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Lamellar Compounds of Graphite with Alkali Metals

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The preparation, structure, and thermodynamic, physical, and chemical properties of lamellar compounds of graphite with alkali metals are surveyed. These compounds are shown to be mostly similar in methods of preparation, structure, and properties to complexes of aromatic hydrocarbons with alkali metals. A list of 100 references is included.

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I. INTRODUCTION

Graphite is an allotropic modification of carbon having a layered structure. The carbon atoms are arranged in parallel planes, in each of which they form a network of hexagons in which the distance between the carbon atoms is close to the length of the carbon–carbon bond in the benzene molecule (1.415 and 1.397 Å respectively). The distance between parallel planes in graphite is rather smaller than the van der Waals thickness of aromatic molecules (3.35 and 3.4–3.5 Å), The absence of chemical bonding between the parallel carbon layers in graphite makes possible the intercalation of monatomic or monomolecular layers of various substances with formation of the so called layer or lamellar compounds of graphite. Alkali metals, halogens, strong acids, and metal halides are able to form such compounds.

Lamellar compounds of graphite with alkali metals were first obtained in 1926. They have continued to attract the attention of research workers, since they have much in common both with "solid solutions" and with the complexes formed by alkali metals with aromatic hydrocarbons. The unusual structure of lamellar compounds of graphite with alkali metals confers on them several interesting properties. Thus those with potassium, rubidium, and caesium are superconductors, react with hydrogen and nitrogen, catalyse the *ortho–para* conversion of hydrogen, and catalyse the isomerisation and the polymerisation of alkenes. We have surveyed methods for the preparation of lamellar compounds of graphite with alkali metals, their structure, and their thermodynamic, physical, and chemical properties.

II. PREPARATION OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

Until recently the only method for preparing lamellar compounds of graphite with alkali metals was to heat a mixture of graphite and the alkali metal in a sealed ampoule. In this way Fredenhagen and his coworkers [1] first obtained compounds of graphite with potassium, rubidium, and caesium, having the compositions C_8M and $C_{16}M$ at 300° and 360–400°C respectively. They also investigated [2] the ability of potassium to be incorporated into graphite as a function of the pressure of its vapour. With graphite at a constant temperature (400° or 450°C) they varied the temperature of the potassium melt from 200° to 400–440°C, and obtained the compounds C_9K and $C_{18}K$. Table 1 shows that the former compound can be obtained with the graphite both at 400° and at 450°C, but this rise in temperature must be accompanied by an increase in the vapour pressure of potassium (i.e. the temperature of the melt).

Table 1. Dependence of composition of lamellar compounds with potassium on reaction conditions.

Temp. of graphite, °C	Temp. of potassium, °C	V.p. of K, mmHg	Composition of cpd.	Refs.
400	320	0.51	C_9K	2
	293	0.20	$C_{18}K$	
450	340	0.91	C_9K	2
	324	0.51	C_8K	
250–310	250	0.06	C_8K	3, 4, 5
390–425	250	0.06	$C_{24}K$	3, 4, 5
490	250	0.06	$C_{40}K$	3, 4, 5

Hérold [3–5] unlike Fredenhagen, investigated the reaction between potassium and graphite with the former at a constant temperature (250°C) while the temperature of the graphite was varied from 250° to 600°C. The isobar for the graphite–potassium system (Fig. 1) contains three plateaux at atomic K/C ratios of 0.125, 0.042, and 0.025, corresponding to the three compounds C_8K, $C_{24}K$, and $C_{40}K$. Compounds containing lower proportions of potassium could not be obtained.

Rüdorff and Schulze [6] heated a mixture of the alkali metal with graphite in a vacuum in a sealed ampoule at 300–400°C, and obtained a large number of lamellar compounds of graphite with potassium and with rubidium— C_8K, $C_{17.7}K$, $C_{21.3}K$, $C_{26.2}K$, $C_{27.7}K$, $C_{28.4}K$, $C_{29.3}K$, $C_{30.4}K$, $C_{32.7}K$, $C_{35.9}K$, $C_{38.3}K$, $C_{40.2}K$, $C_{41.3}K$, $C_{43.9}K$, $C_{44.6}K$, $C_{45.6}K$, $C_{47.9}K$, $C_{52.5}K$, $C_{56.9}K$, C_8Rb, $C_{8.6}Rb$, $C_{16.0}Rb$, $C_{24.3}Rb$, $C_{25.0}Rb$, $C_{34.8}Rb$, $C_{37.4}Rb$, $C_{50.5}Rb$, $C_{16.2}Rb$.

Ottmers and Rose [7] modified this method by using a potassium–sodium alloy, which enabled the reaction temperature to be lowered and the compounds—C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$, and $C_{60}K$—to be obtained. Penetration of sodium into graphite was not observed.

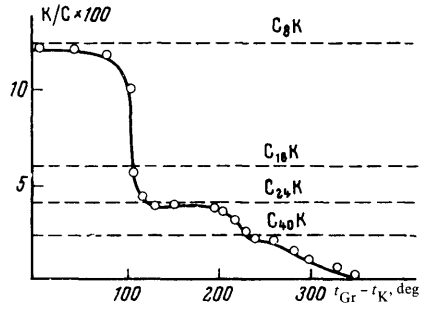


Figure 1. Dependence of composition of lamellar compounds on difference in temperature between graphite and potassium [3–5].

Salzano and Aronson [8,9] investigated the thermal decomposition of lamellar compounds of graphite with potassium, rubidium, and caesium having the composition C_8M, and discovered the existence of $C_{10}M$ between C_8M and $C_{24}M$. However, these compounds are stable only at high temperatures: $C_{10}K$ is stable at 315°C, $C_{10}Rb$ at 293°C, and $C_{10}Cs$ at 324°C.

For a long time it proved impossible [1,2,6] to obtain lamellar compounds by the direct reaction of graphite with lithium and sodium vapours. McDonnell et al. [10] and also Hennig [11] considered the formation of such compounds to be impossible, as the reduction potentials of these metals are lower than that of potassium. This view was regarded as supported by Hérold's observations [5] that a lamellar compound containing both sodium and caesium (ratio Na : Cs = 0.12) is formed by the action of an alloy on graphite, since the reduction potential of the alloy is higher than that of metallic sodium. An alloy of potassium and sodium does not produce the corresponding lamellar compound.

However, Asher and Wilson [12] showed that heating a mixture of graphite with molten sodium in an atmosphere of helium yields the same lamellar compound $C_{64-68}Na$, whose composition is independent of the temperature (120–500°C) or the duration of the reaction (from 15 min to 6 h).

Dzurus et al. [13] were unable to reproduce Asher and Wilson's results [12], and cast doubt on the existence of a lamellar sodium compound. However, Recht et al. [14] investigated the ability of graphite to absorb sodium vapour, confirmed the earlier results [12], and showed that $C_{64}Na$ is formed at 450°C after 7 days. Recht demonstrated also that the low degree of penetration of sodium is mainly kinetic in origin, since a fall in temperature leads to an increase in the equilibrium content of sodium in graphite, but considerably decreases the reaction velocity, so that below 400°C equilibrium is established with extreme difficulty.

A lamellar compound having the same composition ($C_{64}Na$) was obtained by Sleppy [15] by electrolysing molten sodium nitrate with a graphite cathode in an atmosphere of argon at 400°C. Like Hennig [13] this worker considers that the reaction is catalysed by oxygen chemisorbed on the graphite. In a study of the dependence of the diamagnetism of the compounds on the quantity of sodium incorporated Sleppy discovered a compound containing 1.95% of sodium, which corresponds to the formula $C_{96}Na$.

A small quantity of lithium was introduced into graphite [5] by electrolysing an equimolecular melt of potassium and lithium chlorides with a graphite cathode at 400°C. However, a greater amount was introduced [5] by heating lithium with graphite in a high vacuum at 500°C. Thus heating for several hours yielded a product of which the formula C_4Li was assigned. It was contaminated with lithium carbide, and increasing the duration of the reaction to 5 days resulted in complete conversion of the lithium into the carbide.

In 1965 Juza and Wehle [16] investigated the reaction between graphite and lithium vapour, and established that, depending on the conditions, lamellar compounds—C_6Li, $C_{12}Li$, and $C_{18}Li$—were formed, contaminated with lithium carbide and other lamellar graphite–lithium compounds. Bagouin et al. [17] have repeated these results, and also obtained two new compounds—$C_{36}Li$ and $C_{72}Li$.

