

PROPERTIES OF GRAPHITE COMPOUNDS*

G. R. HENNIG

Chemistry Division, Argonne National Laboratory, Lemont, Illinois

(Manuscript received October 25, 1955)

An attempt has been made to classify and interpret various reversible chemical reactions of graphite.

In many chemical reactions, graphite retains those properties which depend upon the covalent carbon layers. These reactions can often be reversed by suitable changes in conditions. Three principal types of such reactions are known: introduction of interstitial reactants into the graphite lattice, introduction of substitutional reactants into the lattice, and reaction with graphite surface atoms.

Compounds of graphite with boron are probably substitutional compounds. Graphite containing lattice vacancies can also be thought of as a substitutional compound.

Most reactions of graphite lead to the formation of interstitial compounds. These are apparently always either considerably better electrical conductors than graphite in which case they are acceptor or donor compounds, or they are insulators. The insulating types of compounds owe their stability to the formation of covalent bonds. The other interstitial compounds are formed because the transfer of electrons between impurity and graphite provides the necessary energy. This dependence of stability on ionization and the resultant peculiar periodicity of the compounds has been investigated.

Surface compounds of graphite have been studied by paramagnetic resonance techniques and by the controlled oxidation of single crystals. Some of the surface atoms of graphite can be stabilized under suitable conditions, the stabilization results in unusual geometric figures at the burned surfaces.

INTRODUCTION

Graphite reacts with many different chemical substances to form compounds which are quite similar in physical properties to the original graphite. In these reactions, the carbon skeleton of the graphite structure remains unchanged, and the chemical reagent is added internally or peripherally to the skeleton. The reactions can be classed into three groups. The first class are surface reactions, and involve only the peripheral surfaces of the graphite crystallites. The second class are interstitial reactions in which the carbon skeleton is retained but is expanded to accommodate the reactant. The third class are substitution reactions in

which a small fraction of the carbon atoms is replaced by foreign atoms.

This report will describe some typical examples of each class of reaction and their effect on the physical properties of graphite. Some attempts at predicting the reactivity of various reagents on graphite will be discussed.

Among the most sensitive tests for chemical reactivity in graphite are the electrical properties. Chemical reactions usually alter the electrical properties considerably because they affect the electron population of the conduction bands. Thus removal of electrons from the graphite creates so-called positive holes, so that the concentration of electrical carriers is increased; addition of electrons also increases

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

this carrier concentration¹. Chemical impurities therefore usually increase the electrical conductivity. They also decrease the diamagnetism and the magneto resistance. The electrical property changes are sufficiently sensitive to detect any chemical reaction which has altered the electron concentration by one in a hundred thousand.

SUBSTITUTIONAL COMPOUNDS

These compounds correspond to solid solutions in metals. In semiconductors, N- or P-type impurities are usually present as substitutional impurities. In graphite, no systematic search has as yet been conducted for substitutional impurities. In analogy with Si or Ge, one would expect nitrogen, phosphorus, antimony, aluminum, boron, and perhaps also silicon and germanium to enter substitutionally. The lack of experimental evidence of such compounds is probably due to the high temperature required to obtain diffusion in graphite. At these high temperatures, where impurities can diffuse into graphite, the impurities have such a high vapor pressure that they react with the container material and do not have a chance to enter into the graphite. There exists some evidence that boron has been substituted in the graphite lattice. Heating graphite with boron compounds usually lowers the resistance. Figure 1 which has been redrawn from data published by Griswald and others² shows the electrical resistance of carbon containing various amounts of boron.

Another impurity which is almost certain to enter the graphite structure under appropriate conditions is the vacancy. If graphite is heated above temperatures where self diffusion can occur in reasonably short times, a concentration of vacancies will automatically establish itself which is

