

8.3 Graphite Intercalation Compounds⁽⁷⁶⁾

The large interlayer distance between the parallel planes of C atoms in graphite implies that the interlayer bonding is relatively weak. This accounts for the ready cleavage along the basal plane and the remarkable softness of the crystals. It also enables a wide range of substances to intercalate between the planes under mild conditions to give lamellar compounds of variable composition. These reactions are often reversible (unlike those with O and F discussed above) and the graphitic nature of the host lattice is retained. The compounds have quite different structures and properties from those previously encountered in this book and so will be described in some detail. They may be compared with the materials formed by intercalation into certain sheet silicates (p. 349).

The first alkali-metal graphite compound was reported in 1926: bronze-coloured C_8K was formed by direct reaction of graphite with K vapour at 300°C . Rubidium and Cs behave similarly. When heated at $\sim 360^\circ$ under reduced pressure the metal is removed in stages to give a series of intercalation compounds C_8M (bronze-red), $C_{24}M$ (steel-blue), $C_{36}M$ (dark blue), $C_{48}M$ (black) and $C_{60}M$ (black). The compounds can also be prepared by electrolysis of fused melts with graphite electrodes, by reaction of graphite with solutions of M in liquid ammonia or amines, and by exchange reactions using M/aromatic radical anions. Intercalation is more difficult to achieve with Li and Na though direct reaction with highly purified graphite at 500° yields $C_6\text{Li}$ (brass coloured), $C_{12}\text{Li}$ (copper), and $C_{18}\text{Li}$ (steel), and reaction with Li/naphthalene in thf yields $C_{16}\text{Li}$ and $C_{40}\text{Li}$. Corresponding reaction of graphite and molten Na at 450° gives $C_{64}\text{Na}$ (deep violet) whereas Na/naphthalene gives $C_{32}\text{Na}$ and $C_{120}\text{Na}$.

The crystal structure of C_8K is shown in Fig. 8.15(a); the graphite layers remain intact but are stacked vertically above each other instead of in the sequence $\dots\text{ABAB}\dots$ found in α -graphite itself. Each graphite layer is interleaved by a layer of K atoms having a commensurate lattice in which the spacing between each K is twice the spacing between the centres of the graphite hexagons (Fig. 8.15(b)). The stoichiometries of the other stages can then be achieved by varying the frequency of occurrence of the intercalated M layers in the host lattice. An idealized representation of this model is shown in Fig. 8.16. Difficulties are encountered in devising a plausible mechanistic route to the formation of these compounds since the direct preparation of one stage from an adjacent stage apparently requires both the complete emptying and the complete filling of inserted layers. It may be that the situation is more complex, with distributions of stages rather than a single uniform arrangement for each stoichiometry. Very recently a new metal-rich phase has been prepared by reacting graphite with molten potassium; the composition is very close to C_4K and the structure comprises double planes of K atoms intercalated between each graphite sheet, with a consequent increase in the interplanar spacing to 850 pm.⁽⁷⁷⁾

The electrical resistance of graphite intercalation compounds is even lower than for graphite itself, resistance along the *a*-axis dropping by a factor of ~ 10 and that along the *c*-axis by ~ 100 ; moreover, in contrast to graphite, which is diamagnetic, the compounds have a temperature-independent (Pauli) paramagnetism and also behave as true metals in having a resistivity that increases with increase in temperature. This is illustrated by the comparative data shown in Table 8.2.

These data, and the other properties of C_nM , suggest that bonding occurs by transfer of electrons from the alkali metal atoms to the conduction band of the host graphite. Consistent with

⁷⁶ L. B. EBERT, *A. Rev. Materials Sci.* **6**, 181–211 (1976). A. HÉROLD, in F. LEVY (ed.), *Intercalated Layered Materials*, pp. 323–421, Reidel, 1979. H. SELIG and L. B. EBERT, *Adv. Inorg. Chem. Radiochem.* **23**, 281–327 (1980); a review with ~ 350 references.

⁷⁷ M. EL GADI, C. HÉROLD and P. LAGRANGE, *Compt. Rend. Acad. Sci. Paris* **316**, 763–9 (1993).

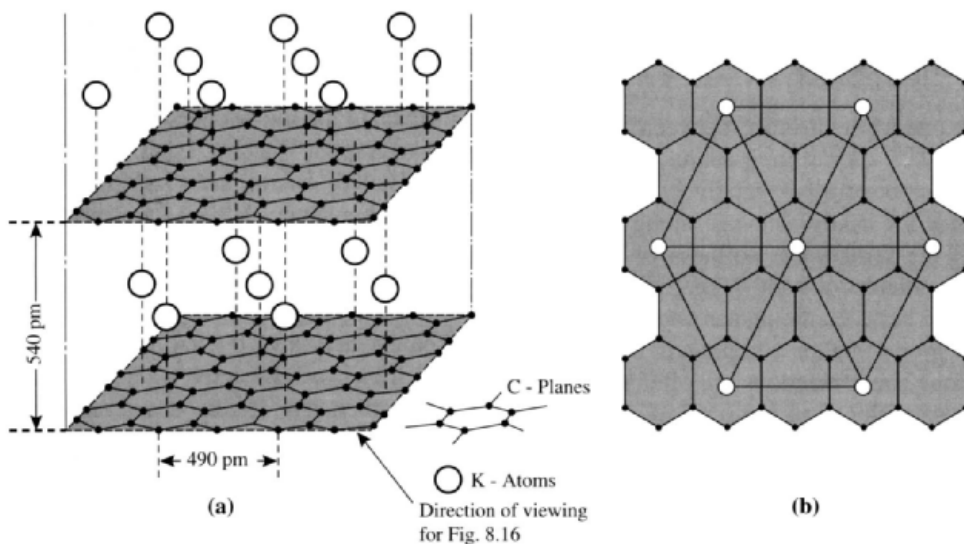


Figure 8.15 (a) Crystal lattice of C_8K showing the vertical packing of graphitic layers. The C-C distance within layers almost identical to that in graphite itself but the interplanar spacing (540 pm) is much larger than for graphite (335 pm) due to the presence of K atoms. The spacing increases still further to 561 pm for C_8Rb and to 595 pm for C_8Cs . (b) Triangular location of K atoms in C_8K showing the relation to the host graphite layers. In the other alkali-metal graphite compounds $C_{12n}M$ the central M atom is missing, leading to a stoichiometry of $C_{12}M$ if every alternate layer is M, $C_{24}M$ if each third layer is M, etc.

