

# Comprehensive Inorganic Chemistry

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The Chemistry of  
**CARBON**

**A. K. Holliday, G. Hughes and S. M. Walker**

**ORGANOMETALLIC  
CHEMISTRY**

**M. L. H. Green and P. Powell**

Chapters 13 and 14 of  
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## PREFACE

The excellent reception that has been accorded to *Comprehensive Inorganic Chemistry* since the simultaneous publication of the five volumes of the complete work has been accompanied by the plea that sections should be made available in a form that would enable specialists to purchase copies for their own use. To meet this demand the publishers have decided to issue selected chapters and groups of chapters as separate editions. These chapters will, apart from the corrections of misprints and the addition of prefatory material and individual indices, appear just as they did in the main work. Extensive revision would delay publication and greatly raise the cost, so limiting the circulation of these definitive reviews.

A. F. TROTMAN-DICKENSON  
*Executive Editor*

## 13. CARBON

A. K. HOLLIDAY, G. HUGHES and S. M. WALKER

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### 1. THE ELEMENT

#### 1.1. GENERAL

Carbon, as charcoal from the combustion of wood, has been known to man from pre-historic times. Its name derives from the Latin *carbo* meaning charcoal. The element is unique in the vast number of its compounds—there are probably more than one million known today. This unique behaviour is in part due to the ability of carbon to form strong chemical bonds not only with itself but with many other elements, particularly those commonly occurring in nature. Some typical bond energy terms are given in Table 1.

TABLE 1. BOND ENERGY TERMS<sup>a</sup> FOR  
CARBON AND SILICON WITH OTHER  
ELEMENTS

X	$D(\text{C-X})$ , kcal	$D(\text{Si-X})$ , kcal
C	83	
Si		53
H	98	76
O	85	108
N	73	
S	65	70
P	63	
Cl	81	91

<sup>a</sup> T. L. Cottrell, *The Strengths of Chemical Bonds*, 2nd ed. Butterworths (1958).

Also shown in Table 1 for comparison are the corresponding values for silicon. It is apparent that although silicon bonds strongly to other elements the Si-Si bond is relatively weak and there is little correspondence, therefore, in silicon chemistry to the vast range of organic compounds. The marked stability of such a wide range of compounds is in part to be attributed to the electronic configuration of carbon (see p. 1189).

#### Occurrence and Distribution

Carbon is widely distributed throughout the universe. Much of the energy of the sun and stars is due to the carbon cycle (see p. 1184). Both black and transparent diamonds have

been found in meteorites. The cosmic abundance is six times that of silicon. In the earth's crust, the most abundant mineral not containing silicon is calcium carbonate. This occurs as limestone, marble, calcite, Iceland spar, chalk, dolomite (with magnesium carbonate) and in shells. Other important carbonate minerals are siderite ( $\text{FeCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ) and smithsonite ( $\text{ZnCO}_3$ ). In its elementary forms, carbon occurs as diamond and graphite.

As early as *c.* 700 B.C. the characteristic hardness of diamond was recognized<sup>1</sup>. Its name derives from a corruption of the Greek word *adamas* meaning invincible. Diamonds are today mined chiefly in South Africa which accounts for 90% of the world's supply, though some are to be found in Brazil, India and Australia. The largest known diamond<sup>2</sup>, the Cullinan, was found near Pretoria in 1905. Before cutting, it weighed 0.57 kg (3106 carats).

Although graphite has been known from prehistory, it was frequently confused with other minerals. Only in 1779 did Scheele, by oxidizing it to carbon dioxide, prove that it was carbon. Its name derives from the Greek word *graphein* meaning to write. It was formerly mined in Borrowdale but these deposits have been largely worked out. Extensive deposits still occur in Ceylon, Madagascar, U.S.A., Siberia and Korea (see p. 1250).

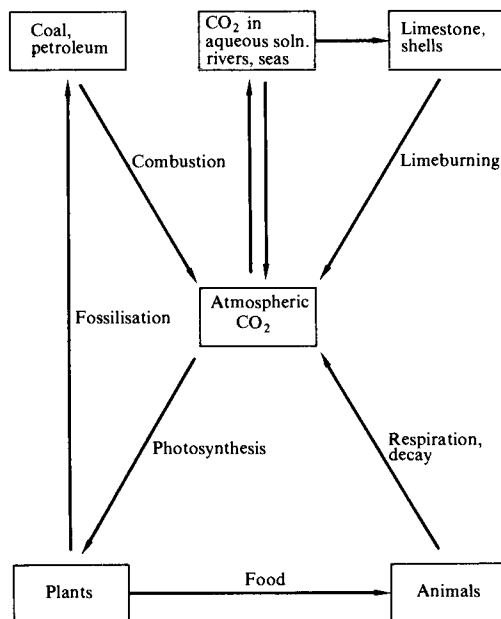


FIG. 1. The carbon dioxide cycle.