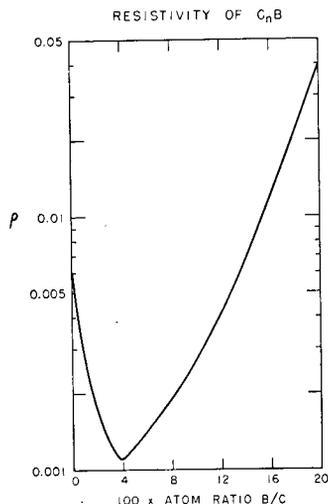


FIG. 1. The resistance of carbon containing boron

approximately given by the equation³

$$N/N_0 = e^{-\Delta H/RT},$$

where the concentration of vacancies per carbon atom is N/N_0 , and the energy content of a vacancy is ΔH . We can make a guess at the magnitude of this energy content. The energy required to remove a carbon atom out of the lattice and place it on the surface is approximately equal to the heat of sublimation. The heat of sublimation is approximately 7.5 ev, thus the vacancy concentration at 3000°K is $\exp\{-7.5/0.25\}$ or 10^{-13} . This is by far too small a concentration to be detected. However, we have neglected in this guess that the vacancy will relax considerably. The bonds of the atoms surrounding the vacancy will in all probability become strengthened so that the energy content of the vacancy will be lowered. There is no certain way to estimate this relaxation but it is not unreasonable to expect that it amounts to, say, 5 ev, so that the concentration of vacancies at 3000°K becomes $\exp\{2.5/0.25\}$ or 10^{-4} . This concentration

¹ G. R. Hennig, J. Chem. Phys. **19**, 922 (1951).

² Griswald, Pfister, and van Roosbroeck, Bell System Tech. J. **30**, 271 (1951).

³ J. Bardeen, and C. Herring, *Imperfections in Nearly Perfect Crystals* (New York, 1952) p. 265.

of vacancies could probably be detected if the graphite can be cooled to room temperature sufficiently rapidly as that the high concentration of vacancies is frozen in. Kinchin⁴ has reported the production of vacancies in graphite in this way, although we have not been able to reproduce his experiments at the temperatures he quoted (2000°C). We ourselves have on occasion quenched single crystals of graphite from 3000° by a rapid stream of helium and found the electrical properties to have changed. The experiments are, however, not yet conclusive. The vacancies can be detected only if they trap electrons or add electrons to the conduction band thereby affecting the electrical properties as described earlier. Again we have to postulate a considerable relaxation around the vacancy, because rearrangement of the electron distribution would be one aspect of such relaxation.

In summary it can be stated that our knowledge concerning substitutional impurities in graphite is still extremely limited. The most promising experiments have been discussed.

INTERSTITIAL COMPOUNDS OF GRAPHITE

The interstitial compounds of graphite are very well known, have been examined and described by a large number of investigators⁵ and nevertheless exhibit many puzzling aspects. Table I lists the type of substances which enter into interstitial compound formation. We have surveyed a considerable number of such compounds but have never found one in which the electron population of the parent graphite has not been altered. The manner in which the population is altered permits classification of the interstitial compounds. Members of the first class are acceptor compounds

and include compounds of bromine, chlorine, ferric chloride, etc. In these compounds, electrons have been removed from the graphite and transferred to the impurity. This transfer increases the electrical conductivity. It also causes the Hall coefficient to change sign, because the predominant carriers become positive holes. Members of the second class of interstitial compounds are donor type. In these, the impurity transfers electrons to the graphite, leaving the Hall coefficient negative, but increasing the conductivity. The third class is entirely different in character. Here the impurity has formed covalent bonds to the carbon atom. This alters the graphite skeleton considerably; the planes are no longer flat but puckered, because the carbon atoms are now tetrahedral. There are no conduction electrons available any more; the compounds are insulators and furthermore are yellow or white. Thus, the third class of interstitial compounds can hardly be considered graphite compounds. Another difference between the three classes is the fact that each reactant in the first two classes can form essentially an infinite number of different compounds, by entering into every interplanar space, or every second interplanar space, every third, etc. The third class of compounds appears to exist only in the most concentrated form, which is often formed with explosive violence.

It was stated above that the interstitial reactions apparently always disturb the electron distribution of the carbon skeleton. It will be shown in the following sections that it is possible to attribute the formation of the interstitial compounds to this electron transfer and to predict the stability of various compounds from elementary considerations. The experimental confirmation of this model is still rather incomplete; a number of observations will be cited which apparently confirm the model, and a

⁴ G. H. Kinchin, Proc. Roy. Soc. A217, 9 (1953).

⁵ H. L. Riley, Fuel 24, 8 (1945).