Thus lamellar compounds of graphite with all the alkali metals can be obtained by direct reaction between the components. With potassium, rubidium, and caesium a whole set of compounds from C_8M to $C_{60}M$ have been prepared. With lithium the series begins at C_4Li and ends at $C_{72}Li$. The sodium series begins at $C_{64}Na$, probably because the conditions have not been found for preparing lamellar compounds with a high sodium content.

Table 2. Redox potentials of various aromatic hydrocarbons relative to biphenyl.

Hydrocarbon	E, V	Hydrocarbon	E, V
Biphenyl	0	Dibenz[a,h]anthracene	0.69
Naphthalene	0.09	Coronene	0.70
Phenanthrene	0.17	Perylene	1.12
Chrysene	0.38	Tetracene	1.28
Pyrene	0.60		

However, a fundamentally different method is possible for obtaining lamellar compounds of graphite with alkali metals, which utilises the aromatic character of the carbon layers in graphite. It is well known that aromatic hydrocarbons (naphthalene, anthracene, coronene, etc.) react with alkali metals in strongly ionising solvents—ammonia, amines, dimethoxyethane, hexamethylphosphoramide, etc.—to form aromatic radical-anions [18,19]. The position of equilibrium and the rate of reaction are substantially dependent on the redox potentials of the aromatic hydrocarbons under otherwise similar conditions. Paul et al. [20] and also Haijitink et al. [21] determined the redox potentials of aromatic hydrocarbons, and arranged the latter according to their electron affinity. Table 2 gives the latter workers' results [21], E being the reduction potential corresponding to formation of a monoanion.

Table 2 shows that the electron affinity increases with the number of fused aromatic rings in the hydrocarbon molecule. Therefore graphite—a compound with an infinite number of aromatic rings in a plane—should have

the highest reduction potential of all fused aromatic hydrocarbons. In such case two new methods become available for preparing lamellar compounds of graphite with alkali metals—by the reaction of graphite with solutions of (1) alkali metals and (2) aromatic radical-anions (of biphenyl, naphthalene, benzophenone, etc.).

Rüdoff et al.[22-24] showed that lamellar compounds could be prepared by the action of solutions of alkali metals on graphite. They examined the reaction of graphite with solutions of lithium, sodium, potassium, rubidium, and caesium in ammonia, methylamine, and pyridine, and found that ~2 moles of solvent per 1 g-atom of alkali metal were both incorporated into the graphite between −100° and −50°C. By using various quantities of alkali metals these workers obtained the following large number of lamellar compounds

$C_{10.6}Li(NH_3)_{1.5}$	$C_{12.5}K(NH_3)_{2.1}$	$C_{13.4}Na(NH_3)_{2.0}$
$C_{13.6}Li(NH_3)_{2.2}$	$C_{12.3}K(NH_3)_{2.3}$	$C_{16.5}Na(NH_3)_{2.2}$
$C_{15.6}Li(NH_3)_{2.0}$	$C_{23.4}K(NH_3)_{2.3}$	$C_{20.5}Na(NH_3)_{2.2}$
$C_{28.8}Li(NH_3)_{1.7}$	$C_{11.4}K(CH_3H_2)_{1.0}$	$C_{26.9}Na(NH_3)_{2.3}$
$C_{12.1}Li(CH_3NH_2)_{1.9}$	$C_{12.2}K(Py)_{1.0}$	$C_{11.9}Rb(NH_3)_{2.0}$
$C_{28}Li(H_2NCH_2CH_2NH_2)_{1.0}$	$C_{20.9}K(Py)_{0.84}$	$C_{13.8}Rb(NH_3)_{2.1}$
		$C_{12.8}Cs(NH_3)_{2.2}$

Rüdoff also found[24] that treating the potassium, rubidium, and caesium lamellar compounds with liquid ammonia resulted in the formation of ternary graphite–alkali-metal–ammonia lamellar compounds. It is interesting that part of the potassium in the compound C_8K passes into solution, and a lamellar compound $C_{12.5}K(NH_3)_2$ is formed. When, however, the compound $C_{24}K$ is treated with liquid ammonia, hardly any potassium is removed from the graphite, and the C : K ratio remains at ~28: i.e. the product has the formula $C_{28}K(NH_3)_{2.8}$. The quantity of a solvent S which is incorporated depends on its molecular size. Thus in the potassium lamellar compounds with ammonia the ratio K : S = 1 : 2; but with methylamine and with pyridine the corresponding ratio is 1 : 1.

Ginderow and Setton[25] used solutions of lithium and sodium in hexamethylphosphoramide to obtain lamellar compounds. The blue solutions of these metals react with graphite within a few seconds to form $C_{32}Li(S)$ and $C_{27}Na(S)$. Attempts to obtain lamellar compounds of potassium, calcium, magnesium, and ytterbium by this method were unsuccessful[25]. Only potassium among these four metals is slightly soluble in hexamethylphosphoramide, but the solution is unstable, and the results are difficult to reproduce. Stabilising the solution by the addition of benzene[26] results in the formation of an intense red solution, from which metal is not absorbed by graphite.

On the basis of the above principles Stein et al.[27-31] showed experimentally that lamellar alkali-metal compounds could be prepared by exchange between graphite and aromatic radical-anions. They found[31] that treating graphite with a 0.114–1.0 *N* solution of the alkali-metal–naphthalene compound in oxolan yields lamellar compounds whose composition, determined by decomposing them with acid, depends on the specimen of graphite used (Table 3).

Later investigations[27-29] indicated the following relations.

1. The equilibrium quantity of alkali metal incorporated into graphite is independent of the nature of the radical-anion (naphthalene, biphenyl, phenanthrene). However, the rate of establishment of equilibrium is sensitive to the radical-anion employed. For example, the equilibrium $ArH^{\cdot-}Li^{+}$ + graphite ⇌ ArH + graphite-Li^{+} is established more rapidly when ArH represents biphenyl than with naphthalene[28]. These results were regarded as consistent with the effect of the electrochemical potential, since the reduction potential of naphthalene relative to biphenyl is +0.9 V.

Table 3. Composition of intrusion products of alkali metals in different varieties of graphite resulting from the action of a solution of naphthalene and the alkali metal in oxolan.

Madagascar (flaky)	Ceylonese (finely ground)
$C_{41.5\pm1.5}Li$	$C_{17.5\pm1.5}Li$
$C_{120\pm4}Na$	$C_{30.5\pm1.5}Na$
$C_{81\pm2}K$	$C_{24.5\pm1}K$

2. The rate of penetration of metal into graphite varies with time during the reaction. Thus 80% of the maximum possible quantity of potassium penetrates into graphite during the first 5 h of the reaction of a potassium–naphthalene solution; the remaining 20% required 35–45 h.

3. The quantity of metal incorporated depends on the sample of graphite, far more penetrating powdered Ceylon graphite than the flaky Madagascar variety.

Table 4. Comparison of methods of analysis of products of the intrusion of an alkali metal into graphite (composition of lamellar compound from analytical data).

Metal	Ceylon graphite—analysis of		Madagascar graphite—analysis of	
	solution	compound	solution	compound
Li	$LiC_{17.6\pm1.0}$	$LiC_{17.5\pm1.5}$	$LiC_{18.8\pm1.0}$	$LiC_{43\pm3}$
Na	$NaC_{30.5\pm0.5}$	$NaC_{30.5\pm0.5}$	$NaC_{50.5\pm1.5}$	$NaC_{121\pm5}$
K		$KC_{24.5\pm1.0}$	$KC_{25.2\pm1.0}$	$KC_{32\pm2}$

4. Neither oxolan nor naphthalene is introduced with the alkali metal into the graphite. This was established by chromatography of the products of extraction at room temperature.

However, other workers have since shown conclusions 3 and 4 above to be incorrect. Thus Nominé and Bonnetain[32] have demonstrated that the different contents of alkali metal in Ceylon and Madagascar graphites are due not to differences in the structure of these specimens but to an incorrect choice of method for analysing the lamellar compounds. Since the particle size of Madagascar graphite considerably exceeds that of Ceylon graphite, the alkali metal separates completely from the latter on hydrolysis, but only partly from the Madagascar specimen. Hence the composition determined was that of the remaining solution of radical-anion, not the lamellar compound formed. Comparative data are given in Table 4.