Combined with hydrogen, carbon occurs extensively as coal, petroleum and natural gas. In spite of its widespread occurrence carbon still only constitutes 0.027% of the earth's crust<sup>3</sup>. As carbon dioxide it constitutes about 0.03% by volume (0.046% by weight) of the earth's atmosphere. Although carbon dioxide is continually being produced in

<sup>1</sup> Jeremiah 17.1.

<sup>2</sup> R. Webster, *Gems*, p. 13, Butterworths, London (1962).

<sup>3</sup> B. Mason, *Principles of Geochemistry*, 3rd ed., p. 45, John Wiley, New York (1966).

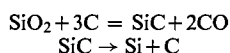
the earth's atmosphere from combustion, it is removed in photosynthesis by plant life to form starches, sugars and other organic compounds. Reactions of this so-called carbon dioxide cycle are summarized in Fig. 1. The distribution of terrestrial carbon is approximately as follows<sup>4</sup>: minerals 99.7%; atmosphere 0.2%; living matter 0.01%.

### Production and Industrial Uses<sup>5</sup>

Diamonds are, of course, highly prized as gemstones. Black diamonds (sometimes known as industrial diamonds), which may be either natural or synthetic, are used in the drilling of rocks and in the cutting and polishing of other gem stones.

Because it is a highly refractory material, graphite is used in making electric furnaces and crucibles for the casting of metals. It is used in pencils since it is soft and is able to mark paper. In this connection, its hardness is varied by the addition of clay. In colloidal dispersion in water (Aquadag) or oil (Oildag) it is used as a lubricant. It is also used extensively because of its electrical conductivity in the manufacture of electrodes, carbon brushes for dynamos and in microphones.

Artificial graphite was first prepared on a large scale by Acheson<sup>6</sup> in 1896. The major part of the technical graphite used today is still produced by the Acheson process<sup>7</sup>. In this, amorphous carbon, e.g. coke, is heated with silica in an electric furnace to  $\sim 2800^\circ\text{K}$  for a prolonged period (24–36 hr). Although it has been suggested that reaction proceeds via the formation of silicon carbide (see p. 1214) which then decomposes, the silicon evaporating off,



it may be that at high temperatures, the growth of graphite crystals, already existing in the coke, is promoted. A cheap, plentiful supply of electricity is required and hence graphite is produced by the Acheson Graphite Company at Niagara.

The capture cross-section of graphite for thermal neutrons is extremely low ( $3.4 \times 10^{-3}$  barn) so that graphite is used extensively as a moderator in the atomic pile<sup>8</sup>. Under the influence of reactor radiation, atomic displacements occur in the crystal (Wigner effect), thus increasing the internal energy. This energy is released on heating at  $1300^\circ\text{K}$  but there is the risk of explosion. The effect is minimized by using graphite of exceptionally good chemical purity and crystal structure. For this purpose, petroleum coke is used as starting material in the Acheson process since this has a lower content of impurities, especially of boron which has a high capture cross-section.

Although coal contains some free carbon, its solubility in pyridine indicates that much of the carbon is chemically combined. Hard coal contains approximately 6% volatile matter, essentially hydrocarbons. Coal is used extensively both combusted directly as a fuel and in the gas industry. In this, coal is heated in the absence of air and gives rise to a gaseous mixture consisting chiefly of  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$  with some  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ , a liquid distillate containing benzene, naphthalene, phenol and other hydrocarbons and leaves a solid residue of coke<sup>9</sup>.

<sup>4</sup> F. H. Day, *Chemical Elements in Nature*, p. 224, Harrap, London (1963).

<sup>5</sup> C. L. Mantell, *Industrial Carbon*, 2nd ed., D. Van Nostrand, New York (1946).

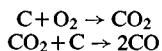
<sup>6</sup> A. G. Acheson, U.S. Patent No. 1,030,372 (1912).

<sup>7</sup> P. A. H. Lee and B. L. Tonge, *J. Chem. Educ.* **40** (1963) 117.

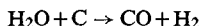
<sup>8</sup> J. K. Dawson and G. Long, *Chemistry of Nuclear Power*, p. 30, Newnes, London (1959).

<sup>9</sup> D. McNeil, *Coal Carbonisation Products*, Pergamon, London (1966).

Coke, charcoal and carbon black are all important forms of amorphous carbon. Coke consists principally of carbon and is used extensively as a reducing agent in a wide variety of metallurgical operations (see p. 1197) and in the production of producer gas and water gas. Producer gas is a mixture of CO and N<sub>2</sub> and is produced when air is blown through incandescent coke. CO<sub>2</sub> is produced at the bottom of the furnace and is further reduced as it passes up the furnace.



The reaction generates sufficient heat to be self-sustaining (see p. 1196). Water gas is a mixture of hydrogen and carbon monoxide formed when steam is passed through heated coke



The process is endothermic ( $\Delta H = +32$  kcal) and a high temperature is maintained by alternate passage of steam and air.