TABLE I
Interstitial Compounds

Acceptors		Donors		Covalent
Reagent	Compound	Reagent	Compound	
Cl ₂	C _n ⁺ ·Cl ⁻ ·3Cl ₂	K	C _n ⁻ ·K ⁺ ·2K (?)	O ₂
Br ₂	C _n ⁺ ·Br ⁻ ·3Br ₂	Rb		F ₂
ICl		Cs		S
FeCl ₃	C _n ⁺ ·Cl ⁻ ·FeCl ₂ ·3FeCl ₃	NH ₃	C _n ⁻ ·NH ₃ ⁺ ·20NH ₃	
SbCl ₅		CH ₃ NH ₂		
UCl ₄	C _n ⁺ ·Cl ⁻ ·UCl ₃ ·3UCl ₄			
H ₂ SO ₄	C _n ⁺ ·HSO ₄ ⁻ ·2H ₂ SO ₄			

few contradictory cases will also be described.

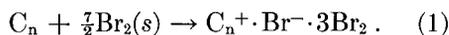
QUALITATIVE CONSIDERATIONS

The energy released in the transfer of electrons between reactant and graphite depends on the difference between the work function of graphite and the ionization potential or electron affinity of the reactant. An additional contribution to the driving force for reaction must be the electrostatic interaction of the ions which are formed. The charged impurity ions will repel one another and attract the charges on the carbon layers. Therefore the stability will be increased if the impurity ions are separated by a larger distance than the average distance from impurity ion to the charge carried by the carbon. If, now, we examine the stoichiometry of some interstitial compounds, we find that inevitably only a fraction of the impurity ionizes; the rest apparently serves as a spacer to keep the ions separated. The formulae for a few compounds have been listed in Table I. Usually each ion is accompanied by two un-ionized impurities, although the ratio appears smaller for some substances. Most of the values in the table were determined by measuring the Hall coefficients and weights of these compounds. This requirement of a spacer between the ions of the impurity permits the introduction of many

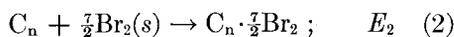
substances⁶ into graphite which do not enter spontaneously. Alkali and alkaline earth metals, for instance, form compounds with graphite in the presence of ammonia, because the NH₃ molecules fulfill this role of spacers. AlCl₃ which does not react by itself, will become the spacer if halogens are also present, which become ionized.

QUANTITATIVE CONSIDERATIONS

The energy of formation of interstitial compounds can be calculated from a Born-Haber type cycle which will be described for the graphite bromide compound. The over-all reaction is



We refer to solid bromine as the standard state. The symbol C_n stands for graphite. We split this reaction (1) into hypothetical partial reactions (2) to (4).

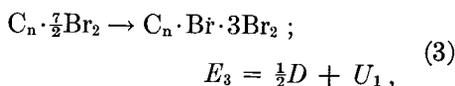


In the first step (2) we separate the carbon planes and insert un-ionized bromine molecules. The change in energy, E_2 , is probably small since it involves only van der Waals terms.

⁶ M. Dzurkus and G. R. Hennig, Bull. Am. Phys. Soc. **29**, No. 7 12 (1954).

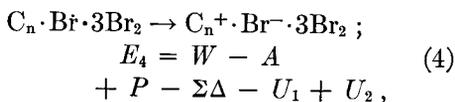
G. R. Hennig, J. Chem. Phys. **20**, 1438 (1952).

The second partial reaction,



is the dissociation of one bromine molecule. U_1 is the difference between the lattice energy of bromine layers in graphite and layers containing molecules and atoms in graphite, and D is the heat of dissociation.

The third step, the transfer of an electron from graphite to the bromine atom,



requires the work function, W , of graphite minus the electron affinity, A , of bromine plus the electrostatic energy, P , which should be strongly negative. U_2 is the change in lattice energy other than electrostatic energy of replacing Br_2 by Br^- . It should be noted that the work function of graphite becomes progressively larger as the conduction band is depleted, so that we have to add for each electron removed a term $-\Delta$, the lowering of the Fermi energy.