Nominé and Bonnetain[33] also showed that the thermal decomposition products of the lamellar compounds are not binary (graphite and alkali metal) but contain also the quantities of oxolan indicated in Table 5. They found that the lamellar compound of graphite with lithium contains three phases—φ_1(Li), φ_2(Li), and φ_3(Li)—differing in the degree of solvation of lithium and in the structure of the solvate sheath of the Li^+ ion. Two phases—φ_1(Na) and φ_2(Na)—were found with sodium. It is interesting that at ~100°C the phases φ_2(Li), φ_3(Li), and φ_2(Na) pass into φ_1(Li) and φ_1(Na) with separation of part of the oxolan.

Table 5. Ratios of carbon to metal and of oxolan to metal in graphite–alkali-metal–oxolan lamellar compounds.

Metal	C/M	Ox/M
K	24±0.5	1.3±0.2
Na	32±1.5	3.5±0.3
Li	20±2.0	2.2±0.2

The graphite–potassium compound exists as a single phase. After standing at room temperature for a long time, this compound loses its oxolan completely, and passes into the binary compound $C_{24}K$. Rose et al.[34] confirmed the presence of oxolan in the compound. They also showed that lamellar compounds of graphite with alkali metals contain also small quantities of naphthalene, 1,2-dihydronaphthalene, and tetrahydronaphthalene.

Table 6. Content of oxolan (molar ratio Ox/M) in compounds formed by different varieties of graphite with alkali metals.

M	Ceylon	Madagascar
Li	0.115	0.122
Na	0.133	0.04
K	0.09	0.5

Thermogravimetric examination[34] of the specimens in a vacuum showed that only part of the oxolan is lost at 20°C and 0.001 mmHg (Table 6). With gradual rise in temperature two inflections appear on the thermogravimetric curve, which supports Bonnetain's suggestion[33] that several phases, differing in degree of solvation, exist in a single compound.

Ketyls, as well as aromatic radical-anions, are able to function as carriers of the alkali metal to the graphite. Genderow and Setton[35] established that sodium and potassium benzophenone ketyls react with graphite (particle size < 50 μm) in oxolan (Ox) solution to form the ternary lamellar compounds $C_{64}Na.Ox$ and $C_{72}K.Ox$ respectively.

Thus the reactions of graphite with solutions of alkali metals and with radical-anions show an analogy between the properties of graphite and those of aromatic hydrocarbons: (1) like aromatic hydrocarbons[36] graphite forms complexes with alkali metals (mainly with potassium) in the absence of a solvent; (2) in the presence of solvents graphite, like aromatic hydrocarbons[37], forms complexes with lithium and sodium; and (3) since the redox potential of graphite would be higher than those of aromatic hydrocarbons, graphite undergoes exchange reactions with the latter

$$ArH\dot{-}M^+ + Ar'H \rightleftarrows ArH + Ar'H\dot{-}M^+$$

to form lamellar compounds.

III. THERMODYNAMIC PROPERTIES OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

Many studies have been made of the thermodynamic properties of the alkali-metal compounds of graphite[2,5,8–10,38–52].

Table 7 gives the calorimetrically determined heats of formation of lamellar compounds C_8M with potassium, rubidium, and caesium and of $C_{24}K$ from graphite and the molten metal. The stability of the C_8M compounds is seen to increase from potassium to rubidium. The heat of reaction is substantially dependent on the type of graphite, the value for the artificial material exceeding by 10 kcal g^{-1} that for natural graphite in the reaction with potassium.

Table 7. Heats of reaction of graphite with alkali metals in the range 66–95°C.

Reaction (solid)	(liq.)	(solid)	kcal g-atom^{-1} M	Ref.
8C	+K	$\rightarrow C_8K$	7.8	38
			8.35	39
			8.35	48
			6.60	52
8C	+Rb	$\rightarrow C_8Rb$	11.1	39
			11.1	48
8C	+Cs	$\rightarrow C_8Cs$	15.3	39
			15.3	48
24C	+K	$\rightarrow C_{24}K$	11.9	52

From the vapour pressure of the metal over the potassium, rubidium, and caesium lamellar compounds Hérold[5] determined the heats of formation of C_8M from $C_{24}M$ [$C_{24}K + 2K(liq.) \rightarrow 3_8K + 2Q$] in the temperature range 417–669°C as respectively 3.4, 5.85, and 10.1 kcal g-atom^{-1} M, where M = K, Rb, Cs. Later, however, Salzano and Aronson[9,40–42] cast doubt on the reliability of these values, since Hérold had been unaware of the existence of the compound $C_{10}M$ between C_8M and $C_{24}M$. Setton[45,50] calculated the work required to separate the carbon networks of graphite and the energy of bonding of 1 g-atom of potassium with carbon as respectively H_C = 2.25 kcal g-atom^{-1} C and H_K = −10.4 kcal g-atom^{-1} K at 420°K; the corresponding values calculated for 620°K were 1.73 and −6.85. The work necessary to separate the carbon networks to infinity has also been determined by several authors, and lies in the range 0.9–1.5 kcal g-atom^{-1} C.[42,53–56] From these data Setton calculated

the heats of formation of C_8K and $C_{24}K$ as respectively 6.87 and 13.3 kcal g-atom^{-1} K, which agreed with the results in Ref. 52 (see Table 7).

The thermodynamic properties of graphite–alkali-metal systems have been investigated in greatest detail by Salzano and Aronson[9,40-44]. They examined the variation in the rate of decomposition of the lamellar compounds C_8M (M = K, Rb, Cs) over the range 400–750°C, and showed that the curve contains a series of breaks corresponding to formation of the compounds $C_{10}M$, $C_{24}M$, $C_{36}M$, $C_{48}M$, and $C_{60}M$. The portions between the breaks were linear, and corresponded to the two-phase regions

(solid) (gas) (solid)

$$4\,C_{10}M + M \rightleftarrows 5\,C_8M$$
$$^5/_7\,C_{24}M + M \rightleftarrows {}^{12}/_7\,C_{10}M$$
$$2\,C_{36}M + M \rightleftarrows 3\,C_{24}M$$
$$3\,C_{48}M + M \rightleftarrows 4\,C_{36}M$$
$$4\,C_{60}M + M \rightleftarrows 5\,C_{48}M$$
$$5\,C_{72}M + M \rightleftarrows 6\,C_{60}M$$

Table 8. Thermodynamic properties of potassium, rubidium, and caesium compounds of graphite ($-\Delta H^\circ$ in kcal g-atom^{-1} M; $-\Delta S^\circ$ in cal deg^{-1} g-atom^{-1} M).

Stage	Equilibrium reaction (solid) (gas) (solid)	Graphite-K		Graphite-Rb		Graphite-Cs	
		$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
Ia	$C_{24}M + M \rightleftarrows C_8M$	27.4	25.7	—	—	—	—
Ib	$4C_{10}M + M \rightleftarrows 5C_8M$	38.0	44	33.9	42.2	43.8	43.4
II	$5/7C_{24}M + M \rightleftarrows 12/7C_{10}M$	24.0	24	25.3	19.2	29.6	19.6
III	$2C_{36}M + M \rightleftarrows 3C_{24}M$	27.7	20.6	27.2	17.0	32.7	18.7
IV	$3C_{48}M + M \rightleftarrows 4C_{36}M$	30.0	20.7	29.5	17.6	34.2	18.6
V	$4C_{60}M + M \rightleftarrows 5C_{48}M$	30.6	20.8	31.0	12.3	34.9	18.6
VI	$5C_{72}M + M \rightleftarrows 6C_{60}M$	—	—	31.8	18.1	35.8	18.8

Salzano and Aronson found that the decomposition curves for lamellar compounds of composition intermediate between C_8M and $C_{24}M$ or between $C_{24}M$ and $C_{36}M$ coincide with those for C_8M: i.e. breaks are observed on the curves at the same compositions, and the rates of decomposition of the intermediate compounds are equal to those of C_8M. This was regarded as indicating that the composition and the structure of any compound are independent of its method of preparation. Thus the decomposition of lamellar compounds with alkali metals is an equilibrium process, since the constancy of the rate of decomposition with time in each two-phase region can be explained by equilibrium between the phase undergoing decomposition and that which is formed. However, the form of the decomposition curve remained unchanged for lamellar compounds with alkali metals and in a vacuum (i.e. in the absence of the metal vapour). From this it was concluded that the rate of decomposition was determined by the rate of removal of metal adsorbed on the surface of the specimen:

$$\text{M (in sample)} \xrightleftharpoons{\text{rapid}} \text{M (on surface)} \xrightleftharpoons{\text{slow}} \text{M (in vapour)}$$

This enabled ΔH° and ΔS° to be calculated for the different stages of decomposition (Table 8). The heat and the entropy of formation of the alkali-metal compounds of graphite from the elements (ΔHform and ΔSform) are given in Table 9.