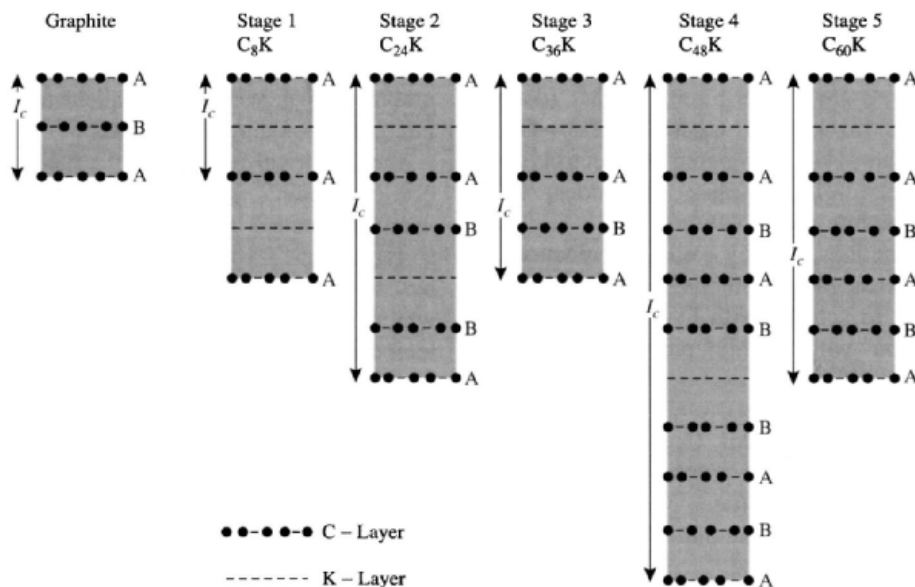


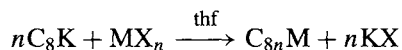
Figure 8.16 Layer-plane sequence along the c -axis for graphite in various stage 1-5 of alkali-metal graphite intercalation compounds. Comparison with Fig. 8.15 shows that the horizontal planes are being viewed diagonally across the figure. I_c is the interlayer repeat distance along the c -axis.

Table 8.2 Resistivity of graphite and its intercalates

Material	ρ (90 K)/ohm cm	ρ (285 K)/ohm cm	ρ_{90}/ρ_{285}
α -graphite	37.7	28.4	1.33
C ₈ K	0.768	1.02	0.75
C ₁₂ K	0.932	1.15	0.81

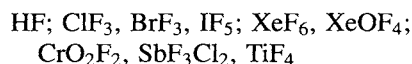
this, direct metal intercalation has only been observed with the most electropositive elements (Group 1) though Ba, with a first-stage ionization energy intermediate between those of Li and Na, was recently (1974) found to give C₆Ba.

Alkali-metal graphites are extremely reactive in air and may explode with water. In general, reactivity decreases with ease of ionization of M in the sequence Li > Na > K > Rb > Cs. Under controlled conditions H₂O or ROH produce only H₂, MOH and graphite, unlike the alkali-metal carbides M₂C₂ (p. 297) which produce hydrocarbons such as acetylene. In an important new reaction C₈K has been found to react smoothly with transition metal salts in tetrahydrofuran at room temperature to give the corresponding transition metal lamellar compounds:⁽⁷⁸⁾



Examples include reaction of Ti(OPrⁱ)₄, MnCl₂·4H₂O, FeCl₃, CoCl₂·6H₂O, CuCl₂·2H₂O, and ZnCl₂ to give C₃₂Ti, C₁₆Mn, C₂₄Fe, C₁₆Co, C₁₆Cu and C₁₆Zn, respectively.

A quite different sort of graphite intercalation compound is formed by the halides of many elements, particularly those halides which themselves have layer structures or weak intermolecular binding. The first such compound (1932) was with FeCl₃; chlorides, in general, have been the most studied, but fluoride and bromide intercalates are also known. Halides which have been reported to intercalate include the following:



MF₅ (M = As, Sb, Nb, Ta); UF₆
 MCl₂: M = Be; Mn, Co, Ni, Cu; Zn, Cd, Hg
 MCl₃: M = B, Al, Ga, In, Tl; Y; Sm, Eu,
 Gd, Tb, Dy; Cr, Fe, Co; Ru, Rh, Au; I
 MCl₄: M = Zr, Hf; Re, Ir; Pd, Pt
 MCl₅: M = Sb; Mo; U
 MCl₆: M = W, U; also CrO₂Cl₂, UO₂Cl₂
 Mixtures of AlCl₃ plus Br₂, I₂, ICl₃,
 FeCl₃, WCl₆
 Bromides: CuBr₂; AlBr₃, GaBr₃; AuBr₃

The intercalates are usually prepared by heating a mixture of the reactants though sometimes the presence of free Cl₂ is also necessary, particularly for "non-oxidizing" chlorides such as MnCl₂, NiCl₂, ZnCl₂, AlCl₃, etc. Many of the compounds appear to show various stages of intercalation, the first stage usually exhibiting a typical blue colour. A common feature of many of the intercalated halides is their ability to act as electron-pair acceptors (Lewis acids). Low heat of sublimation is a further characteristic of most of the intercalating compounds. It may be that an important feature is an ability of the guest molecule to form a layer lattice commensurate with the host graphite. For example, in C_{6,69}FeCl₃ the intercalated FeCl₃ has a layer structure similar to that in FeCl₃ itself with Cl in approximately close-packed arrangement though with some distortion, and with extensive stacking disorder. The "first-stage" compound varies in composition in the range C_{~6-7}FeCl₃; in addition a "second-stage" compound corresponding to C_{~12}FeCl₃ is known, and also a "third-stage" with composition in the range C_{~24-30}FeCl₃. Another well-characterized phase occurs with MoCl₅: layers of close-packed Mo₂Cl₁₀ molecules alternate with sets of 4 graphite layers along the *c*-axis.