ΔH of reaction (1) should be the sum of the individual E_i terms plus a (pv) term which is small. The free energy is

$$\Delta F = \Delta H - T\Delta S. \quad (5)$$

The entropy change, ΔS , is probably small because the reaction product is highly ordered; thus the free energy change is about equal to the sum of the E_i terms. A more useful value than ΔF is the partial molar free energy $\Delta \bar{F}$ per ion. This value differs from ΔF only in the Fermi energy terms; instead of containing $\Sigma \Delta$, it only counts the final, largest value of Δ :

$$\Delta \bar{F} = E_2 + U_2 + \frac{1}{2} D$$

$$+ W - A + P - \Delta. \quad (6)$$

For donor compounds and for metal halide compounds of graphite the expressions for the partial molar free energy are

TABLE II
Energy Terms

$C_n + 3K \rightarrow C_n^- \cdot K^+ \cdot 2K$ $\Delta \bar{F} = -W + I + [E_2 + U_2 + P + \Delta_d]$
$C_n + \frac{7}{2} Br_2 \rightarrow C_n^+ \cdot Br^- \cdot 3Br_2$ $\Delta \bar{F} = W + \frac{1}{2} D - A + [E_2 + U_2 + P - \Delta_a]$
$C_n + 4UCl_4 \rightarrow C_n^+ \cdot Cl^- \cdot UCl_3 \cdot UCl_4$ $UCl_4(S) \rightarrow UCl_3(S) + \frac{1}{2} Cl_2(S) + Q$ $\Delta \bar{F} = W + \frac{1}{2} D - A - Q + [E_2 + U_2 + P - \Delta_a]$

\wedge A = Electron Affinity; P = Electrostatic Energy; Δ = Change in Fermi Level; Q = Heat of Reaction; E_2 = Van der Waals Energy; U_2 = Change of Crystal Energy; I = Ionization Potential; W = Work Function of Graphite.

somewhat different. The equations have been summarized in Table II. The validity of these equations will be examined by two tests: the variation of stability with chemical impurity, and the concentration dependence of stability. For a series of different acceptor compounds, or donor compounds, the terms inside the square brackets (Table II) probably vary much less than the other terms. Therefore, the sum of these other terms should be a rough index of the relative stability of the compounds. Such a tabulation of various compounds is shown in Table III. The acceptor and donor compounds⁷ are separately arranged in the order of increasing energy, i.e., in the predicted order of decreasing stability. The acceptor compounds were selected at random from a considerably larger list of substances which had been examined by Croft.⁸

It is apparent from the table that the calculated energy differences for acceptors are not a reliable index of compound stability, although they appear to be correct for donor compounds. In the acceptor compounds there is at most a trend of decreasing reactivity with increasing energy

⁷ M. A. Herold, *Compt. rend.* **232**, 838, 1484 (1951).

⁸ R. C. Croft, *Nature* **172**, 725 (1953).

TABLE III
Stability of Lamellar Compounds

Acceptor	Probable Compound	$W + \frac{1}{2}D - A - Q$	Observed Reaction	U_2 Large
Cl ₂	$C_n^+Cl^- \cdot (Cl_2)_m$	+2.06	+	
Br ₂	$C_n^+Br^- \cdot (Br_2)_m$	+2.18	+	
SO ₂ Cl ₂	$C_n^+Cl^- \cdot \frac{1}{2}SO_2 \cdot (SO_2Cl_2)_m$	+2.19	-	*
SbCl ₃	$C_n^+Cl^- \cdot \frac{1}{2}SbCl_3 \cdot (SbCl_3)_m$	+2.27	+	
CCl ₄	$C_n^+Cl^- \cdot \frac{1}{4}C \cdot (CCl_4)_m$	+2.28	-	*
AuCl ₃	$C_n^+Cl^- \cdot \frac{1}{2}AuCl \cdot (AuCl_3)_m$	+2.36	+	
I ₂	$C_n^+I^- \cdot (I_2)_m$	+2.45	-	
PCl ₅	$C_n^+Cl^- \cdot \frac{1}{2}PCl_3 \cdot (PCl_5)_m$	+2.51	+	
FeCl ₃	$C_n^+Cl^- \cdot FeCl_2 \cdot (FeCl_3)_m$	+2.54	+	
TlCl ₃	$C_n^+Cl^- \cdot \frac{1}{2}TlCl \cdot (TlCl_3)_m$	+2.61	+	
CuCl ₂	$C_n^+Cl^- \cdot \frac{1}{2}Cu_2Cl_2 \cdot (CuCl_2)_m$	+2.74	+	
SnCl ₄	$C_n^+Cl^- \cdot \frac{1}{2}SnCl_2 \cdot (SnCl_4)_m$	+2.76	+	
HgCl ₂	$C_n^+Cl^- \cdot HgCl \cdot (HgCl_2)_m$	+2.77	-	
SbCl ₅	$C_n^+Cl^- \cdot \frac{1}{3}Sb \cdot (SbCl_5)_m$	+3.25	-	*
Cu ₂ Cl ₂	$C_n^+Cl^- \cdot Cu \cdot (Cu_2Cl_2)_m$	+3.34	-	*
SiCl ₄	$C_n^+Cl^- \cdot \frac{1}{4}Si \cdot (SiCl_4)_m$	+3.54	-	*
UCl ₄	$C_n^+Cl^- \cdot UCl_3 \cdot (UCl_4)_m$	+3.57	+	
CrCl ₃	$C_n^+Cl^- \cdot CrCl_2 \cdot (CrCl_3)_m$	+3.65	+	
InCl ₃	$C_n^+Cl^- \cdot InCl_2 \cdot (InCl_3)_m$	+3.73	+	
PbCl ₂	$C_n^+Cl^- \cdot \frac{1}{2}Pb \cdot (PbCl_2)_m$	+3.78	-	*
CdCl ₂	$C_n^+Cl^- \cdot \frac{1}{2}Cd \cdot (CdCl_2)_m$	+3.94	-	*
MgCl ₂	$C_n^+Cl^- \cdot \frac{1}{2}Mg \cdot (MgCl_2)_m$	+5.26	-	*
BaCl ₂	$C_n^+Cl^- \cdot BaCl \cdot (BaCl_2)_m$	+5.99	-	
Donor	Probable Compound	$-W + I$	Observed Reaction	U_2 Large
Cs	$C_n^-Cs^+ \cdot Cs_m$	-0.69	+	
Rb	$C_n^-Rb^+ \cdot Rb_m$	-0.40	+	
K	$C_n^-K^+ \cdot K_m$	-0.24	+	
Na	$C_n^-Na^+ \cdot Na_m$	+0.56	-	
Li	$C_n^-Li^+ \cdot Li_m$	+0.80	-	