Charcoal is produced by the dry distillation of wood (wood charcoal) or bones (animal charcoal). Whereas wood charcoal is predominantly carbon, animal charcoal consists of only 20% carbon in a fine state of subdivision on a matrix of calcium and magnesium phosphates. Because of its very high surface area, charcoal is used as an adsorbent both for gases, e.g. in the production of high vacua and in the separation of gases, and for liquid solutions, e.g. the purification of molasses and the decolorization of solutions. Activated charcoal is produced by heating charcoal in steam at 1200°K. This removes obstructions from the pores of the solid and thus enhances its adsorbent property<sup>10</sup>.

Carbon black is produced by burning natural gas or other carbon-containing compounds, e.g. residual petroleum oils, in a limited supply of air. The smoke thus produced, after being cooled by spraying with water, is passed through an electrostatic precipitator. Some of the carbon collects on the electrodes and the remaining larger particles are recovered in a series of cyclone operators<sup>11</sup>. Most of the carbon black produced is used as a reinforcing agent for natural and synthetic rubber though some is used as a pigment in printing inks, etc.

The use of carbon fibres to produce materials of low density and high tensile strength is currently being developed and is likely to lead to important technological developments (see p. 1252).

Recent estimates of the world consumption of carbon are given in Table 2 and indicate the importance of this element.

The consumption of carbon in its elemental form is probably more than that of any other element. Its industrial and theoretical importance is also evidenced by the growing literature devoted to it. It has been the subject of five international conferences<sup>12</sup> and these have led to the subsequent publication<sup>13</sup> of the journal *Carbon*. In addition there is a well-known review series<sup>14</sup>.

### Preparation of Pure Material

Reasonably pure material can be obtained by heating sucrose in the absence of air.

<sup>10</sup> H. W. Davidson, P. K. C. Wiggs, A. H. Churchhouse, F. A. P. Maggs and R. S. Bradley, *Manufactured Carbon*, Pergamon, Oxford (1958).

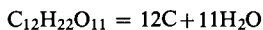
<sup>11</sup> D. M. Samuel, *R.I.C. Monographs for Teachers*, No. 10, p. 11 (1966).

<sup>12</sup> *Proceedings of the 1st, 2nd, 3rd, 4th and 5th Conferences on Carbon*, Vols. 1-5, Pergamon, London (1956-1963).

<sup>13</sup> *Carbon*, 1 (1963) to present date.

<sup>14</sup> *Chemistry and Physics of Carbon*, vols. 1-4, Ed. P. L. Walker, Arnold, London (1965-68).





Ordinarily available carbon contains as impurities compounds with H, N, O and S as well as adsorbed gases. Because of the ease with which carbon adsorbs gases, very high purity carbon can only be prepared and studied in high vacuum apparatus<sup>15</sup>. For this purpose, it can be obtained by igniting carbon at red heat in a current of chlorine, followed by heating for several hours at 600°K in high vacuum.

TABLE 2. WORLD CONSUMPTION OF CARBON<sup>a</sup>

Form of carbon	Consumption, tons
Diamond	6
Graphite	$3 \times 10^5$
Coal	$1.8 \times 10^9$
Petroleum	$0.9 \times 10^9$
Natural gas	$0.4 \times 10^9$

<sup>a</sup> B. Mason, *Principles of Geochemistry*, 3rd ed., p. 301. Wiley, New York (1966).

## 1.2. ALLOTROPY

Carbon can be obtained in three different crystalline forms:  $\alpha$ - (or hexagonal) and  $\beta$ - (or rhombohedral) graphite and diamond<sup>16</sup>. Carbon black and other amorphous forms of carbon consist essentially of microcrystalline graphite with various impurities adsorbed on the surface.

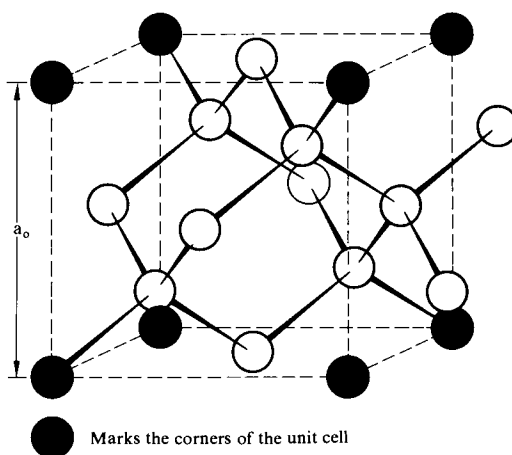


FIG. 2. Structure of diamond.

The structure of diamond is shown in Fig. 2. It is essentially a giant molecule with each atom bonded tetrahedrally to four other carbon atoms, the whole possessing cubic symmetry with  $a_0 = 0.356679$  nm at 293°K<sup>17</sup>. The C–C bond length is then given by  $a_0\sqrt{3}/4$ , viz.

<sup>15</sup> A. Stock, *Z. anorg. und allgem. Chem.* **195** (1931) 158.

<sup>16</sup> S. Ergun, *Carbon*, **6** (1968) 141.

<sup>17</sup> D. M. Donaldson and J. M. Robertson, *Proc. Roy. Soc. (London)*, **220A** (1953) 157.