There appears to be a small but definite transfer of electron charge from the graphite to the guest species and this has led to formulations such as C₇₀⁺Cl⁻.FeCl₂.5FeCl₃. Similarly, the intercalate of AlCl₃ (which is formed in the presence of free Cl₂) has been formulated as C₂₇⁺Cl⁻.3AlCl₃ or C₂₇⁺AlCl₄⁻.2AlCl₃. This would explain the enhanced conductivity of the graphite-metal

⁷⁸ D. BRAGA, A. RIPAMONTI, D. SAVOIA, C. TROMBINI and A. UMANI-RONCHI, *J. Chem. Soc., Dalton Trans.*, 2026-8 (1979).

8.4 Carbides

Carbon forms binary compounds with most elements: those with metals are considered in this section whilst those with H, the halogens, O, and the chalcogens are discussed in subsequent sections. Alkali metal fullerides and encapsulated (endohedral) metallafullerenes have already been considered (pp. 285, 288 respectively) and metallocarbohedrenes (metcars) will be dealt with later in this section (p. 300). Silicon carbide is discussed on p. 334. General methods of preparation of metal carbides are:⁽⁸³⁾

- (1) Direct combination of the elements above $\sim 2000^\circ\text{C}$.
- (2) Reaction of the metal oxide with carbon at high temperature.
- (3) Reaction of the heated metal with gaseous hydrocarbon.
- (4) Reaction of acetylene with electropositive metals in liquid ammonia.

Attempts to classify carbides according to structure or bond type meet the same difficulties as were encountered with hydrides (p. 64) and borides (p. 145) and for the same reasons. The general trends in properties of the three groups of compounds are, however, broadly similar, being most polar (ionic) for the electropositive metals, most covalent (molecular) for the electronegative non-metals and somewhat complex (interstitial) for the elements in the centre of the d block. There are also several elements with poorly characterized, unstable, or non-existent carbides, namely the later transition elements (Groups 11 and 12), the platinum metals, and the post transition-metal elements in Group 13.

Salt-like carbides containing individual C "anions" are sometimes called "methanides" since they yield predominantly CH_4 on hydrolysis. Be_2C and Al_4C_3 are the best-characterized examples, indicating the importance of small

compact cations. Be_2C is prepared from BeO and C at $1900\text{--}2000^\circ\text{C}$; it is brick-red, has the antifluorite structure (p. 118), and decomposes to graphite when heated above 2100° . *Ab initio* calculations suggest that the structure is predominantly ionic with charges close to the nominal $\text{Be}^{2+}_2\text{C}^{4-}$.⁽⁸⁴⁾ Al_4C_3 , prepared by direct union of the elements in an electric furnace, forms pale-yellow crystals, mp 2200°C . It has a complex structure in which $\{\text{AlC}_4\}$ tetrahedra of two types are linked to form a layer lattice: this defines two types of C atom, one surrounded by a deformed octahedron of 6 Al at 217 pm and the other surrounded by 4 Al at 190–194 pm and a fifth Al at 221 pm. The closest C...C approach is at the nonbonding distance of 316 pm. Although it is formally possible to describe the structure as ionic, $(\text{Al}^{3+})_4(\text{C}^{4-})_3$, such a gross separation of charges is unlikely to occur over the observed interatomic distances.

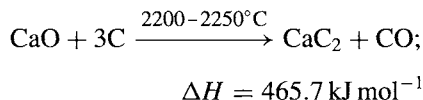
Carbides containing a C_2 unit are well known; they are exemplified by the acetylides (ethynides) of the alkali metals, $\text{M}^{\text{I}}_2\text{C}_2$, alkaline earth metals, $\text{M}^{\text{II}}\text{C}_2$, and the lanthanoids LnC_2 and Ln_2C_3 i.e. $\text{Ln}_4(\text{C}_2)_3$. The corresponding compounds of Group 11 (Cu, Ag, Au) are explosive and those of Group 12 (Zn, Cd, Hg) are poorly characterized. $\text{M}^{\text{I}}_2\text{C}_2$ are best prepared by the action of C_2H_2 on a solution of alkali metal in liquid NH_3 ; they are colourless crystalline compounds which react violently with water and oxidize to the carbonate on being heated in air. $\text{M}^{\text{II}}\text{C}_2$ can be prepared by heating the alkaline earth metal with ethyne above 500°C . By far the most important compound in this group is CaC_2 — it is manufactured on a huge scale, 6.4 million tonnes worldwide in 1982 and is used as a major source of ethyne for the chemical industry and for oxyacetylene welding. US production peaked at 1.03 Mt in 1964 but then declined substantially as ethyne became available from petrochemical feedstocks, from the thermal cracking of hydrocarbons and as a byproduct of C_2H_4 manufacture. US production of CaC_2

⁸³ Reference 2, pp. 841–911: Carbides (p. 841); Cemented carbides (p. 848); Industrial hard carbides (p. 861); Calcium carbide (p. 878); Silicon carbide (p. 891).

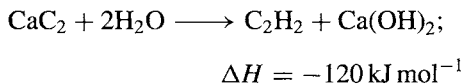
⁸⁴ P. W. FOWLER and P. TOLE, *J. Chem. Soc., Chem. Commun.*, 1652–4 (1989).

has been below 250 000 tonnes per annum for the past 20 years and was 236 000 tonnes in 1990 (price \$515/t). Europe (3.25 Mtpa) and Asia/Australia (2.42 Mtpa) are currently the major producers.