The heats of formation of C_8M (M = K, Rb, Cs) found by these workers agree with calorimetric values[9] when it is remembered that the heats of evaporation of these three alkali metals (in kcal g-atom^{-1} M) are respectively 20.2 (at 550°), 17.8 (800°), and 16.8 (800°C) (cf. Tables 7 and 9). Comparison of the enthalpy and the entropy of reaction between the gaseous metal and the alkali-metal–graphite compounds (Table 8) for potassium, rubidium, and caesium shows that compounds at the same stages are formed in all three systems.

Table 9. Entropy and heat of formation of alkali-metal compounds of graphite from the elements ($-\Delta H$form in kcal g-atom^{-1} M; $-\Delta S$form in cal deg^{-1} g-atom^{-1} M).

Reaction (solid) (gas) (solid)	Graphite-K		Graphite-Rb		Graphite-Cs	
	$-\Delta H_{form}$	$-\Delta S_{form}$	$-\Delta H_{form}$	$-\Delta S_{form}$	$-\Delta H_{form}$	$-\Delta S_{form}$
$8C + M \rightarrow C_8M$	28.5	24.0	28.8	23.3	34.2	24.0
$10\,C + M \rightarrow C_{10}M$	27.0	22.5	27.5	18.5	32.2	19.2
$24C + M \rightarrow C_{24}M$	30.4	20.7	30.6	17.6	34.8	18.7
$36C + M \rightarrow C_{36}M$	31.7	20.7	32.2	18.0	35.8	18.7
$48C + M \rightarrow C_{48}M$	32.3	20.7	33.1	18.1	36.4	12.8
$60C + M \rightarrow C_{60}M$	32.8	20.8	33.6	18.1	36.7	18.8

The heat of reaction is largest for stage (Ib), is least for stage (II), and increases slightly on passing from stage (III) to stage (VI). The entropy of reaction is approximately the same for the lower stages, and has the approximate values 20.7, 17.8, and 18.7 kcal deg^{-1} g-atom^{-1} M for the potassium, rubidium, and caesium lamellar compounds. Nevertheless, the entropy is very high (42–44 kcal deg^{-1} g-atom^{-1} M) for stage (Ib) (Table 8). The large entropy changes for this stage are regarded by the authors as attributable both to the increase in concentration of alkali-metal ions in a layer and to a strengthening of interaction between adjacent layers of alkali-metal atoms.

IV. STRUCTURE OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

The X-ray method usually employed for studying lamellar compounds with alkali metals enables us to determine the stage reached in compound formation, i.e. to determine the number of carbon networks of graphite associated with one layer of the metal (Fig. 2), to calculate the identity period I_c along the c-axis, to determine the thickness I_c' of a filled layer, to determine the structure of a layer of alkali metal in the graphite, and also to ascertain whether the carbon layers undergo mutual displacement on the intrusion of alkali metal.

1. Structure of Binary Systems formed by Graphite with Potassium, Rubidium, and Caesium

Several investigations have been made on the structure of lamellar compounds of graphite[5-7,57-59]. Schleede and Wellmann[59] showed that the structure of the compounds C_8M (M = K, Rb, Cs) corresponds to stage (I): i.e. a

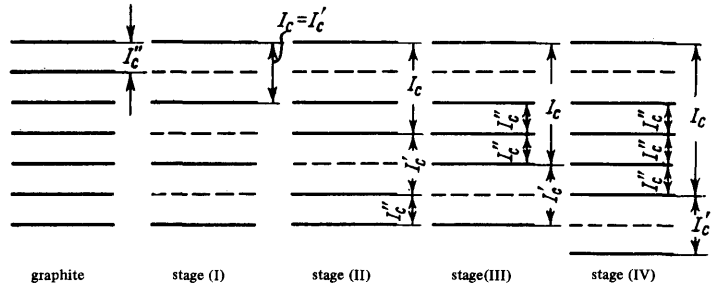


Figure 2. Arrangement of layers of graphite and of alkali metals in lamellar compounds: full line = carbon layer; broken line = intercalated metal layer; I_C'' = thickness of unfilled layer in lamellar compound; I_C = identity period in inclusion compounds; I_C' = thickness of filled layer in lamellar compound.

metal layer alternates with a graphite layer. The composition $C_{16}M$ represents the second stage of lamellar compounds. In both cases the metal atoms form a monatomic layer midway between adjacent carbon layers of the graphite. In an actual layer the metal atoms form a triangular network, the distance between them being 4.90 Å (Fig. 3). It was assumed that the carbon networks underwent no relative displacement on penetration of the alkali metal, and the identity period I_C for these compounds was determined from reflections of the type $00l$ (Table 10). If the thickness of a filled layer (Fig. 3) is assumed to be the same in compounds of both stages (I) and (II), the interplanar distance in an unfilled graphite layer is the same as in the original graphite (Table 10).

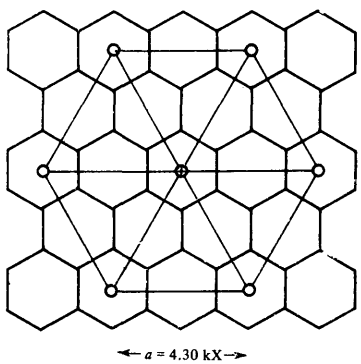


Figure 3. Triangular arrangement of potassium atoms relative to carbon network of graphite.

Subsequently Hérold [5] and especially Rüdorff and Schulze [6] made a more detailed investigation of the structure of the potassium and rubidium lamellar compounds, with the results indicated below.

1. The composition $C_{16}M$ represents a mixture of compounds of stages (I) and (II) (Table 11), the latter compound having the formula $C_{24}M$. Thus the lamellar compounds have the following compositions depending on the stages—C_8M (stage I), $C_{24}M$ (II), $C_{36}M$ (III), $C_{48}M$ (IV), and $C_{60}M$ (V).

Table 10. Identity period I_C, thickness of filled layers I_C', and thickness of unfilled layers I_C'' in lamellar compounds of graphite with potassium, rubidium, and caesium.

Metal	Colour	Stage	I_C, Å	I_C', Å	I_C'', Å
K	brown	I	5.33	5.33	3.41
	black	II	8.74	5.33	
Rb	brown	I	5.68	5.68	3.29
	black	II	8.97	5.68	
Cs	brown	I	5.94	5.94	3.31
	black	II	9.25	5.94	

Table 11. Composition and stages of compounds of graphite with potassium and rubidium.

Potassium compounds				Rubidium compounds	
composition	stage	composition	stage	composition	stage
C_8K	I	$C_{38,3}K$	III	$C_{8.2}Rb$	I
$C_{17.7}K$	II+I	$C_{40,2}K$	III+IV	$C_{8,8}Rb$	I
$C_{21.3}K$	II	$C_{41.3}K$	III+IV	$C_{16.0}Rb$	I+II
$C_{26.2}K$	II	$C_{43.9}K$	IV+III	$C_{24.3}Rb$	II
$C_{27.7}K$	II	$C_{44,6}K$	IV+III	$C_{26.6}Rb$	II
$C_{28.9}K$	II+III	$C_{45.6}K$	IV	$C_{34.8}Rb$	III
$C_{29.3}K$	II+III	$C_{47,9}K$	IV	$C_{37.4}Rb$	III
$C_{30.4}K$	II+III	$C_{52,5}K$	V+IV	$C_{50.5}Rb$	IV
$C_{32.7}K$	III+II	$C_{56.9}K$	V	$C_{61.2}Rb$	V
$C_{35.9}K$	III				

2. Determination of the identity periods for the lamellar compounds of stages (I)–(V) (Table 12) indicated that the thickness of a filled graphite layer is the same for all stages with a given metal, and depends only on the nature of the metal. These workers also confirmed that interplanar distances in an unfilled graphite layer were the same as in graphite itself (Table 12).

