, the experimental evidence appears to favor relatively low carrier-generation (*H29*), the high *a*-axis conductivity seems to result from a proportionally smaller decrease in mobility over that of the parent graphite. Infrared optical-reflectance measurements (*H29, H35*) confirmed the metallic character of the compounds. Interpretation of the spectra in terms of a one-carrier model yielded high optical conductivities, in good agreement with dc measurements. Similar conclusions were reached on the basis of resistivity and magnetoresistance data (*Z3*). Further confirmation of the metallic character of graphite–AsF_5 was obtained from conduction electron-spin resonance (*K3*). The results implied a very small density of states at the Fermi energy. The temperature dependence of the line widths show order–disorder transitions of the intercalant layers, implying delocalization of conduction electrons.

Of the other Group V pentafluorides, PF_5 does not intercalate (*H32, H35*), and BiF_5 has not been studied, because it is a nonvolatile solid that decomposes to BiF_3 at higher temperatures. In the presence of chlorine or bromine, NbF_5 and TaF_5 yield $C_{16.6}NbF_5$ and $C_{17.6}TaF_5$ (*M5*).

2. *Reactions of Graphite with Metal Hexafluorides*

Hexafluorides run the gamut of reactions with graphite, from no intercalation except in the presence of a catalyst (WF_6), through intercalation with partial reduction (UF_6), to intercalation with complete reduction (OsF_6).

Interest in UF_6 as a nuclear material first stimulated a study of intercalation of UF_6 into graphite (*M10*). Based on weight increases of graphite, the nominal stoichiometries $C_{16.8}UF_6$ and $C_{9.8}UF_6$ were obtained with natural and artificial graphites, respectively. Desorption of UF_6 was strongly dependent on initial conditions of formation, becoming appreciable only above 300°C. Later work (*B23*) confirmed these results, although a stoichiometry $C_{9.1}UF_6$ was reported. However, it was found that very little UF_6 could be recovered, the evolved gases being fluorocarbons, or, at higher temperatures, UF_4, indicating the reaction:

$$C_{9.1}UF_6 \rightarrow C_{8.6}UF_4 + \tfrac{1}{2}\,CF_4.$$

Magnetic-susceptibility measurements showed the presence of UF_4 in heated samples. Ebert *et al.* (*E14*) reported a nominal stoichiometry $C_{13}UF_6$, magnetic-susceptibility measurements indicating partial reduction at room temperature, with ~10% of the uranium species present as U(IV). Wide-line NMR demonstrated the presence of both U(VI) and U(IV).

In contrast, MoF_6 has been found to intercalate without reduction, giving first- and second-stage compounds, depending on reaction times (*O6, H33*). Stoichiometries of C_8MoF_6 (*O6*) and $C_{(11\pm1)n}MoF_6$(*H33*) have been reported, with a *c*-axis repeat-distance $I_c = 5.0 + 3.35n$ (n = stage). Most of the MoF_6 can be desorbed as a function of temperature.[2] Tungsten hexafluoride intercalates only in the presence of gaseous or liquid Cl_2, F_2, or HF, giving a second-stage compound formulated as $C_{14\pm1}WF_6\,(HF)_x$ ($x \geq 0$), as it was not determined whether HF is inserted as well (*H33*).

At room temperature, osmium hexafluoride yields a blue material of approximate composition C_8OsF_6 (*B22*). Its magnetic susceptibility obeys the Curie–Weiss law, with a magnetic moment, $\mu_{eff} = 3.5$ BM,

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[2] The ^{19}F-NMR spectrum of C_nMoF_6 is, however, quite different from that of pure MoF_6 (*E1*).

corresponding to OsF_6^-. The repeat distance is 8.06 Å, consistent with alignment of the threefold axis of the OsF_6^- species with the graphite *c*-axis.

The reactions of hexafluorides with graphite may thus involve both intercalation and oxidation, a phenomenon that has been encountered to a greater or lesser degree with other fluorides, depending on their reactivities.

F. GRAPHITE–METAL OXIDES

Attention has now been accorded the graphite–chromium trioxide intercalation compound, considered to be of use as a cathode material in high-energy-density batteries (*A2, A10, G12*), as a reagent for the oxidation of primary alcohols to aldehydes (*L10, N10*), and as a reforming catalyst (*H37*). Whereas the synthetic method of Platzer (*P9*) is generally considered to yield a true intercalation compound, the direct, "dry" combination technique of Croft has aroused controversy (*E13*). Although X-ray diffraction, differential thermal analysis (*E13*), electron-spin resonance (*E11*), and electrochemical techniques (*E15, B25*) suggested that the Croft method yields reduced chromium oxides unaccompanied by intercalation of graphite, there is some evidence for the success of the dry method (*H38*). Unfortunately, characterization was made after heating with 6 *M* hydrochloric acid, which may have caused intercalation in the solution phase (*E16*). It so happens that all of the technical applications just discussed refer to the product arising from the dry synthesis, with the Platzer material being useless in each case; thus, it is possible that one of the more economically valuable, "intercalation" compounds is not an intercalation compound at all.