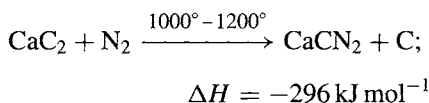
Industrially, CaC_2 is produced by the endothermic reaction of lime and coke:



Subsequent hydrolysis is highly exothermic and must be carefully controlled:

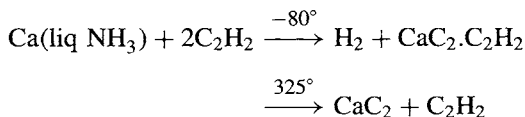


Another industrially important reaction of CaC_2 is its ability to fix N_2 from the air by formation of calcium cyanamide:



CaCN_2 is widely used as a fertilizer because of its ready hydrolysis to cyanamide, H_2NCN (p. 323).

Pure CaC_2 is a colourless solid, mp 2300°C . It can be prepared on the laboratory scale by passing ethyne into a solution of Ca in liquid NH_3 , followed by decomposition of the complex so formed, under reduced pressure at $\sim 325^\circ$:



It exists in at least four crystalline forms, the one stable at room temperature being a tetragonally distorted NaCl-type structure (Fig. 8.17) in which the C_2 units are aligned along the c -axis. The ethynides of Mg, Sr and Ba have the same structure and also hydrolyse to give ethyne. In addition, BaC_2 absorbs N_2 from the atmosphere to give $\text{Ba}(\text{CN})_2$ (cf. CaC_2 above).

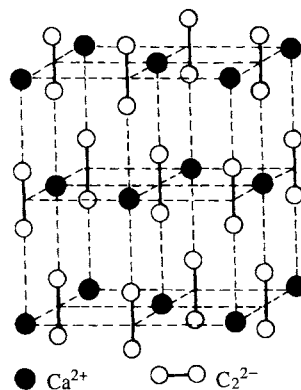


Figure 8.17 Crystal structure of tetragonal CaC_2 showing the resemblance to NaCl (p. 242). Above 450°C the parallel alignment of the C_2 units breaks down and the structure becomes cubic.

Carbides containing the essentially linear C_3^{4-} unit are known, e.g. Li_4C_3 , Mg_2C_3 , and the recently characterized $\text{Ca}_3\text{C}_3\text{Cl}_2$ and Sc_3C_4 .⁽⁸⁵⁾ Thus $\text{Ca}_3\text{C}_3\text{Cl}_2$ forms as transparent red crystals when CaCl_2 is heated with graphite in sealed Ta capsules at 900°C for 1 day (C–C 134.6 pm, angle 169.0°). By contrast Sc_3C_4 is a grey-black metallic substance with Pauli paramagnetism: it contains C^{4-} and C_2^{2-} ions, and supernumerary electrons e^- in addition to C_3^{4-} (C–C 134.2 pm, angle 175.8°). It can best be represented as $10\text{Sc}_3\text{C}_4 \equiv [(\text{Sc}^{3+})_{30}(\text{C}^{4-})_{12}(\text{C}_2^{2-})_2(\text{C}_3^{4-})_8(e^-)_6]$.⁽⁸⁵⁾

The carbides of the lanthanoids and actinoids can be prepared by heating M_2O_3 with C in an electric furnace or by arc-melting compressed pellets of the elements in an inert atmosphere. They contain the C_2 unit and have a stoichiometry MC_2 or $\text{M}_4(\text{C}_2)_3$. MC_2 have the CaC_2 structure or a related one of lower symmetry in which the C_2 units lie at right-angles to the c -axis of an orthogonal NaCl-type cell.⁽⁸⁶⁾ They are more reactive than the alkaline-earth metal

⁸⁵ R. HOFFMANN and H.-J. MEYER, *Z. anorg. allg. Chem.* **607**, 57–71 (1992).

⁸⁶ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984, 1382 pp.

carbides, combining readily with atmospheric oxygen and hydrolysing to a complex mixture of hydrocarbons. This derives from their more complicated electronic structure and, indeed, LnC_2 are metallic conductors (not insulators like CaC_2); they are best regarded as ethynides of Ln^{III} with the supernumerary electron partly delocalized in a conduction band of the crystal. This would explain the evolution of H_2 as well as C_2H_2 on hydrolysis, and the simultaneous production of the reduced species C_2H_4 and C_2H_6 together with various other hydrocarbons up to C_6H_{10} :



An interesting feature of the ethynides MC_2 and $\text{M}_4(\text{C}_2)_3$ is the variation in the C–C distance as measured by neutron diffraction. Typical values (in pm) are:

CaC_2 119.2	YC_2 127.5	CeC_2 128.3	LaC_2 130.3	UC_2 135.0
$\text{La}_4(\text{C}_2)_3$ 123.6	$\text{Ce}_4(\text{C}_2)_3$ 127.6	$\text{U}_4(\text{C}_2)_3$ 129.5		

The C–C distance in CaC_2 is close to that in ethyne (120.5 pm) and it has been suggested that the observed increase in the lanthanoid and actinoid carbides results from a partial localization of the supernumerary electron in the antibonding orbital of the ethynide ion $[\text{C}\equiv\text{C}]^{2-}$ (see p. 932). The effect is noticeably less in the sesquicarbides than in the dicarbides. The compounds EuC_2 and YbC_2 differ in their lattice parameters and hydrolysis behaviour from the other LnC_2 and this may be related to the relative stability of Eu^{II} and Yb^{II} (p. 1237).

The lanthanoids also form metal-rich carbides of stoichiometry M_3C in which individual C atoms occupy at random one-third of the octahedral Cl sites in a NaCl-like structure. Several of the actinoids (e.g. Th, U, Pu) form monocarbides, MC , in which all the octahedral Cl sites in the NaCl structure are occupied and this stoichiometry is also observed for several other carbides of the early transition elements, e.g. $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; \text{V}, \text{Nb}, \text{Ta}; \text{Mo}, \text{W}$. These

are best considered as interstitial carbides and in this sense the lanthanoids and actinoids occupy an intermediate position in the classification of the carbides, as they did with the hydrides (p. 66).