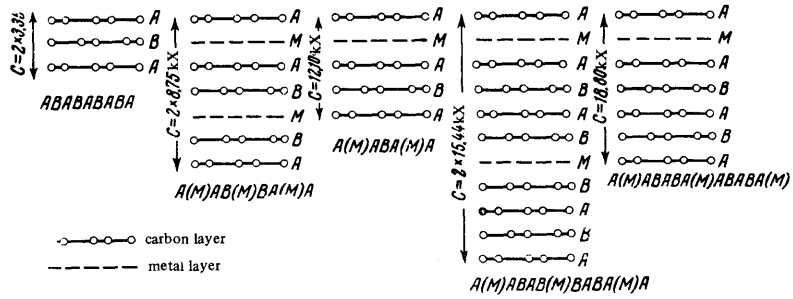


Figure 4. Relative positions of carbon networks and layers of alkali metal in lamellar compounds of graphite.

3. On passing from (I) to higher stages not only does the number of carbon networks per metal layer increase, but also the structure of the metal layer changes. Whereas the metal atoms in the compound C_8M are arranged in a triangular pattern (Fig. 3), on passing to stage (II) they are rearranged into a hexagonal network.

Table 12. Repeat periods of lamellar compounds of graphite with potassium found from 00*l* reflections.

Stage	Potassium cpd.	Rubidium cpd.
I	5.40=5.40	5.65=5.65
II	8.75=5.40+3.35	9.02=5.67+3.35
III	12.10=5.40+2·3.35	12.34=5.64+2·3.35
IV	15.46=5.41+3·3.35	15.75+5.70+3·3.35
V	18.80=5.40+4·3.35	19.08=5.68+4·3.35

This requires that the central atom (denoted by a "plus" in Fig. 3) should move out of the lattice. This could not be demonstrated by means of X-rays, since the lines *h*0*l* and *hkl* were absent from the Debye diagrams. Their absence was attributed to the great mobility of the metal atoms in the graphite planes.

4. On the formation of lamellar compounds with alkali metals the carbon networks adjacent to a metal layer shift and become superimposed (AA...BB). The remaining carbon networks are arranged as in graphite (ABAB...) (Fig. 4).

5. The identity period for the first stage should be quadrupled in comparison with that found from 00*l* reflections, since the 10*l* and 11*l* reflections have established that the alkali-metal layers are displaced relative to one another by $\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}$, and $0\frac{1}{2}$. For stages (II) and (IV) the identity period I_C calculated from 00*l* reflections should be doubled, as is indicated by the value of I_C calculated from 10*l* reflections. For stages (III) and (V) the same value of I_C is obtained by calculation from 00*l* and from 10*l* reflections.

6. Metal atoms are located below the centres of the carbon hexagons in the graphite network, and the distance between the metal atom and a carbon atom is 3.05 and 3.16 Å in the compounds C_8K and C_8Rb respectively.

More recent investigations by Nixon and Parry[57] have shown that the carbon networks adjacent to a potassium layer undergo a complete displacement: i.e. these carbon networks are equivalent. However, carbon networks remote from the potassium layer are only partly displaced. Thus some turbostrasis is observed in the arrangement of the carbon networks in lamellar compounds of graphite with potassium of stages (I)–(IV). These workers therefore suggest the arrangement

II stage — AB (K) BC (K) CA (K) A
III stage — ABA (K) ACA (K) A
IV stage — ABAB (K) BCBC (K) CACA (K) A

for the carbon networks in the potassium compounds of stages (II)–(IV).

The identity period I_C calculated by these workers for the potassium compound of stage (II) would cover three filled layers (each 5.4 Å) and three unfilled layers (each 3.3 Å), and should be 26.25 Å. In stage (III) it would contain two filled and four unfilled layers and be 24.2 Å in stage (IV) three filled and nine unfilled layers would make the identity period 46.35 Å. Good agreement was found between experimental and calculated values of the identity period.

2. Structure of Binary Compounds of Graphite with Sodium

In studying the structure of the lamellar compounds with sodium Asher and Wilson[12,60] found that graphite lines of the type 00*l* had disappeared from the Debye powder diagrams, while the graphite lines 10*l*, 112, 202, and 123 remained; i.e. the lattice parameter varied along the *c*-axis, but the structure of the carbon network of graphite remained unchanged. Indexing the X-ray diagram showed that a compound of stage (VIII) had been formed with an identity period I_C = 28 Å. On the assumption that the interplanar spacing in the unfilled graphite layer was the same (3.35 Å) as in graphite itself, the thickness of an unfilled layer was found to be I'_C = 4.5 Å (28 − 7 × 3.35). Carbon networks adjacent to sodium layers are arranged similarly (AA, BB), but the others alternate as in graphite (ABAB...). The sodium atoms in a layer are arranged in a triangular pattern, like the potassium atoms in C_8K.[6] It is not clear why the sodium atoms are most densely packed (C_8Na) in the stage (VIII) compound, whereas the packing is less compact ($C_{12}M$) in the graphite compounds of potassium, rubidium, and caesium beginning with stage (II); and in the lithium compound, beginning from stage (IV), one metal atom in a layer is associated with twelve carbon atoms from each graphite network adjacent to the lithium layer, although the atomic radius of lithium is smaller than that of sodium.

3. Structure of Binary Compounds of Graphite with Lithium

Juza and Wehle [16] found that the compounds C_6Li, $C_{12}Li$, and C_8Li all have a hexagonal crystal lattice. Table 13 gives the parameters along the a- and c-axes (I_a and I_c) together with the thickness of a filled layer (I'_c). These workers found [16] that the carbon layers are arranged in the same sequence (ABAB...) as in graphite. The carbon–carbon distance in a layer is somewhat greater than in graphite.

Table 13. Structure of lamellar compounds of graphite with lithium.

Compound	I_a, Å	I_c, Å	Stage	I'_c, Å
C_6Li	4.29_0	3.73_7	I	3.73_7
$C_{12}Li$	4.29_0	7.02_9	II	3.67_9
$C_{18}Li$	4.2_8	10.4_4	III	3.7_4

Bagouin et al. [17] have since established that the compounds— C_6Li, $C_{18}Li$, $C_{36}Li$, and $C_{72}Li$—also have a hexagonal lattice. Table 14 gives the parameters I_a and I_c together with I'_c. These authors attribute the composition $C_{18}Li$ to a compound of stage (II), and consider that the transition from stage (I) to stage (II) is accompanied by an increase in the number of carbon layers per metal layer and a decrease in the lithium content of a layer, as in the potassium compound [6]. The carbon–carbon distance in a layer is the same as in graphite.

Table 14. Structure of lamellar compounds of graphite with lithium.

Compound	I_a, Å	I_c, Å	Stage	I'_c, Å
C_6Li	4.28	3.70	I	3.70
$C_{18}Li$	7.40	7.05	II	3.70
$C_{36}Li$	—	13.75	IV	3.70
$C_{72}Li$	—	27.05	VIII	3.65

4. Structure of Graphite–Metal–Solvent Ternary Compounds

The structure of lamellar compounds of graphite with alkali metals and ammonia or amines was investigated by Rüdorff et al. [22-24], who determined the identity periods (Table 15) and established the following generalisations.

1. Intrusion of a solution of a metal into the graphite lattice yields inclusion compounds analogous in structure to those formed in the absence of a solvent (stages I, II, etc.), with the ammonia or amine molecules situated in the same layer as the metal atoms.

2. The carbon networks adjacent to a metal layer are arranged similarly, but the other networks alternate, as in the original graphite. Hence the identity period must be doubled for even stages.

3. The thickness of a filled layer in a graphite–alkali-metal–ammonia compound is 6.6 Å, and is independent of the nature of the metal (lithium, sodium, potassium, or rubidium) or the stage of the compound (I or II). It is considerably larger than the thickness of a filled layer in an alkali-metal compound containing no solvent (cf. Tables 12–14): i.e. the size of the metal atom does not affect the interplanar spacing, which is determined by the size of the solvated ion. The increase in molecular size of the solvent on passing from ammonia to methylamine and to ethylenediamine leads to an increase in thickness of the filled layer to 6.9 and 8.5 Å respectively.

Table 15. Composition and identity period I_c of alkali-metal compounds of graphite containing ammonia and amines (py = pyridine; en = ethylenediamine).