index, but there appear to be numerous exceptions. We must conclude therefore, that the terms inside the square brackets of Table II do not remain constant for different acceptors. Since E_2 is probably small and Δ can hardly be affected much by the impurities, one must conclude that the electrostatic energy, P , is quite sensitive to the size of the impurity molecules and probably also to the effective dielectric constant of the impurity layer.

The term U_2 which measures the energy of introducing a reduced or oxidized species into a crystal lattice, will probably be small when the parent and reduced species are isomorphic but may be quite large, for

instance, for a lattice of CCl₄ containing some carbon, or MgCl₂ containing Mg. The substances for which U_2 can be anticipated to be large have been marked with an asterisk in column 5 of Table III, and should lie lower in the table than indicated. This improves the agreement between measured and predicted stability considerably.

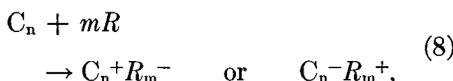
The experimentally determined reactivities in column 4 of Table III are also open to some doubt. Unfortunately, no systematic study of relative stabilities or concentrations are available. The measurements of Croft⁸ may be biased because excess chlorine had apparently not been

excluded in some of the reactions tested, so that some of the compounds may merely have acted as spacers in chloride compounds as discussed earlier.

A second test of the equation of Table II is the concentration dependence of the stability. The concentration dependence is most conveniently measured by the equilibrium vapor pressure of the impurity over the graphite compound. This pressure, p , is related to the equilibrium pressure, p_0 , of unreacted impurity at the temperature T and the free energy of the impurity at pressure p by

$$F = RT \ln p/p_0 + O, \quad (7)$$

where terms in O are usually small as long as T does not exceed the boiling point. This free energy, F , of the reactant in equilibrium with a graphite compound is proportional to the partial molar free energy, $\Delta\bar{F}$. It is, in fact, related to the $\Delta\bar{F}$ of a reaction written schematically as,



by

$$\Delta\bar{F} = mF \cong mRT \ln (p/p_0). \quad (9)$$

This dependence of free energy on concentration has been plotted in Figs. 2 and 3 for two graphite compounds. The value of m is $\frac{1}{2}$ for the bromide and unknown for