Interstitial carbides are infusible, extremely hard, refractory materials that retain many of the characteristic properties of metals (lustre, metallic conductivity).⁽⁸⁷⁾ Reported mps are frequently in the range 3000–4000°C. Interstitial carbides derive their name from the fact that the C atoms occupy octahedral interstices in a close-packed lattice of metal atoms, though the arrangement of metal atoms is not always the same as in the metal itself. The size of the metal atoms must be large enough to generate a site of sufficient size to accommodate C, and the critical radius of M seems to be ~ 135 pm: thus the transition metals mentioned in the preceding paragraph all have 12-coordinate radii > 135 pm, whereas metals with smaller radii (e.g. Cr, Mn, Fe, Co, Ni) do not form MC and their interstitial carbides have a more complex structure (see below). If the close-packed arrangement of M atoms is hexagonal (h) rather than cubic (c) then the 2 octahedral interstices on either side of a close-packed M layer are located directly above one another and only one of these is ever occupied. This gives a stoichiometry M_2C as in V_2C , Nb_2C , Ta_2C and W_2C . Intermediate stoichiometries are encountered when the M atom stacking sequence alternates, e.g. Mo_3C_2 (hcc) and V_4C_3 (hhcc). Ordered defect NaCl-type structures are also known, e.g. V_8C_7 and V_6C_5 , thus illustrating the wide range of stoichiometries which occur among interstitial carbides. Unlike the “ionic” carbides, interstitial carbides do not react with water and are generally very inert, though some do react with air when heated above 1000° and most are degraded by conc HNO_3 or HF. The extreme hardness and inertness of WC and TaC have led to their extensive use as high-speed cutting tools.

⁸⁷ H. H. JOHANSEN, *Survey of Progress in Chemistry* **8**, 57–81 (1977). See also A. COTTRELL, *Chemical Bonding in Transition Metal Carbides*, Inst. of Materials, London, 1995, 99 pp.

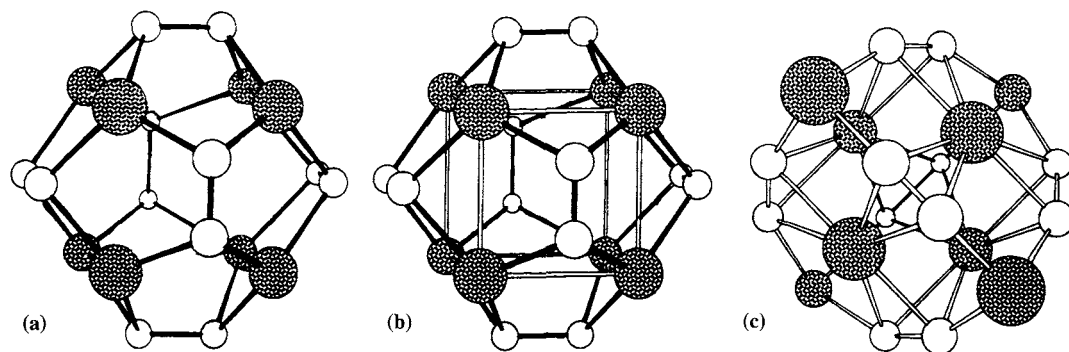


Figure 8.18 (a) Proposed pentagonal dodecahedral structure of Ti_8C_{12} . (b) The same structure viewed as a Ti_8 cube with each face capped by a C_2 group. (c) An alternative T_h structure (see text).

Table 8.3 Stoichiometries of some transition element carbides

V_2C , V_4C_3	$Cr_{23}C_6$	$Mn_{23}C_6$, $Mn_{15}C_4$	Fe_3C , Fe_7C_3	Co_3C	Ni_3C
V_6C_5 , V_8C_7	Cr_7C_3	Mn_3C , Mn_5C_2	Fe_2C	Co_2C	
VC	Cr_3C_2	Mn_7C_3			

The carbides of Cr, Mn, Fe, Co and Ni are profuse in number, complicated in structure, and of great importance industrially. Cementite, Fe_3C , is an important constituent of steel (p. 1075). Typical stoichiometries are listed in Table 8.3 though it should be noted that several of the phases can exist over a range of composition.

The structures, particularly of the most metal-rich phases, are frequently related to those of the corresponding metal-rich borides (and silicides, germanides, phosphides, arsenides, sulfides and selenides), in which the non-metal is surrounded by a trigonal prism of M atoms with 0, 1, 2, or 3 additional neighbours beyond the quadrilateral prism faces (p. 148). e.g. Fe_3C (cementite), Mn_3C and Co_3B ; Mn_5C_2 and Pd_5B_2 ; Cr_7C_3 and Re_7B_3 . Numerous ternary carbides, carbonitrides, and oxocarbides are also known.

The carbides of Cr, Mn, Fe, Co and Ni are much more reactive than the interstitial carbides of the earlier transition metals. They are rapidly hydrolysed by dilute acid and sometimes even by water to give H_2 and a mixture of hydrocarbons. For example, M_3C give H_2 (75%), CH_4 (15%)

and C_2H_6 (8%) together with small amounts of higher hydrocarbons.

Metallo-carbohedrenes (met-cars)

An entirely novel group of binary metal carbides, reminiscent of the fullerenes (p. 279), were discovered by accident in 1992.⁽⁸⁸⁾ When Ti metal is vaporized in a laser plasma reactor in the presence of He gas containing a hydrocarbon such as methane, ethene, ethyne or benzene, the mass spectrum of the emerging beam contains a single dominant peak at 528 corresponding to Ti_8C_{12} [isotope ^{48}Ti 73.8% abundant: $(8 \times 48) + (12 \times 12) = 528$]. Detailed isotope distribution studies confirmed the molecular formula. The proposed structure, shown in Fig. 8.18a, is a pentagonal dodecahedron of T_h symmetry comprising 12 mutually fused Ti_2C_3 pentagons.

⁸⁸ B. C. GUO, K. P. KERNS and A. W. CASTLEMAN, *Science* **255**, 1411–3 (1992). B. C. GUO, S. WEI, J. PURNELL, S. BUZZA and A. W. CASTLEMAN, *Science* **256**, 515–6 and 818–20 (1992), *J. Chem. Phys.* **96**, 4166–8 (1992).