IV. Residue Compounds

True graphite intercalation compounds are frequently not stable in the absence of a given activity (pressure, concentration) of free intercalant, and thus decompose to lower stage and, ultimately, so-called "residue" compounds. This process can be accelerated by thermal or *in vacuo* treatment. Although intercalant binding in residue compounds has been considered to exist primarily at defects, electronic and magnetic properties of residue compounds often differ greatly from those of graphite (*B26, H39*).

Experimental results now suggest that the intercalant species in residue compounds may be ordered (*S31, I3, C10*). Detailed electron-diffraction and microscopy work by Chung on residue compounds arising either from highly oriented, pyrolytic graphite or natural crystals suggested that residue compounds have intralayer ordering similar to that of more concentrated, lamellar compounds. In particular, the previous concept that 99% of the residual intercalant resides on defect sites was rejected in favor of a model involving layers of intercalant. This new view is consistent with magnetoreflection (*C14*) and Raman (*S13*) results that indicated a similarity between lamellar compounds and residue compounds.

Although residue compounds are difficult to characterize experimentally, they should constitute only a minor perturbation on the band structure of pure graphite. Efforts to model the electronic properties in the dilute-concentration limit by perturbing the Slonczewski–Weiss–McClure model for graphite have been made (*D5*).

V. Applications of Intercalation Compounds

A. CHEMICAL REAGENTS

Recent investigations have indicated that graphite compounds may become useful as chemical reagents; the results are summarized in several reviews (*W1, K6, K7, S32*). It is not always clear whether, in a given system, intercalates behave as catalysts or as chemical reagents. Moreover, it is often difficult to determine whether a given effect arises from the specific properties inherent in intercalation, or from the diluent effect of the graphite. The possible role of the latter as an inert solvent had been suggested earlier (*E12*), as applied to the system graphite–SbF_5, which was proposed as a mild reagent for halogen exchange in organic chlorides (*L11*). The advantages of intercalates could arise from slow release of the chemical reagent, thus moderating its activity; or from specific, stereochemical effects peculiar to graphite. From a technical standpoint, graphite compounds may be useful because they can be readily separated from the reaction medium, and can often be stored and handled more easily than the neat chemical reagent. The latter property has been used to advantage in fluorination reactions of aromatic compounds by graphite intercalated with XeF_6 (*S18, R8*), XeF_4 (*S19*), and $XeOF_4$ (*R8*). Graphite–XeF_6 seems to be a more selective fluorinating agent than XeF_2 (*A9*). Specificity has also been found in certain bromination reactions using bromine–graphite (*P10*). Other systems that have been studied include graphite–$SbCl_5$, which has particular advantages as a halogen-exchange reagent, with properties quite different from those of neat $SbCl_5$ (*B27*). Graphite bisulfate has been found to promote esterification of carboxylic acids with alcohols (*B14*). In some cases, yields of 80–90% were obtained without use of an excess of the reagents. It is assumed that the graphite compound acts both as an acid catalyst and a dehydrating agent. However, another study indicated that graphite bisulfate exerts no specific influence as a component, compared with that of free sulfuric acid (*B28*). Graphite bisulfate also promotes the formation of acetals or ethyl esters from ethyl orthoformate, as well as the nitration of aromatic compounds with nitric acid (*A11*).

The system studied most intensively is that of graphite–potassium. According to Lalancette *et al.* (*L10*), $C_{24}K$ causes condensation of benzene to biphenyl, as well as isomerization of 2-alkynes to 1-alkynes. It is not clear, however, whether reaction takes place within or outside of the graphite. Evidence that, for C_8K, reaction occurs within the matrix was obtained by Beguin and Setton (*B9*). The reaction is apparently driven by the high affinity of C_8K for hydrogen; this effect probably also plays a role in reactions of C_8K with such weak protic acids as water and alcohols. Only small proportions of hydrogen were found to be evolved, resulting in formation of partially reduced graphite (*B10*). For larger alcohols, however, larger proportions of hydrogen are released, suggesting that the reactivity of C_8K towards protonic acids is substrate-dependent (*B11*). The acid–base chemistry of rubidium–graphite and cesium–graphite is similar to that of C_8K (*B11*). Reduction of alkyl halides with C_8K was also studied (*B11*).

B. ELECTROCHEMICAL APPLICATIONS

Intercalation compounds are logical candidates for application as reversible electrodes in cells. Possessing electroactive, but possibly nonconducting, species in electronic contact with the graphite matrix, the intercalation compound is expected to be insoluble in the electrolyte, conductive in the charged and discharged states, and mechanically stable with respect to cycling. Somewhat ironically, although this concept has been thoroughly explored (*A8, A10, A12, D7*), a nonconducting graphite compound has been the most economically successful.