Stage I		Stage (II)	
composition	I_c, Å	composition	I_c, Å
$C_{10.6}Li(NH_3)_{1.6}$	6.6_2	$C_{28.8}Li(NH_3)_{1.7}$	9.9_3
$C_{13.4}Na(NH_3)_{2.0}$	6.6_3	$C_{26.7}Na(NH_3)_{2.3}$	9.9_7
$C_{12.5}K(NH_3)_{2.1}$	6.5_6	$C_{28.7}K(NH_3)_{2.8}$	9.9_4
$C_{11.9}Rb(NH_3)_{2.0}$	6.5_8		
$C_{12.0}Cs(NH_3)_{2.2}$	6.5_8		
$C_{12.1}Li(CH_3NH_2)_{1.9}$	6.9		
$C_{11.4}K(CH_3NH_2)_{1.0}$	6.8		
		$C_{28}Li(en)_{1.0}$	11.85=8.5+3.35
$C_{12.2}K$ (py) $_{1.0}$		$C_{20.9}K(py)_{0.84}$	

4. In the ternary graphite compounds of stage (I) one alkali-metal atom is associated with twelve carbon atoms, as in the binary lamellar compounds of stages (II)–(V). This is due to the presence of solvent molecules between alkali-metal atoms in the layer.

5. The metal atoms in the lattice are solvated, the number of solvent molecules per alkali-metal atom decreasing with increase in size of the solvent molecule (Table 15).

These conclusions have been confirmed by Ginderow and Setton's investigation [25] of the structure of the lithium and sodium compounds containing hexamethylphosphoramide $C_{32}Li.HMP$ and $C_{27}Na.HMP$. These compounds were found to be of stage (I), with the parameters

$C_{32}Li \cdot HMP$: $I_a = 19.68$ Å; $I_c = 30.48$ Å
$C_{27}Na \cdot HMP$: $I_a = 12.73$ Å; $I_c = 15.24$ Å

The alternation of carbon networks in the compound is AAA..., not ABAB... as in graphite itself. One metal atom is solvated by one solvent molecule, with the P=O bond perpendicular to the carbon lamellae. As a consequence, the thickness of a filled layer is the same in the two compounds: $I'_c = 7.62$ Å, considerably greater than for the binary compounds (4.5 and 3.7 Å) and for compounds of graphite with the alkali metals and ammonia ($I_c = 6.6$ Å). The layers of solvated atoms are displaced relative to one another. Therefore the identity period for this compound must be quadrupled: $I_c = 4 \times 7.62 = 30.48$ Å.

5. Structure of Compounds of Graphite with Alkali Metals and Oxolan

The structure of interstitial products of graphite with a metal and oxolan was investigated by Stein et al. [27-29] (cf. also Ref. 38) by means of X-rays. However, they were

unable to index the powder diagrams obtained or to determine the identity periods. From the diagrams these workers established that the products were indeed lamellar compounds, since the most characteristic lines of graphite 002 and 004 were absent (indicating a change in the identity period along the c-axis, i.e. penetration of the alkali metal between the carbon networks), while the "graphite" lines 100, 110, and 112 were present (indicating the unchanged structure of the carbon networks).

Nominé and Bonnetain [33,61] discovered that three phases were present in the lithium compound, two phases with sodium, and one phase with potassium, distinguished by their degrees of solvation. Table 16 gives the identity periods for these phases. Independently of the phase, all are stage (I) compounds. Consequently the differences in identity periods are due to differences in structure between the solvate sheaths of the alkali-metal ions. On the assumption that the thickness of a filled layer is the sum of the thicknesses of a graphite layer (3.35 Å) and a layer of solvated ions e_I, these workers calculated values of $e_I = I_c - 3.35$ (Table 16).

Table 16. Structural parameters of various phases in graphite–alkali-metal–oxolan compounds.

Phase	I_c, Å	e_I
φ_1(Li)	7.24	3.89
φ_2(Li)	12.45	9.10
φ_3(Li)	17.2	13.85
φ_1(Na)	7.24	3.89
φ_2(Na)	11.12	7.77
φ_1(K)	7.18	3.88

The use of models to study the structure of the solvated ions showed that, in the phases φ_1(Li), φ_1(Na), and φ_1(K), the oxolan molecules are oriented parallel to the plane of the graphite. Each alkali-metal layer is surrounded by three oxolan molecules. In the phases φ_2(Li) and φ_2(Na) a metal ion is surrounded by four oxolan molecules located at the vertices of a tetrahedron. With lithium the tetrahedron is regular, but in the case of sodium it is somewhat flattened between two graphite layers. In the phase φ_3(Li) the lithium ion is surrounded by oxolan molecules at the corners of an octahedron, a diagonal of which, like the planes of the oxolan molecules, is perpendicular to the graphite layers.

V. PHYSICAL PROPERTIES AND NATURE OF BONDING

1. Electrical Conductivity of Compounds of Graphite with Alkali Metals

The electrical conductivity of alkali-metal lamellar compounds has been investigated only on binary systems [7,10,62–69,74]. Since detailed discussions of the results will be found in reviews [70–72], we shall consider here only the main conclusions.

1. Incorporation of an alkali metal into graphite leads to an increase in the conductance of the latter, by factors of 10 and 200 along the a- and c-axes respectively.

2. Alkali-metal complexes of graphite exhibit a considerable positive temperature coefficient of the resistance.

3. Increase in the potassium content is accompanied by a continuous fall in resistance along the c-axis, whereas the resistance reaches a limit along the a-axis at compositions far removed from saturation [62].

It is interesting that similar generalisations apply to the solid alkali-metal compounds of aromatic hydrocarbons [73,74]. Thus the solid complexes of anthracene with lithium, sodium, and potassium have a considerable positive temperature coefficient of resistance. The graphite compounds C_8M (where M = K, Rb, Cs) are superconductors [63,75], their superconductivity appearing at 0.55°, 0.151°, and 0.135°K respectively. The compound $C_{24}K$ is not a superconductor, which was explained on the assumption that only every other interlayer space was occupied by potassium. However, Salzano and Strongin have since shown [63] that this may be due to a decrease in the potassium content of a layer on passing from C_8K to $C_{24}K$.

Table 17. Magnetic susceptibilities of graphite, potassium, and their lamellar compounds (χ_m calculated as 10^{-6} c.g.s. g-atom^{-1} C).

Material	90° K		195° K		288° K		Bulk density, g cm^{-3}
	χ_s	χ_m	χ_s	χ_m	χ_s	χ_m	
K	+0.540	+21.1	+0.538	+21.0	+0.539	+21.1	0.849
Graphite	−7.909	−94.81	−6.757	−81.08	−6.04	−72.48	0.783
$KC_{8.47}$	+1.01	+16.78	+1.01	+16.78	+1.00	+16.61	0.730
$KC_{7.79}$	+0.953	+16.23	+0.951	+16.17	+0.953	+16.23	0.713

2. Magnetic Susceptibility of Lamellar Compounds of Graphite with Alkali Metals

Measurements of the magnetic susceptibility of lamellar compounds of graphite with potassium [10,76–78] showed that intercalation of the metal had replaced the abnormally high diamagnetism of graphite by weak paramagnetism, which remained unchanged when the compound was treated with liquid ammonia. McDonnel et al. [10] found that the paramagnetism of these lamellar compounds exceeded the additive value calculated from the contributions of potassium and of graphite. However, the paramagnetism is independent of temperature, like the susceptibility of potassium (Table 17), and cannot be explained by the presence of isolated potassium atoms, whose susceptibility would be inversely proportional to the temperature. Rüdorff et al. [6,23,24] found that the susceptibility of lamellar compounds of graphite with potassium and with rubidium of stages (I)–(V) was strongly dependent on the field strength. Comparable values (Table 18) were obtained by extrapolating the results to H_∞. In contrast to previous papers, these workers showed that the paramagnetism of the compounds diminished with fall in temperature. No explanation was given for this fact. Measurement of the magnetic susceptibility of the sodium compound has shown [15] that the diamagnetism of graphite decreases with increase in the sodium content (Fig. 5), and completely disappears when 1.95% of sodium, corresponding to the composition $C_{96}Na$, has been incorporated.

The electron spin resonance spectra of compounds of graphite with lithium, sodium, and potassium [76] prepared from solutions of the metals in liquid ammonia showed

that the line width was unaffected by the presence of ammonia. Furthermore, the relaxation time was found to be of the same order as predicted by theory for metallic conductors. The metallic character of the bond in the compounds was confirmed also by the temperature dependence of the line width (Table 19).

Table 18. Magnetic susceptibility of lamellar potassium and rubidium compounds at 295°K.