Table 8.4 Some properties of methane and CX₄

Property	CH ₄	CF ₄	CCl ₄	CBr ₄	CI ₄
MP/°C	-182.5	-183.5	-22.9	90.1	171 (d)
BP/°C	-161.5	-128.5	76.7	189.5	~130 (subl)
Density/g cm ⁻³ (at T°C)	0.424 (-164°)	1.96 (-184°)	1.594 (20°)	2.961 (100°)	4.32 (20°) (s)
-ΔH _f ^o /kJ mol ⁻¹	74.87	679.9	106.7 (g) 139.3 (l)	160 (l)	—
D(X ₃ C-X)/kJ mol ⁻¹	435	515	295	235	—

Each Ti bonds to 3C via σ bonds and each C bonds to 2Ti and one C. The all-carbon analogue, C₂₀, is not expected to be stable because of severe internal strain; (it would be the smallest possible fullerene, p. 280). Note, however, that dodecahedrane, C₂₀H₂₀, is known.⁽⁸⁹⁾ An alternative description of the structure (Fig. 8.18b) would be as a weakly bonded cube, Ti₈, each face of which is capped by a C₂ unit. The calculated distances⁽⁹⁰⁾ are Ti...Ti 302 pm, Ti-C 199 pm and C-C 140 pm (implying some multiple bonding; cf. 140 pm in benzene). An alternative *T_h* structure for Ti₈C₁₂, which is calculated to have a lower energy, has also been proposed.⁽⁹⁰⁾ In this, the Ti₈ array is a tetracapped tetrahedron containing six Ti₄ faces in butterfly conformation; each of these Ti₄ faces can then accommodate a C₂ unit as shown in Fig. 8.18c.

Other met-cars that have been detected mass spectrometrically are M₈C₁₂ (M = V, Zr, Hf) and there is some evidence for higher members such as Zr₁₃C₂₂, Zr₁₄C₂₃, Zr₁₈C₂₉ and Zr₂₃C₃₂ which may feature fused clusters of clusters. The possibility of a super-pentagonal cluster, M₃₀C₄₅, of *D_{5h}* symmetry has also been mooted.⁽⁹¹⁾

As with the fullerenes, further detailed studies will depend on the discovery of viable bulk preparations of the met-cars. Macroscopic

amounts of Ti₈C₁₂ and V₈C₁₂ have indeed been made by DC arc discharge techniques using electrodes of compacted metal and graphite powders and He as the quenching carrier gas.⁽⁹²⁾ The resulting soot contains about 1% of air-stable M₈C₁₂ plus some C₆₀ (unstable in air). Solution studies have not yet been reported but there is mass spectrometric evidence for Ti₈C₁₂L₈ (L = NH₃, ND₃, H₂O) as well as for Ti₈C₁₂(MeOH)₄.

8.5 Hydrides, Halides and Oxohalides

The ability of C to catenate (i.e. to form bonds to itself in compounds) is nowhere better illustrated than in the compounds it forms with H. Hydrocarbons occur in great variety in petroleum deposits and elsewhere, and form various homologous series in which the C atoms are linked into chains, branched chains and rings. The study of these compounds and their derivatives forms the subject of organic chemistry and is fully discussed in the many textbooks and treatises on that subject. The matter is further considered on p. 374 in relation to the much smaller ability of other Group 14 elements to form such catenated compounds. Methane, CH₄, is the archetype of tetrahedral coordination in molecular compounds; some of its properties are listed in Table 8.4 where they are compared with those of the

⁸⁹ R. J. TERNANSKY, D. W. BALOGH and L. A. PAQUETTE, *J. Am. Chem. Soc.* **104**, 4503-4 (1982). J. C. GALLUCCI, C. W. DOECKE and L. A. PAQUETTE *J. Am. Chem. Soc.* **108**, 1343-4 (1986).

⁹⁰ I. G. DANCE, *J. Chem. Soc., Chem. Commun.*, 1779-80 (1992).

⁹¹ I. G. DANCE, *Aust. J. Chem.* **46**, 727-30 (1993).

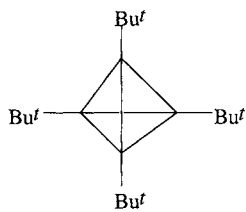
⁹² S. F. CARTIER, Z. Y. CHEN, G. J. WALDER and A. W. CASTLEMAN, *Science* **260**, 195-6 (1993).

corresponding halides. Unsaturated hydrocarbons such as ethene (C_2H_4), ethyne (C_2H_2), benzene (C_6H_6), cyclooctatetraene (C_8H_8) and homocyclic radicals such as cyclopentadienyl (C_5H_5) and cycloheptatrienyl (C_7H_7) are effective ligands to metals and form many organometallic complexes (pp. 930–43).

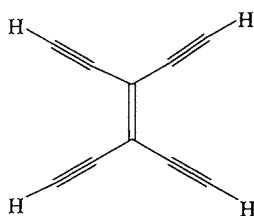
Methane is unique among hydrocarbons in being thermodynamically stable with respect to its elements. It follows that pyrolytic reactions to convert it to other hydrocarbons are energetically unfavourable and will be strongly equilibrium-limited. This is in marked contrast to the boranes where mild thermolysis of B_2H_6 or B_4H_{10} , for example, readily yields mixtures of the higher boranes (p. 164). Vast natural reserves of CH_4 gas exist but much is wasted

by flaring (direct burning off at the petroleum production site) because of the uneconomical cost of transport. However, in convenient locations such as the North Sea, natural gas is piped ashore for use as domestic or industrial fuel or as chemical feedstock. After CO_2 , methane is the most important “greenhouse gas” (p. 273) accounting for an estimated 15–20% of the atmospheric global warming ($CO_2 > 50\%$). The major sources of atmospheric CH_4 are natural wetlands (25%), rice cultivation (22%), animals (mainly domestic ruminants) (17%) and the mining of fossil fuels (16%), the total “production” being some 460 million tonnes per annum.