0.15545 nm. This is similar to that observed for ethane<sup>18</sup>, viz. 0.1533 nm, and indicates that the bonding is similar. This strong bonding throughout the crystal makes cleavage of the crystal difficult and diamond is one of the hardest known substances. Its involatility and low coefficient of cubical expansion are due to this bonding.

The diamond has a highly symmetrical structure so that a large number of crystal faces may be formed and it is therefore an attractive gemstone. In the absence of impurities there is a large energy gap ( $\sim 6$  eV) between the filled electron band and the next vacant band so that it is colourless and does not conduct electricity. Coloured diamonds contain some impurity and are valuable because of their relative scarcity. Colour may be induced in diamonds on exposure to ionizing radiation, but since this colour arises from the production of trapped electrons such diamonds, usually green or blue, may be decolorized<sup>19</sup> on heating at 800°K.

In addition to the ideal diamond structure (known as type I), X-ray analysis shows that a mosaic structure (type II) is sometimes formed. This latter structure consists of a large number of mosaic blocks, approximately  $10^2$  nm wide in which the structure is ideal, but the blocks are not perfectly packed.

The structure of  $\alpha$ -graphite is shown below.

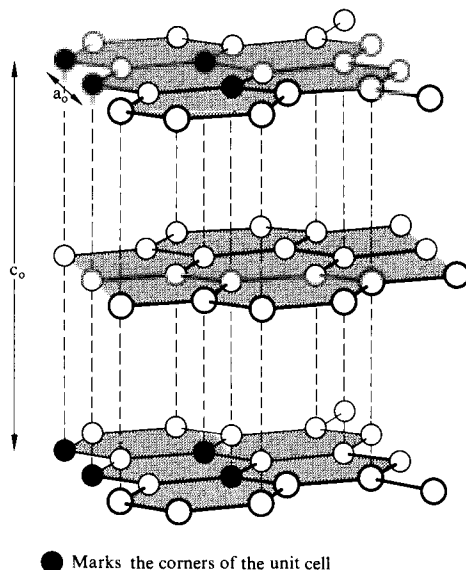


FIG. 3. Structure of  $\alpha$ -graphite.

In Fig. 3 the atoms of the unit cell are indicated by solid circles and it will be seen that the unit cell has hexagonal symmetry. The dimensions of the unit cell are<sup>20</sup>  $a_0 = 0.24611$  nm and  $c_0 = 0.67078$  nm at 288°K. This corresponds to a C–C bond length within the plane of 0.14210 nm indicating a bond order of 1.33<sup>21</sup>. Within the plane each carbon atom, in

<sup>18</sup> K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.* **73** (1951) 1482.

<sup>19</sup> *Encyclopedia of Chemical Technology*, vol. 4, p. 289, Ed. A. Standen, Interscience, New York (1964).

<sup>20</sup> J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* **57** (1945) 477, 486.

<sup>21</sup> L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., p. 235, Cornell University Press, Ithaca, N.Y. (1960).

its  $sp^2$  hybridized state, is bonded to three other carbon atoms. The non-bonded  $p_z$  atomic orbitals overlap to give a completely delocalized system of molecular orbitals thus allowing the transport of electrons throughout the crystal. Hence graphite, unlike diamond, is a good conductor though the conductivity, as with many other of its physical properties, is markedly dependent on the axis of measurement. The black colour of graphite also arises from the excitation of these delocalized electrons.

The distance between planes is 0.33539 nm, though this distance is increased slightly in poorly crystalline carbons<sup>22</sup>. This distance is too great for normal valence forces to be operative and successive planes are held together only by weak van der Waals' forces. The virtual lack of bonding between planes leads to ready cleavage along the planes and thus accounts for the softness of the solid. Moreover, because of the lack of interaction between planes it is possible to insert other chemical groups into the crystal, giving rise to the lamellar chemistry of graphite (see p. 1262). In fact, the well-known lubricating properties of graphite probably arise as a result of the bonding of oxygen or organic molecules to the graphite layers, thus reducing still further the interaction between planes. Very pure graphite is actually abrasive<sup>23</sup>.

In normal (or  $\alpha$ -) graphite the planes are so arranged that the carbon atoms of alternate layers are vertically above each other. However, in  $\beta$ -graphite the planes are staggered such that the carbon atoms of every third layer are vertically above each other (see p. 1254). Although some naturally occurring graphites contain traces of the  $\beta$ -form, all synthetic graphites are formed in the  $\alpha$ -form. The  $\beta$ -form is produced by mechanical treatment, such as grinding, of the  $\alpha$ -form, but is converted to the more stable  $\alpha$ -form by heating above 1300°K.  $\Delta H$  for the transition<sup>24</sup>  $\alpha \rightarrow \beta$  is  $0.14 \pm 0.04$  kcal g atom<sup>-1</sup>.

The density of diamond<sup>25</sup> is 3.514 g cm<sup>-3</sup>. The calculated density of the ideal hexagonal graphite lattice is considerably lower<sup>26</sup> than this, viz. 2.266 g cm<sup>-3</sup>. However, the densities of both naturally occurring and synthetic graphites are often less than  $\sim 2$  g cm<sup>-3</sup>. This would indicate considerable defects in packing. Data for some typical carbons are given in Table 3.