Stage	Potassium compounds		Rubidium compounds	
	composition	$10^6\chi_{mol}$	composition	$10^6\chi_{mol}$
Graphite		−110		−110
I	$CK_{0.120}$	+10.0	$CRb_{0.119}$	+5.0
II	$CK_{0.037}$	+8.7	$CRb_{0.040}$	+5.1
III	$CK_{0.027}$	+8.5	$CRb_{0.028}$	+5.6
IV	$CK_{0.021}$	+5.7	$CRb_{0.019}$	+6.2
V	$CK_{0.015}$	+4.0	$CRb_{0.014}$	+3.7

Ginderow and Setton [25] examined the e.s.r. spectra of the lithium and sodium compounds with hexamethylphosphoramide (HMP), and detected a signal. With H = 280 Mc/s the g-factor and the line width were found to be

$C_{32}Li \cdot HMP$ $g = 2.0023$ $\Delta H = 0.470$ G
$C_{27}Na \cdot HMP$ $g = 2.0023$ $\Delta H = 0.436$ G

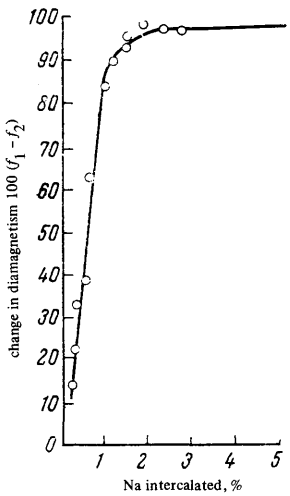


Figure 5. Dependence of diamagnetism of graphite on quantity of intercalated sodium.

The calculated spin densities of the lithium and sodium compounds were respectively 2.1×10^{22} and 7.0×10^{22} spins mole^{-1}. On the assumption that the spin density was due solely to unionised atoms, these workers calculated the percentage of unionised metal as respectively 4% and 15% for lithium and for sodium. They investigated also [35] the e.s.r. spectra of the inclusion products obtained by the action of a solution of sodium or potassium benzophenone ketyl on graphite (Table 20), and obtained rather different contents of unionised metal (9% with sodium, and 6% with potassium).

Table 19. Line widths in e.s.r. spectra of alkali-metal lamellar compounds.

Metal	ΔH_1 (300°K), mG	ΔH_2 (77°K), mG
Li (conc.)	100	70
Li (dil.)	86	60
Na	115	77
K[a]	350[b]	—
K	275	275

[a] Compound obtained in a vacuum; it contains no ammonia.
[b] Measured at 425 Mc/s.

However, Rose et al. [79] suggested that the signals in the e.s.r. spectra were due, not to compounds of graphite with alkali metals, but to complexes of the latter with aromatic hydrocarbons which had penetrated the graphite. They examined [79] the e.s.r. spectra of inclusion products obtained by the action of oxolan solutions of the lithium, sodium, and potassium derivatives of naphthalene, and found that the paramagnetism of all the compounds disappeared irreversibly when they were heated in a vacuum to 180–300°C. This was accompanied by separation of all the oxolan and a small quantity of naphthalene from the compound (Fig. 6). Values of the g-factor close to 2 were obtained for the different graphite compounds—2.0023, 2.0028, and 2.0023 for lithium, sodium, and potassium respectively—which are characteristic of the free radical-anion of naphthalene (g = 2.0026) (Table 21).

Table 20. Data on e.s.r. spectra of alkali-metal lamellar compounds obtained from benzophenone ketyls and graphite.

Property	Compound	
	$NaOxC_{64}$	$KOxC_{12}$
ΔH, G	~1.3	~2.5
g-factor	1.999	1.997
Spins g^{-1}	$6.21 \cdot 10^{19}$	$3.44 \cdot 10^{19}$
Spins mole^{-1}	$5.34 \cdot 10^{22}$	$3.41 \cdot 10^{22}$
Unionised metal, %	8.9	5.7

The graphite complexes are relatively insensitive to traces of water vapour. This is regarded [79] as indicating that the complex of naphthalene with the alkali metal is not simply adsorbed on the graphite but enclosed between its planes. The absence of hyperfine splitting in the spectra of these compounds is explained by the absence of free movement of the naphthalene molecules enclosed between the graphite planes.

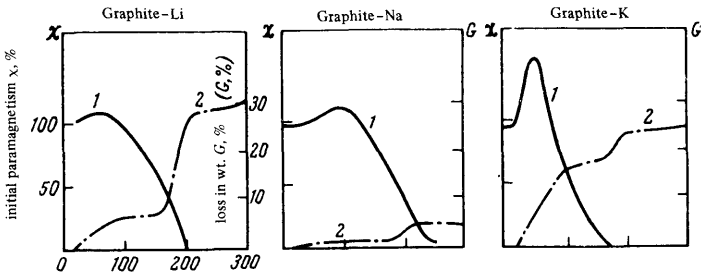


Figure 6. Dependence of paramagnetism of alkali-metal lamellar compounds on temperature of specimen: 1) paramagnetism; 2) loss in weight (oxolan, naphthalene).

3. Nature of Bond in Lamellar Compounds of Graphite with Alkali Metals

Salzano and Aronson have proposed a model [9,41-44], representing the type of bonding in lamellar compounds of graphite with potassium, rubidium, and caesium, in which the compounds comprise "metallic" carbon networks and layers of metal ions M^+. They suggest that a positive ion is formed by transfer of an electron from a metal atom to the conduction band of an adjacent graphite layer. Thus the metal atoms in the lamellar compounds are completely ionised, and the bond between the alkali metal and the carbon network is formed by electrostatic interaction of positive metal ions with free electrons in the conduction band of adjacent graphite layers, as in the bond between metal ions and aromatic radical-anions and dianions. This model is supported by the facts indicated below.

Table 21. Data on e.s.r. spectra of alkali-metal lamellar compounds prepared from radical-anions of naphthalene and graphite.

Parameter	Proportion of spins of various compounds		
	$C_{18}LiOx_{1.4}\cdot Naph_{0.020\pm0.010}$	$C_{50}NaOx_{0.6}\cdot Naph_{0.10\pm0.005}$	$C_{24}KOx_{1.6}\cdot Naph_{0.003}$
10^{-19} spins g^{-1}	2.1 2.5 2.5 —	— 0.9 0.4 —	0.2 0.4 0.6 1.6
10^{-19} spins g^{-1} based on naphthalene	3.7±1.8	0.9±0.4	0.4±0.25
g-factor	2.0029 2.0028	2.0027 2.0029	2.0021 2.0025

1. The lamellar compounds of graphite with alkali metals are more highly conducting than graphite itself [7,10], and those of composition C_8M are even superconducting [75].

2. The resistance of the compounds has a positive temperature coefficient [69-71]. A similar relation is observed with the solid alkali-metal compounds of aromatic hydrocarbons [72,73].

3. Investigation of the optical properties of the compounds has revealed [80] that electrons are transferred from the alkali metal to the carbon networks.

4. The Mössbauer spectra of the caesium compounds indicate [81] that the metal in them is completely ionised.

5. Calculations by Setton show [82] that the interplanar spacing in a filled layer is the sum of the radii of the metal ions M^+ and the van der Waals thickness of a carbon layer.

6. The thickness of a filled layer is the same for compounds of different stages.

This model enabled Salzano and Aronson [43,44] to explain the variation in the heat and entropy of decomposition of the lamellar compounds with potassium, rubidium, and caesium. According to Table 8 the formation of C_8M from $C_{10}M$ is accompanied by the largest heat effect, since work must be done, in all stages other than (Ib), to increase the separation between the carbon networks from 3.35 Å (in the original graphite) to 5.4–6.0 Å (in the alkali-metal compounds) so that metal is able to penetrate into the space between the planes. The formation of C_8M from $C_{10}M$ does not require the separation of graphite planes, since in $C_{10}M$ all the planes are already separated. The compound C_8M is formed by the incorporation of additional M atoms into each layer. Therefore the heat evolved in the formation of C_8M from $C_{10}M$ exceeds the heat of formation of other phases by the work required to move the carbon layers apart from 3.35 to 5.4–6.0 Å. The increased heats of formation of compounds from $C_{10}M$ to $C_{60}M$ was explained by these workers by a diminution in the repulsion between adjacent layers of metal ions, since they are separated by increasing numbers of carbon layers. On the basis of this model they used a Born–Haber cycle to calculate the energy of bonding of caesium with graphite in the lamellar compounds [42] as between −67 and −55 kcal g-atom^{-1} Cs, in agreement with the value found from thermodynamic data (55 kcal mole g-atom^{-1} Cs).