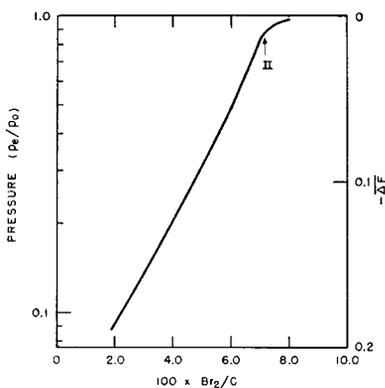


FIG. 2. Free energy of graphite bromide

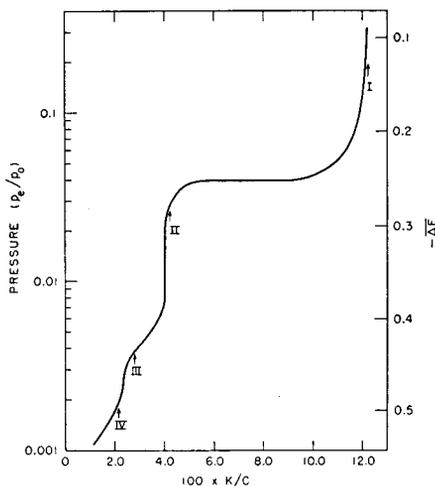


FIG. 3. Free energy of potassium graphite

the potassium compound, for which it was assumed to be 3. The partial molar free energy can also be determined from electrode potentials for some graphite compounds. The electrode potential which is a direct measure of $\Delta\bar{F}$ in units of ev , has been plotted in Fig. 4 for the graphite bisulfate compound $C_n^+HSO_4^- \cdot 2H_2SO_4$. The free energies of the bisulfate and the potassium compounds show a characteristic structure; it becomes nearly constant in the vicinity of ordered compounds, indicated in the graphs by Roman numerals. (In a compound III, f.i., three carbon layers alternate with one impurity layer.) The data for the bromine compound⁹ are not sufficiently precise to show such structure. Aside from this structure, the curves show a free energy change from extreme dilution up to a compound of stage II of 0.2 ev for the bromide, 0.3 ev for the potassium and 0.4 ev for the bisulfate compound. From the equations of Table II, these values must be due to changes in the terms inside the square brackets, because the terms outside the brackets are concentration independent. The term E_2 inside the brackets is also concentration independent.

⁹ Juza, Lübke, and Heinlein, *Z. anorg. Chem.* **258**, 104 (1949);

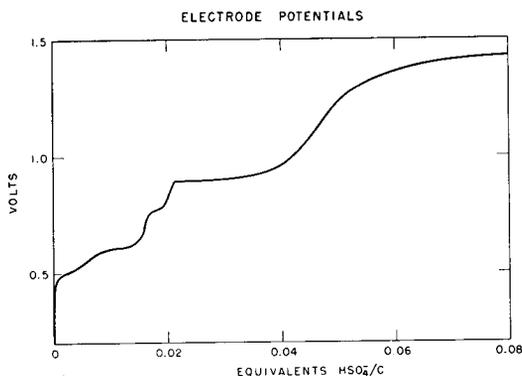


FIG. 4. Free energy of graphite bisulfate

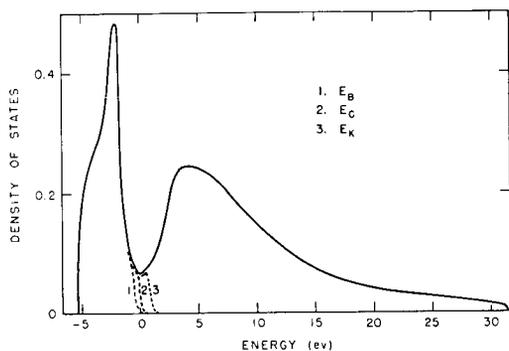


FIG. 5. Band structure (Coulson, Taylor)

The value of Δ , the increase in the Fermi energy due to electron addition or removal, is very difficult to evaluate. Figure 5 shows an approximate contour of the electron bands in graphite. This contour was evaluated by Coulson¹⁰ for a 3 dimensional graphite structure. In the second stage bisulfate compound, $C_{48}^+HSO_4^- \cdot 2H_2SO_4$, 1/48 electrons have been removed; its Fermi energy is therefore lowered to E_B , so that Δ is about -0.3 eV. For the bromide of composition $C_{56}^+Br^-(Br_2)_3$, the value of Δ is about -0.2 eV. These values of Δ are sufficient to explain nearly the total observed concentration dependence (Fig. 2 and 3) of these compounds, and seem to show that the electrostatic energy, P , is concentration independent. Before discussing P further, we have to note another