TABLE 3. DENSITIES OF SOME CARBONS<sup>a</sup>

Type of carbon	Density, g cm <sup>-3</sup>
Activated carbon	1.46
Sugar carbon	1.50-1.58
Hardwood carbon	1.87
Bone carbon	1.94
Acetylene black	2.04
Petroleum coke	2.23

<sup>a</sup> L. M. Currie, V. C. Hamister and H. G. McPherson, *Int. Conf. on Peaceful Uses of Atomic Energy*, vol. 8, p. 451, United Nations, New York (1956).

<sup>22</sup> G. E. Bacon, *Acta Cryst.* **4** (1951) 558.

<sup>23</sup> T. J. Lewis and P. E. Secker, *Science of Materials*, p. 159, Harrap, London (1965).

<sup>24</sup> H. P. Boehm and R. W. Coughlin, *Carbon*, **2** (1964) 1.

<sup>25</sup> J. A. Bearden, *Phys. Rev.* **54** (1938) 198.

<sup>26</sup> U. Hofmann, D. Wilm and E. Csalen, *Z. Elektrochem.* **42** (1936) 506.

### Graphite–Diamond Equilibrium

At ordinary temperatures, graphite is the stable form of carbon. Thus its heat of combustion at 298°K is 94·052 kcal g atom<sup>-1</sup> compared with 94·505 kcal g atom<sup>-1</sup> for diamond<sup>27</sup>. However, the transition from graphite to diamond involves a considerable rearrangement of structure and its rate at normal temperatures and pressures is negligibly slow—to the relief of diamond owners! Naturally considerable interest has attached to the possibility of transforming graphite to diamond. The earliest claims to have achieved this were by Hannay<sup>28</sup> and Moissan<sup>29</sup>. Although these claims have since been refuted, the question cannot be regarded as definitely closed<sup>30</sup>. Diamond crystals were successfully synthesized<sup>31</sup> by the General Electric Company of America in 1955.

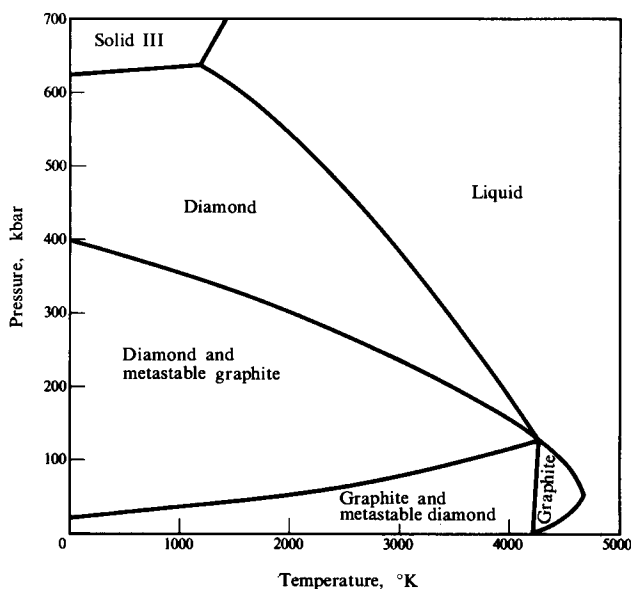


FIG. 4. Phase diagram of carbon.

The high-pressure phase diagram<sup>32</sup> for carbon is shown in Fig. 4. Graphite sublimes<sup>33</sup> at atmospheric pressure at  $3640 \pm 25^\circ\text{K}$  and the triple point (graphite–liquid–gas) is  $4020 \pm 50^\circ\text{K}$  at  $126 \pm 15$  bar. From Fig. 4 it may be seen that a second triple point (diamond–graphite–liquid) occurs at  $4100 \pm 100^\circ\text{K}$  and 125–130 kbar. The transition from graphite to diamond involves considerable reorganization of structure and is only likely to proceed at a significant rate at high temperature. However, as the temperature increases, so does the equilibrium pressure, as may be seen from Fig. 4. It is clear that diamonds are only likely to be synthesized under extreme conditions of temperature and pressure and this is why the earliest claims have been doubted.

<sup>27</sup> E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33** (1944) 447.

<sup>28</sup> J. B. Hannay, *Proc. Roy. Soc. (London)*, **30** (1880) 188, 450.

<sup>29</sup> H. Moissan, *Compt. Rend.* **116** (1893) 218.

<sup>30</sup> E. P. Flint, *Chem. and Ind. (London)*, **47** (1968) 1618.

<sup>31</sup> E. A. D. White, *Quart. Revs. (London)*, **15** (1961) 1.

<sup>32</sup> F. P. Bundy, *J. Chem. Phys.* **38** (1963) 618, 631.

<sup>33</sup> C. A. Hampel (Ed.), *Encyclopedia of the Chemical Elements*, p. 106, Reinhold, New York (1968).

No significant transformation of pure graphite to diamond was observed by the General Electric team even at a pressure of 121 kbar. As indicated earlier, kinetic as well as thermodynamic factors must be significant. Although all the details of the successful synthesis have not been published the following points are of interest<sup>31</sup>.