Calculation of the thermodynamic stability of the caesium compounds of various stages has shown [40] that the phases—$C_{24}M$ (stage II), $C_{36}M$ (III), $C_{48}M$ (IV), and $C_{60}M$ (V)—should be the most stable. For stage (I), however, the model predicts that the phases $C_{12}M$, $C_{16}M$, and $C_{20}M$ should be more stable by an order of magnitude than C_8M and $C_{10}M$. Thus the proposed model represents correctly the composition, the structure, and the nature of the bond in compounds from $C_{24}M$ to $C_{60}M$. Yet it is of little use for compounds C_8M and $C_{10}M$ (*a*) repulsion between adjacent layers of metal ions should be strongest for these compounds, since they are separated by only one carbon network, so that C_8M should have the smallest heat of formation, which is contrary to the experimental result; (*b*) this model does not predict the stability of these compounds C_8M and $C_{10}M$, although it has been shown experimentally that C_8M—not $C_{12}M$ or $C_{16}M$—is formed; and (*c*) heats of formation of C_8M and $C_{10}M$ from the elements, calculated on the basis of models, differ substantially from the experimental values [40].

Nevertheless, the suggested model provides a qualitative explanation of the fact that lamellar compounds are formed either with difficulty or not at all by the direct reaction of lithium and sodium vapours with graphite. According to the views of McDonnel et al.[10] the incorporation of an alkali metal into graphite can be represented by the scheme

$$K_{gas} \rightarrow K^+_{gas} + [\bar{e}];\ \Delta H_1 = +101{,}1$$
$$[\bar{e}] + [C]_{lamell} \rightarrow [C]^-_{lamell}$$
$$K^+_{gas} + [C]_{lamell} \rightarrow C_8K + \Delta H_2$$
$$K_{gas} + [C]_{lamell} \rightarrow C_8K + \Delta H;\quad \Delta H = \Delta H_2 + 101{,}1$$

The calculated value of ΔH_2 is -126 kcal g-atom^{-1} K. These authors assume that the energy evolved (ΔH_2) is necessary to balance the ionisation energy of potassium. In view of the ionisation potentials of the alkali metals, they consider that the energy evolved in the third stage is sufficient for the formation of compounds of graphite with potassium, rubidium, and caesium, and insufficient to form the compounds C_8Li and C_8Na. Since Salzano and Aronson's model is similar to that of the alkali-metal compounds of aromatic hydrocarbons, solvation may be supposed to be the additional energetic factor favouring the formation of lamellar compounds with lithium and sodium. Indeed, results obtained by Rüdorff[22-24] and also by Ginderow and Setton[25] show that lithium and sodium atoms, solvated by ammonia, amines, or hexamethylphosphoramide, penetrate graphite at $-50°$ and 20°C respectively, to form stage (I) compounds.

VI. CHEMICAL PROPERTIES

Little information has been published on the chemical properties of the alkali-metal lamellar compounds. Rüdorff[6] reported that hydrogen was evolved by the action of water on the potassium, rubidium, and caesium compounds. Hydrogen is evolved also by the action of water on the compounds of graphite with lithium[16,17], on the ternary compounds with an alkali metal and oxolan[27,31], and on the ternary compounds containing lithium, potassium, or sodium and ammonia[24]. It is interesting that hydrogen is evolved also when these graphite complexes are heated, amides of the alkali metals being formed[24]. In none of these cases was the quantity of hydrogen determined, although it may be expected (from the similarity between the alkali-metal lamellar compounds and aromatic radical-anions) that the graphite will be hydrogenated by the action of water.

Saehr and Hérold[83-85] have shown that the compound C_8K absorbs hydrogen slowly even at room temperature, the reaction being accelerated by heating. Products C_8KH_x are formed in which x varies with temperature to a limiting value of 0.67. The compounds of C_8Rb and C_8Cs are less active than C_8K: the maximum value of x in C_8RbH_x is 0.05, reached at 60°C; C_8Cs does not react with hydrogen between $-78°$ and $+150°$C. The compound $C_{24}K$ absorbs hydrogen to form $C_{24}KH_{0.25}$. Investigation of the structure of $C_8KH_{0.67}$ by the Debye–Scherrer method showed that the lines corresponding to C_8K had disappeared, while potassium hydride and graphite phases were not formed. The powder photographs contained distinct lines due to a new phase with identity periods I_c = 11.9 Å and I_a = 4.92 Å. The authors give no interpretation of this structure. The heat of sorption of hydrogen is found to be 8.1 kcal g-atom^{-1} K for the compound C_8K. Although C_8Cs does not absorb hydrogen[84], this compound catalyses the isotopic exchange of hydrogen with deuterium and the conversion of *ortho*-hydrogen into *para*-hydrogen[86].

According to Diebold and Hérold[87,88] gaseous chlorine and also the vapours of bromine and iodine react very vigorously with C_8K and C_8Cs to form the metal halides, the structure of the lamellar compound being completely destroyed. X-Ray examination shows that the product comprises a graphite phase and a metal-halide phase. Almost all the salt can be washed out with water. Thermogravimetric results show[89] that the salt in the graphite melts at the same temperature as the pure salt.

In 1969 it was reported[90] that oxygen and carbon monoxide react with C_8K to form a KO_2 or K_2CO_3 phase mixed with graphite. According to Sudo et al.[91] C_8K absorbs nitrogen at room temperature.

Jensen et al.[92] demonstrated the reducing properties of C_8K in its reaction with bis(trialkyl phosphite)nickel(II) dichlorides and excess of the trialkyl phosphite to form a zerovalent nickel complex—tetrakis(triethyl phosphite) nickel(0).

The alkali-metal lamellar compounds catalyse the polymerisation of alkenes[84,93-96], the isomerisation of alkenes[97], and also the alkylation by alkenes of benzene derivatives in the ring and in the side-chain[98]. With ethylene at 1000 atm on C_8K at 200°C the products are C_8–C_{14} *trans*-monoalkenes together with a small quantity of a solid polyethylene of low molecular weight[93]. Greater catalytic activity is found with C_8K than with pure potassium dispersed in its chloride or oxide. According to Hambling and Alderson[95] treatment of the compounds—C_8K, $C_{16}K$, $C_{24}K$, $C_{36}K$, $C_{48}K$, $C_{60}K$, and $C_{64}K$—with alkyl or aryl halides and halides of transition metals (titanium, zirconium, vanadium, chromium, molybdenum) modifies them in such a way that the products catalyse the polymerisation of ethylene, propene, and butene at 50–250°C with the formation of products of high molecular weight. The rate of polymerisation of styrene on C_8K and $C_{24}K$ is lower[94], but the molecular weight of the polymer is higher, than in the presence of pure, finely divided potassium.

Golé and Stein[96] have shown that $C_{32}K$ also catalyses the polymerisation of styrene in various solvents (oxolan, benzene, cyclohexane, hexane, carbon tetrachloride) at 25–30°C. In the polymerisation of dienes—butadiene and isoprene[94,96,99]—on C_8K, $C_{24}K$, and $C_{32}K$, the mode of addition is 1,2 and *trans*-1,4 with the former compound, and 1,2, *trans*-1,4, and 3,4 with isoprene. No *cis*-1,4-addition product is formed.

In 1958 Podal and Foster[98] discovered that C_8K catalyses not only the polymerisation of ethylene but also the alkylation of benzene and toluene in the ring and in the side chain. With ethylene at 700 atm and 110°C benzene yields 2-butylbenzene (35%), dialkylbenzenes, and higher monoalkylbenzenes. Ethylbenzene was not detected. These results are opposite to those obtained with organosodium compounds as catalysts[100]. Raising the temperature to 200°C leads to the formation of biphenyl (19%) together with s-butylbenzene (23%). The appearance of biphenyl was attributed to dimerisation of benzene radical-anions formed from benzene and the graphite–potassium complex. The reaction between toluene and ethylene yields triphenylpentane (at 120°C) or n-propylbenzene (55°C). t-Pentylbenzene is formed from isopropylbenzene (200°C).

Ottmers and Rase[97] studied the isomerisation of pent-1-ene into *cis*- and *trans*-pent-2-enes in the presence of

C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$, and $C_{60}K$ at temperatures between 75° and 235°C. They found that the reaction velocity and the *trans/cis* ratio increased with rise in temperature. At a given temperature the activity of the catalysts varied in the sequence—$C_{60}K > C_{48}K > C_{36}K > C_{24}K > C_8K$. The activity of the catalyst decreases during the reaction, and this decrease is more rapid the higher the temperature.

Comparison of the catalytic activity of these compounds with that of an industrial aluminosilicate catalyst [97] shows that the potassium complex of graphite is more active at low temperatures, and the aluminosilicate catalyst at high temperatures.

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