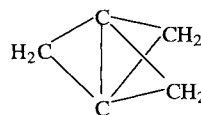
Notable recent advances in the chemistry of hydrocarbons include the synthesis and



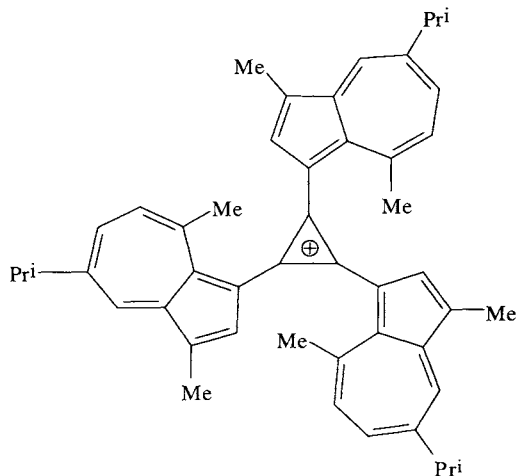
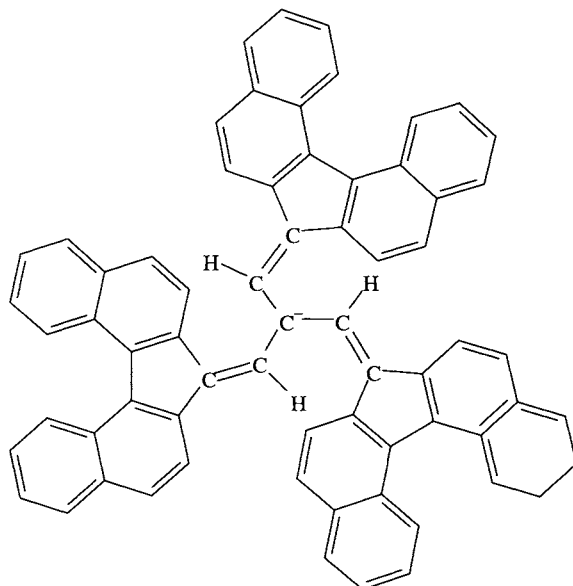
(1)

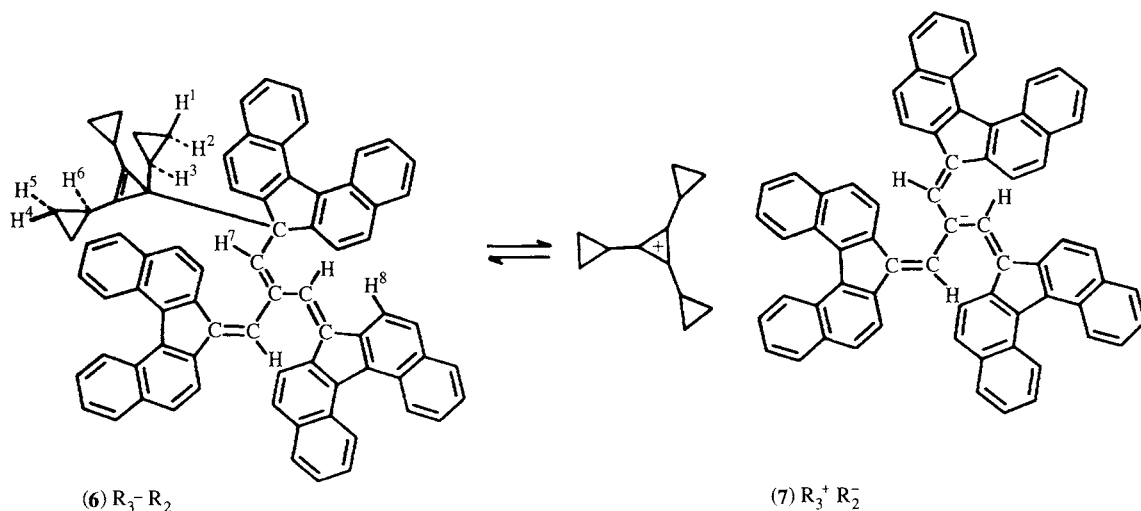


(2)



(3)

(4) R_1^+ (5) R_2^-



molecular structure determination of the tetrahydride derivative, $C_4Bu_4^+$ (1),⁽⁹³⁾ the carbon-rich molecules tetraethynylmethane, $C(C\equiv CH)_4$ i.e. C_9H_4 ⁽⁹⁴⁾ and tetraethynylethene, $C_2(C\equiv CH)_4$ i.e. $C_{10}H_4$,⁽⁹⁵⁾ the highly strained [1.1.1]propellane (3)⁽⁹⁶⁾ and the preparation of the largest discrete hydrocarbon molecules yet synthesized, the polyphenylethyne dendrimers $C_{1134}H_{1146}$ and $C_{1398}H_{1278}$ (mol wts 14 777.6 and 18 079.6).⁽⁹⁷⁾ There is also increasing interest in hydrocarbon salts $R_1^+R_2^-$. The first example was the stable, greenish-black crystalline compound $C_{48}H_{51}^+C_{61}H_{39}^-$ (mp $230^\circ C$ decomp.) obtained by mixing the solutions of Agranat's carbocation (4) and Kuhn's carbanion (5).⁽⁹⁸⁾ Of special interest is the covalent molecular hydrocarbon

R_3-R_2 (6) which exists in chloroform solution but which crystallizes on evaporation or cooling to give the ionic salt $R_3^+R_2^-$ (7).⁽⁹⁹⁾ This reversible ionic-covalent equilibrium is reminiscent of similar behaviour in certain halides such as $AlCl_3$ (p. 234), PCl_5 (p. 499) and $TeCl_4$ (p. 772), etc.

Fullerene derivatives such as $C_{60}H_n$ (p. 283), $C_{60}H_2$ (p. 287), and $C_{61}H_2$ (p. 287), and hypercoordinated non-classical carbonium ions (p. 290) have already been briefly mentioned.