1. Work was carried out in the phase region for stability of diamond, viz. 5.5–100 kbar pressure and temperatures of 1200–2400°K.
2. Molten metal catalysts, e.g. Cr, Fe, Ni, were used.
3. Commercial graphite gave better crystals.

Growth rates of approximately 0.1 mm min<sup>-1</sup> and crystal sizes of 0.5 mm could be obtained. The colour of the diamonds obtained varied from black at the lowest temperatures used through dark green, light green, yellow and colourless at the highest temperatures. More recently<sup>32</sup>, the conversion of pure graphite to diamond has been observed at pressures greater than 126 kbar using flash heating to achieve transient temperatures of ~5000°K. The conversion has also been reported using a shock wave<sup>34</sup> and a spark discharge shock<sup>35</sup> to achieve the necessary temperatures and pressures. Although it is now clear that diamonds may be synthesized at high temperatures and pressures, the origin of naturally occurring diamonds is still not clear.

Considerable effort has been made to produce metastable diamond though this has been largely unsuccessful. If methane is passed over diamond powder at 1300°K at very low pressures, the diamonds are covered with a black coating which is predominantly graphite. The coating may be removed by treatment with a sulphuric acid–chromic acid mixture when the resulting powder shows a weight gain of 1–4%. That this is due to diamond formation is confirmed by electron diffraction study of the treated surface<sup>36</sup>. Similarly diamond is reported to deposit during the decomposition of methylchlorosilane on silica though the deposits did not exceed thicknesses of 10 nm with diameters of the order of 0.1 mm.

Attempts are being made to grow diamonds by spraying 1 carat natural cut diamonds with carbon vapour in very high vacuum<sup>37</sup>. It is essential for the surface of the diamond to be kept free from impurities. Impurities, when detected by examining the surface using electron diffraction, are removed by bombardment of the surface with noble gas ions. Ultimately it is hoped to use the high vacuum of outer space for successful growing.

The conversion of diamond to graphite by heating in the absence of oxygen at approximately 1300°K has also been investigated<sup>38</sup>. Under conditions of complete conversion, the graphite is always polycrystalline and does not always retain preferred orientation effects.

As indicated in Fig. 4, the existence of a third form of carbon, solid III, has been proposed<sup>32</sup>. This would be stable at pressures >630 kbar and temperatures 0–1000°K. It is suggested that this would be a metallic state, 20% more dense than diamond, though there is, as yet, no experimental evidence for its existence.

<sup>34</sup> B. J. Alder and R. H. Christian, *Phys. Rev. Letters*, **7** (1961) 367.

<sup>35</sup> H. Honda, Y. Sanada and K. Inoue, *Carbon*, **1** (1963) 127.

<sup>36</sup> R. H. Wentorf, in *Advances in Chemical Physics*, vol. 9, p. 365, Ed. I. Prigogine, Interscience, New York (1965).

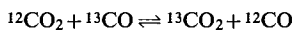
<sup>37</sup> *Scientific Research*, p. 21, McGraw Hill, New York (1968).

<sup>38</sup> K. Lonsdale and H. J. Milledge, in *Physical Properties of Diamond*, p. 12, Ed. R. Berman, Clarendon Press, Oxford (1966).

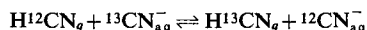
## 1.3. NUCLEAR PROPERTIES

The stable isotopes of carbon are  $^{12}\text{C}$  and  $^{13}\text{C}$ ; the radioactive isotopes  $^9\text{C}$ ,  $^{10}\text{C}$ ,  $^{11}\text{C}$ ,  $^{14}\text{C}$ ,  $^{15}\text{C}$  and  $^{16}\text{C}$  have been synthesized.

Naturally occurring carbon consists<sup>39</sup> of 98.892%  $^{12}\text{C}$  and 1.108%  $^{13}\text{C}$ , though there are minor variations in this distribution. Complete separation of  $^{12}\text{C}$  and  $^{13}\text{C}$  is difficult to achieve. Enrichment of  $^{13}\text{C}$  can be obtained via the reaction



for which it has been calculated<sup>40</sup> that the equilibrium constant is 1.098 at 273°K. The reaction



for which  $K = 1.012$  at 298°K, has been used<sup>41</sup> as the basis for commercial production of up to 65 at. % of  $^{13}\text{C}$ . The process is rapid, but is, of course, extremely toxic and is complicated by polymerization of the HCN (see p. 1243). Distillation of CO may also be used since the vapour pressure ratio  $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$  is 1.01 at 70°K and at this temperature a production rate of 0.4 g per day of 60 at. %  $^{13}\text{C}$  has been obtained<sup>42</sup>. Algae preferentially absorb  $^{12}\text{CO}_2$  and this can be used<sup>43</sup> to produce enriched  $^{13}\text{CO}_2$  (see p. 1230).