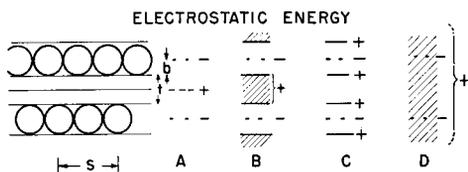
uncertainty in the Δ values, however. The energy contours of Fig. 5 were evaluated for pure graphite and may well be altered by the introduction of impurities. In fact it is very likely that a superlattice is formed; this may cause the band to become split into several bands, and cause the energy contours to become sawtoothed.¹¹ Thus the density of states may be altered specifically near concentrations corresponding to ordered compounds. The change in Δ with concentration will then not be linear anymore, but show abnormalities near ordered compounds. This conclusion may qualitatively explain the wriggles which were found in the free energy curves.

The electrostatic energy, P , has to be examined next. We have already concluded earlier that P cannot change much with impurity concentration. To evaluate P we must know the charge distribution in the compound. Four possible charge distributions have been represented in Fig. 6 for an acceptor compound. The corresponding electrostatic energies have been listed. These values are crude approximations for an infinitely large crystal of the compound, where edge effects can be neglected. None of these models can be correct, however, because the energies of model A, B, and D become infinitely large at low concentrations (large t), while model C is a two phase system which would show no concentration dependence of P or Δ and thus no concentration dependence of $\Delta\bar{F}$. It is also uncertain whether the use of an average, concentration independent dielectric constant, k , is justified.

In both tests of the model discussed here, the quantity E_2 was assumed small. The neglect of this energy term may be a rather serious approximation. Although the van der Waals energy per carbon atom is small, about 0.2 eV, and the difference between C—C bonds and C—Br₂ or

¹⁰ C. A. Coulson, and R. Taylor, Proc. Phys. Soc. **A64**, 815 (1952).

¹¹ A. H. Wilson, *The Theory of Metals* (Cambridge, 1953) p. 44.



$$A: P = \frac{3.64 e^2}{K} \left[\frac{b+1/4}{S^2} - \frac{1.02}{S} \right]$$

$$B: P = \frac{3.64 e^2}{K} \left[\frac{b+1/8}{S^2} - \frac{1.02}{S} \right]$$

$$C: P = \frac{3.64 e^2}{K} \left[\frac{b}{S^2} - \frac{1.02}{S} \right]$$

$$D: P = \frac{3.64 e^2}{K} \left[\frac{2b+1}{8S^2} - \frac{0.51}{S} - \left(\frac{0.04}{S^2} \right)^{1/3} \right]$$

FIG. 6. The electrostatic energy

C—H₂SO₄ bonds probably even smaller, this energy per carbon atom is counted n times where n is the ratio of carbon atoms to ions in the stage I compound. The value n per ion introduced is 24 for the bisulfate and probably for most of the other impurities. That this energy is by no means negligible is indicated by the type of packing observed in those compounds for which the arrangement of molecules in the impurity layers is known. These molecules are usually not close packed, but seem to prefer to lie on points of the carbon lattice. This effect is probably also responsible for the replacement of ABAB stacking of pure graphite by A—A—A stacking of the carbon planes in some of the lamellar compounds. On the other hand, an evaluation of E_2 for the various compounds listed would present great difficulties. Also related to the quantity E_2 is probably the observation that in several compounds, i.e., the FeCl₃,¹² K,¹³ Br₂,¹⁴ compounds, the density of the impurity in the interlamellar space abruptly changes between the first and the second stage.

In summation, it might be said that the calculation of free energies from an electro-

¹² J. A. Barker and R. C. Croft, Australia J. of Chem. **6**, 302 (1953).

¹³ W. Rudorff and E. Schulze, Z. anorg. u. allgem. Chem. **277**, 156 (1954).

¹⁴ J. Mering, private communication.

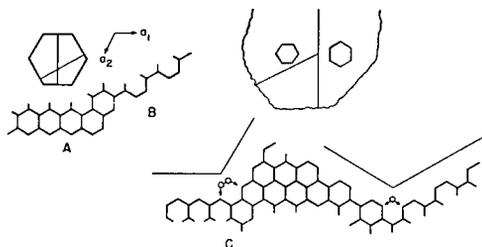


FIG. 7. Graphite surfaces

static model of lamellar compounds has not been satisfactorily accomplished. Some trends have been predicted, but the main obstacle is the necessity of an electrostatic energy which differs for different compounds having the same ion concentration but different chemistry, and which is rather concentration independent. It should be emphasized that the calculations assumed a truly ionic character of the lamellar compounds. An experiment has recently come to the author's attention,¹⁵ in which the formation of a lamellar compound between graphite and aluminum chloride has been accomplished, without the addition of free halogen which could act as an electron acceptor. It will be extremely interesting to measure the Hall coefficients of the compound. If such a compound exhibits P-type behavior, it is difficult to see how it could be a truly ionic compound, and its existence would cast doubt on any electrostatic model of lamellar compounds.