Thus, although the use of graphite compounds as cathodes in electrochemical cells antedates the use of other layered materials (*B29, B30*), it was not until 1973, with the commercial introduction of the CF_x cathode in a lithium–nonaqueous electrolyte system (*F19, W2*), that graphite compounds achieved widespread publicity. Possessing a nominal voltage of 2.8 V, an energy weight density of 804 W-h/lb (CF) [or

1443 W-h/kg (LiCF)], and a volume density of 10 W-h/in.^{3}, the battery is currently marketed by Matsushita in six different capacities. The most popular of these, the BR-435, is a cylindrical cell 4 mm in diameter by 30 mm long; 4 million of these cells were produced in 1977 (*B31*).

Other covalent compounds of graphite have been investigated as cathode materials. Most thorough has been the work of the United States Army Electronics Command on graphite oxide, graphite oxyfluoride, and various graphite fluorides (*H40, H41, H42, L12, B32*). A new graphite fluoride compound, "C_2F", made from the action of ClF_3 and HF on graphite, has been suggested for yielding voltages and discharge characteristics superior to those of CF (*M11, M12, R13*).

Why do true intercalation-compounds not work better as reversible electrodes? In fact, the C_8K–K cell is reversible, but its room temperature emf of only 0.2 V (*A13*) is suggestive of the large "atomic" character of the intercalated potassium in C_8K. In contrast, in the Li–TiS_2 system (*W1*), in which the intercalated lithium is best considered ionic, there are observed an open-circuit emf of 2.5 V, complete reversibility, and an energy density of 455 W-h/kg ($LiTiS_2$). With intercalated oxidants, Lalancette found that bromine compounds can be used as electrodes in concentration cells, yielding voltages of the order of 50 mV, with thermal gradients of 60–75°C, in the range of 0–100°C (*L13*). If, however, a concentrated acceptor-compound, such as $C_{13}CrO_3$, is run against lithium, the oxidant, which is primarily *molecular* in graphite, leaves the graphite on reaction with lithium, or displacement by electrolyte-solvent molecules (*E16*). Thus, the concept of using graphite–acceptor compounds as cathodes fails, because of the large fraction of non-ionized species that is not in close, electronic contact with the graphite matrix. Existing as "spacers" to screen the coulombic repulsions among the intercalated ions, these molecules are reasonably mobile and may react to form a nonintercalated species, while solvent molecules from the electrolyte intercalate as new spacers.

For a more-detailed treatment of the use of intercalation compounds in electrochemistry, more-specialized reviews (*W1, E15, B33*) may be consulted.

C. Intercalation Compounds as Highly Conducting Materials

A great deal of excitement has been generated by the assertion that some intercalation compounds of graphite possess a conductivity greater than that of copper (*V10, F13, T11*). Much of this work was based upon earlier researches by Ubbelohde, who found that the a-axis conductivity of the semi-metal graphite increases, and develops a metallic temperature-dependence, on intercalation either by donors or acceptors; he thus referred to graphite intercalation compounds as "synthetic metals" (*U11*).

Currently, there is disagreement concerning the actual magnitude of the conductivity increase, but there is no doubt that an effect, most pronounced for such acceptors as AsF_5, does exist (*T10, V13*). Models evolved in order to account for the magnitude of the conductivity increase included intergraphite layer-separation (*F5*), the intercalant concentration (*F10*), and carrier-mobility enhancement (*F5*).

The actual utility of this discovery depends on the ability to go from hosts consisting of expensive, highly oriented, pyrolytic graphite to hosts composed of cheap graphite powders or fibers. Care must be taken on intercalation, because defects in such low-rank graphites may affect not only the intrinsic conductivity of the host (*Z4*) but may also serve as sites for oxidative reactions that may disrupt the host (*E11*).

D. Catalysis by Graphite Intercalation Compounds

Graphite compounds have been described as catalysts for ammonia synthesis from nitrogen and hydrogen (*I4, P11*), for Fischer–Tropsch chemistry (*M13, R14*), for paraffin isomerization (*R15*), and for Friedel–Crafts chemistry (*O7*).

Unfortunately, it is difficult to ascertain the identity of the actual catalytic species, and it is not clear whether catalysis by a true intercalation compound has been established. For instance, a frequent method for ammonia and Fischer–Tropsch catalyst generation is the following:

$$C_nMX_y + y\,M' \rightarrow \text{"}C_nM\text{"} + y\,(M'X),$$

where M = transition metal, M′ = alkali metal, and X = halogen. This technique is more apt to lead to a finely dispersed metal than to an intercalated one, although the characterization of such materials is difficult (*B19, E1, E11, V1, V2, V14, V15*). A thorough discussion of the catalytic behavior of graphite compounds has appeared (*W1*).

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