The isotope  $^{12}\text{C}$  is of interest because it is now the basis of all atomic weight determinations. Prior to 1961, two separate scales of atomic weights existed. The physical scale was based on  $^{16}\text{O} = 16.0000$ , but the chemical scale was based on the atom of naturally occurring oxygen  $\text{O} = 16.0000$ . Oxygen consists of isotopes of mass 16, 17 and 18, however, so that atomic weights on the chemical scale were heavier than those on the physical scale by a factor  $r = 1.000273$ . Moreover, the isotopic abundance of oxygen in nature varies from source to source<sup>44</sup> so that  $r$  varied from 1.000268 to 1.000278. It was clearly desirable to establish a unified scale of atomic weights and at a meeting of the IUPAC in 1961 the choice was made<sup>45</sup> of  $^{12}\text{C} = 12.0000$  rather than  $^{16}\text{O} = 16.0000$ .  $^{12}\text{C}$  was chosen largely for physical reasons<sup>46</sup>. Thus in the determination of nuclear masses by mass spectroscopy more nuclei may be related to  $^{12}\text{C}$  and the ratio of their masses to  $^{12}\text{C}$  are more accurately known than the ratio of  $^{12}\text{C}$  to  $^{16}\text{O}$ . Moreover, several nuclear masses are determined by measurement of the energy changes in nuclear reactions and for these  $^{12}\text{C}$  is a more satisfactory basis.

The practical effect of this change is that previous chemical atomic weights are now reduced by 43 ppm. Although this small change is within the limits of accuracy of present atomic weight determinations, it must be taken into account when considering very precise physicochemical data, e.g. Avogadro's number, the Faraday. Revised tables of atomic weights have been published<sup>47</sup>. On this new scale, the atomic weight of naturally occurring carbon is 12.01115. In future, for all atomic weight determinations to an accuracy of 50 ppm or better, it will be necessary to specify the isotopic composition of the material under investigation.

<sup>39</sup> A. O. Nier, *Phys. Rev.* **77** (1950) 789.

<sup>40</sup> H. C. Urey and L. Grieff, *J. Am. Chem. Soc.* **57** (1935) 321.

<sup>41</sup> D. W. Stewart, *Nucleonics*, **1** (1947) 18.

<sup>42</sup> T. F. Johns, H. Kromberger and H. London, *Mass Spectrometry*, p. 141, Institute of Petroleum, London (1952).

<sup>43</sup> M. Calvin and J. W. Weigh, *Concentrating Isotopic Carbon*, U.S. Patent 2,602,047 (1952).

<sup>44</sup> M. Dole, *Chem. Revs.* **51** (1952) 263.

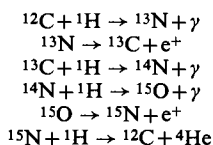
<sup>45</sup> A. Labbauf, *J. Chem. Ed.* **39** (1962) 282.

<sup>46</sup> D. H. Whiffen, *Proc. Chem. Soc.* (1960) 97.

<sup>47</sup> *J. Chem. Ed.* **38** (1961) 625.

Before the discovery of  $^{14}\text{C}$ ,  $^{13}\text{C}$  was used as a tracer in chemical kinetics. Subsequent analysis was by mass spectroscopy. However, the more convenient radio-chemical assay of  $^{14}\text{C}$  has led largely to the replacement of  $^{13}\text{C}$  by  $^{14}\text{C}$ . However,  $^{13}\text{C}$  is still used in experiments where double labelling is important<sup>48</sup>, since compounds containing 60 at. % of  $^{13}\text{C}$  can be produced. The activities of  $^{14}\text{C}$  compounds that can be conveniently handled are such that the percentage of doubly labelled species is negligible. Because of its nuclear spin, compounds labelled with  $^{13}\text{C}$  are useful in nuclear magnetic resonance studies<sup>49</sup>. From measurements of the spin-spin coupling of  $^{13}\text{C}$  nuclei at natural abundance with the protons bonded to them, it is possible by high resolution n.m.r. studies to determine the amount of *s* character of the C-H bond<sup>50</sup>.

$^{12}\text{C}$  and  $^{13}\text{C}$  are important intermediates in the liberation of energy in the sun and other hot stars ( $T > 5 \times 10^8$  °K). Energy release is postulated<sup>51</sup> as occurring by the following cycle of reactions:

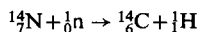


Four hydrogen atoms are converted into one helium atom and two positrons and the consequent reduction in mass results in the liberation of 30 meV per cycle.

The ions  $^{12}\text{C}^{6+}$  and  $^{13}\text{C}^{6+}$  are used in nuclear chemistry. They possess the advantage that at high energies ( $> 100$  MeV) relatively large changes in the atomic number of the particles being bombarded can be achieved.

In Table 4 are listed the methods of production, the half-lives and the particles emitted on decay of the radioactive nuclides of carbon.

$^{14}\text{C}$  is by far the most stable and is the isotope of major interest. As indicated in Table 4 it is prepared by neutron bombardment of  $^{14}\text{N}$ .