Recent attempts in our laboratory to repeat these syntheses have not been successful. We found instead that graphite compounds containing AlCl₃ inevitably also contained excess halogen or other electron acceptors.

SURFACE COMPOUNDS

To understand the surface compounds of graphite, the structure of clean graphite

¹⁵ R. C. Croft, J. Appl. Chem. (London) **2**, 557 (1952).

W. Rudorff and R. Zeller, Z. anorg. u. allgem. Chem. **279**, 182 (1955).

surfaces has to be understood. The planar surfaces perpendicular to the c axis (also called d or a_2 axis) are very probably surfaces of low chemical activity, because they will bond foreign substances with only van der Waals forces. Even these surfaces can, however, adsorb as work by Ruess and Vogt¹⁶ has shown. The edge atoms of the carbon planes are expected to be more active because of their residual valence bonds. The preferred orientation of the surfaces formed by these edge atoms has been determined by Palachi.¹⁷ The most perfect single crystals of graphite have well-developed $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ surfaces and weak $\{10\bar{1}0\}$ planes, while $\{11\bar{2}i\}$ planes are subordinate. Translated into a chemists language this means that the edge atoms of a given carbon plane appear to prefer the arrangement A (Fig. 7) over the arrangement B (referred to in the following as zigzag and armchair surfaces). It is of interest whether this preferred surface structure remains the more stable one during oxidation in various chemical agents. When a clean crystal is burned, the edge structure is usually obliterated, planes parallel to the c axis, however, appear to remain shiny and unaltered. If the crystals are not perfectly clean, one observes holes or pits burned into the flat planes; these holes are often perfect hexagons. The orientation of these hexagons depends upon the burning gases. I have conducted some preliminary investigation on this orientation. The crystals were touched with the finger to introduce the required catalytic impurity. They were burned in air to introduce pits and holes. The impurity was then removed by heating in chlorine at 1100°C. That this treatment was sufficient was shown by heating new, impure crystals first in chlorine and then in air. No pits or holes appeared in these crystals. The

hexagons produced by the catalytic impurities were nearly always abnormal, i.e., their surfaces were bounded by $(11\bar{2}i)$ planes or "armchair" surfaces. Subsequent burning in air or water vapor caused the hexagons to become rounded off. Burning in pure CO₂ caused rotation of the hexagon to the normal orientation, i.e. $(10\bar{1}i)$ surfaces or "zigzag" structure. Burning in CO₂ containing chlorine or HCl or CCl₄ retained the abnormal armchair structure.

Although more experimental evidence on other burning gases and varied conditions are required, it is tempting to postulate that the abnormal, armchair structure occurs only when it is protected by a bridging surface compound, drawn in C (Fig. 7) as an adsorbed phosgene molecule. This postulate agrees with the observation that chlorine compounds considerably inhibit burning in CO₂. The abnormal orientation of the hexagons during catalytic burning cannot be explained by this postulate.

Information about the structure of graphite surface compounds has been obtained from paramagnetic resonance studies. As pointed out earlier, the peripheral atoms of clean graphite crystallites must have free valence bonds and can therefore be expected to be paramagnetic. This paramagnetism can best be demonstrated by paramagnetic resonance absorption techniques because these are not masked by the large diamagnetism of the graphite conduction electrons. The formation of surface compounds by peripheral atoms can be expected to alter or annihilate their paramagnetism. These studies have been carried out jointly by Dr. B. Smaller and the author, and are described in the attached note which has been submitted for publication elsewhere.

In conclusion I wish to emphasize that many of the speculations in this report are preliminary theorems only, which await further experiment for confirmation or rejection.

¹⁶ G. Ruess and F. Vogt, Monatshefte f. Chem. **78**, 222 (1949).

¹⁷ C. Palache, American Mineralogist **27**, 709 (1941).