Turning next to the simple halides of carbon: tetrafluoromethane (CF_4) is an exceptionally stable gas with mp close to that of CH_4 (see Table 8.4). It can be prepared on a laboratory scale by reacting SiC with F_2 or by fluorinating CO_2 , CO or $COCl_2$ with SF_4 . Industrially it is prepared by the aggressive reaction of F_2 on CF_2Cl_2 or CF_3Cl , or by electrolysis of MF or MF_2 using a C anode. CF_4 was first obtained pure in 1926; C_2F_6 was isolated in 1930 and C_2F_4 in 1933; but it was not until 1937 that the various homologous series of fluorocarbons were isolated and identified. Replacement of H by F greatly increases both thermal stability and chemical inertness because of the great strength of the $C-F$

⁹³ H. IRNGARTINGER, A. GOLDMANN, R. JAHN, M. NIXDORF, H. RODEWALD, G. MAIER, K.-D. MALSCH and R. EMRICH, *Angew. Chem. Int. Edn. Engl.* **23**, 993–4 (1984).

⁹⁴ K. S. FELDMAN and C. M. KRAEBEL, *J. Am. Chem. Soc.* **115**, 3846–7 (1993).

⁹⁵ Y. RUBIN, C. B. KNOBLER and F. DIEDERICH, *Angew. Chem. Int. Edn. Engl.* **30**, 698–700 (1991).

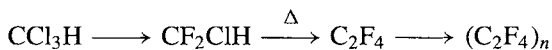
⁹⁶ J. E. JACKSON and L. C. ALLEN, *J. Am. Chem. Soc.* **106**, 591–9 (1984).

⁹⁷ Z. XU and J. S. MOORE, *Angew. Chem. Int. Edn. Engl.* **32**, 246–8 (1993), and *Abstracts*, ACS Denver Meeting, April 1993.

⁹⁸ K. OKAMOTO, T. KITAGAWA, K. TAKEUCHI, K. KOMATSU and K. TAKAHASHI, *J. Chem. Soc., Chem. Commun.*, 173–4 (1985).

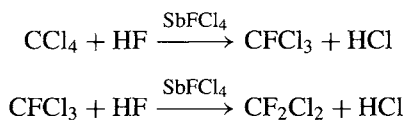
⁹⁹ K. OKAMOTO, T. KITAGAWA, K. TAKEUCHI, K. KOMATSU and A. MIYABO, *J. Chem. Soc., Chem. Commun.*, 923–4 (1988).

bond (Table 8.4). Accordingly, fluorocarbons are resistant to attack by acids, alkalis, oxidizing agents, reducing agents and most chemicals up to 600°. They are immiscible with both water and hydrocarbon solvents, and when combined with other groups they confer water-repellance and stain-resistance to paper, textiles and fabrics.⁽¹⁰⁰⁾ Tetrafluoroethene (C₂F₄) can be polymerized to a chemically inert, thermosetting plastic PTFE (polytetrafluoroethene); this has an extremely low coefficient of friction and is finding increasing use as a protective coating in non-stick kitchen utensils, razor blades and bearings. PTFE is made by partial fluorination of chloroform using HF in the presence of SbFCl₄ as catalyst, followed by thermolysis to C₂F₄ and subsequent polymerization:



As a ligand towards metals, C₂F₄ and other unsaturated fluorocarbons differ markedly from alkenes (p. 931).

CCl₄ is a common laboratory and industrial solvent with a distinctive smell, usually prepared by reaction of CS₂ or CH₄ with Cl₂. Its use as a solvent has declined somewhat because of its toxicity, but CCl₄ is still extensively used as an intermediate in preparing "Freons" such as CFCl₃, CF₂Cl₂ and CF₃Cl:⁽¹⁰⁰⁾

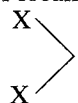


The catalyst is formed by reaction of HF on SbCl₅. The Freons have a unique combination of properties which make them ideally suited for use as refrigerants and aerosol propellants. They have low bp, low viscosity, low surface tension and high density, and are non-toxic, non-flammable, odourless, chemically inert and thermally stable. The most commonly used is CF₂Cl₂, bp, -29.8°. The market for Freons

and other fluorocarbons expanded rapidly in the sixties: production in the USA alone exceeded 200 000 tonnes in 1964 (417 000 tonnes in 1990) and global production was about three times this amount. Already in 1977 there was an annual production of 2.4 × 10⁹ spray-cans. However, there has been growing concern that chlorofluorocarbons from spray-cans gradually work their way into the upper atmosphere where they may, through a complex chemical reaction, deplete the earth's ozone layer (p. 608). For this reason there was an enforced progressive elimination of this particular application in the USA starting 15 October 1978 and production of CFCs will effectively be completely phased out following the Montreal Protocol of September 1981.

CBr₄ is a pale-yellow solid which is markedly less stable than the lighter tetrahalides. Preparation involves bromination of CH₄ with HBr or Br₂ or, more conveniently, reaction of CCl₄ with Al₂Br₆ at 100°. The trend to diminishing thermal stability continues to Cl₄ which is a bright-red crystalline solid with a smell reminiscent of I₂. It is prepared by the AlCl₃-catalysed halogen exchange reaction between CCl₄ and EtI.

Carbon oxohalides are reactive gases or volatile liquids which feature planar molecules of C_{2v} symmetry; they are isoelectronic with BX₃ (p. 196) and the bonding is best described in terms of molecular orbitals spanning all 4 atoms rather than in terms of localized orbitals as

implied by the formulation  C=O. Some

physical properties and molecular dimensions are in Table 8.5. The values call for little comment except to note that the XCX angle is significantly less (as expected) than the value of 120° found for the more symmetrical isoelectronic species BX₃ and CO₃²⁻. The C-Br distance is unusually long; it comes from a very early diffraction measurement and could profitably be checked.

Mixed oxohalides are also known and their volatilities are intermediate between those of the

¹⁰⁰ Kirk-Othmer Encyclopedia of Chemical Technology, 4th edn., Vol 11, 1994, pp. 467-729.