For this purpose the nitride of beryllium or aluminium is used<sup>52</sup>. The reaction is complex and a wide variety of single C atom compounds have been extracted from the target material<sup>53</sup> as may be seen from Table 5. Products are usually oxidized to  $^{14}\text{CO}_2$  which is dispensed as  $\text{Ba}^{14}\text{CO}_3$ . Because of the low cross-section of the  $^{14}\text{N}$  (*n, p*) reaction and the long half-life of  $^{14}\text{C}$ , the production of high specific activity material requires exposure of the targets to high neutron fluxes over long periods and is relatively expensive.  $^{14}\text{C}$  labelled compounds are used extensively<sup>54</sup>, particularly in kinetics, and a wide variety of such compounds is now available<sup>55</sup>.

Assay of the  $^{14}\text{C}$  content of naturally occurring materials is used to determine their age<sup>56</sup> (see also refs. j and k, Table 4). In the upper atmosphere  $^{14}\text{N}$  is converted into  $^{14}\text{C}$  by bombardment with neutrons derived from the cosmic radiation. Subsequently these atoms

<sup>48</sup> C. E. Melton and G. A. Ropp, *J. Am. Chem. Soc.* **80** (1958) 5573.

<sup>49</sup> E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur and J. D. Roberts, *J. Am. Chem. Soc.* **83** (1961) 1987.

<sup>50</sup> N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31** (1959) 768.

<sup>51</sup> H. A. Bethe, *Phys. Rev.* **55** (1939) 103, 434.

<sup>52</sup> J. R. Catch, *Carbon-14 Compounds*, p. 6, Butterworths, London (1961).

<sup>53</sup> P. E. Yankwich and W. R. Cornman, *J. Am. Chem. Soc.* **78** (1956) 1560.

<sup>54</sup> V. F. Raaen, G. A. Ropp and H. P. Raaen, *Carbon*, p. 14, McGraw Hill, New York (1968).

<sup>55</sup> *The Radiochemical Manual*, 2nd ed., p. 38, Radiochemical Centre, Amersham (1966).

<sup>56</sup> A. G. Maddock and E. H. Willis, *Adv. in Inorg. and Radiochem.* **3** (1961) 287.

TABLE 4. RADIOACTIVE NUCLIDES OF CARBON

Isotope	Production	Half-life	Decay
$^9\text{C}$	$^{10}\text{B}(p, 2n)^a$ $^{11}\text{B}(p, 3n)^a$	0.127 s <sup>a</sup>	$\beta^+$ <sup>a</sup>
$^{10}\text{C}$	$^{10}\text{B}(p, n)^b$	19.48 s <sup>c</sup>	$\beta^+$ <sup>d</sup>
$^{11}\text{C}$	$^{10}\text{B}(p, \gamma)^e$ $^{10}\text{B}(d, n)^f$ $^{11}\text{B}(p, n)^e$ $^{14}\text{N}(p, \alpha)^e$	20.34 m <sup>g</sup>	$\beta^+$ <sup>h</sup>
$^{14}\text{C}$	$^{14}\text{N}(n, p)^i$ $^{13}\text{C}(d, p)^j$	5685 y <sup>k</sup>	$\beta^-$ <sup>l</sup>
$^{15}\text{C}$	$^{14}\text{C}(d, p)^m$	2.5 s <sup>n</sup>	$\beta^-$ <sup>m</sup>
$^{16}\text{C}$	$^{14}\text{C}(t, p)^o$	0.74 s <sup>o</sup>	$\beta^-$ <sup>o</sup>

<sup>a</sup> J. C. Hardy, R. I. Verrall, R. Barton and R. E. Bell, *Phys. Rev. Letters*, **14** (1965) 376.

<sup>b</sup> R. Sherr, H. R. Muether and M. G. White, *Phys. Rev.* **74** (1948) 1239A.

<sup>c</sup> L. G. Earwater, J. G. Jenkin and E. W. Titterton, *Nature*, **195** (1962) 271.

<sup>d</sup> R. Sherr, H. R. Muether and M. G. White, *Phys. Rev.* **75** (1949) 282.

<sup>e</sup> W. H. Barkas, *Phys. Rev.* **56** (1939) 287.

<sup>f</sup> J. D. Cockroft, G. W. Gilbert and E. T. S. Walton, *Proc. Roy. Soc. (London)*, **148A** (1935) 225.

<sup>g</sup> T. M. Kavanagh, J. K. P. Lee and W. T. Link, *Can. J. Phys.* **42** (1964) 1429.

<sup>h</sup> J. Scobie and G. M. Lewis, *Phil. Mag.* **2** (1957) 1089.

<sup>i</sup> S. Ruben and M. D. Kamen, *Phys. Rev.* **59** (1941) 349.

<sup>j</sup> W. F. Libby, *Radio Carbon Dating*, 2nd ed. University of Chicago Press, Chicago (1955).

<sup>k</sup> I. U. Olsson and I. Karlen, *Radioactive Dating*, p. 3, International Atomic Energy Agency, Vienna (1963).

<sup>l</sup> M. D. Kamen and S. Ruben, *Phys. Rev.* **58** (1940) 194A.

<sup>m</sup> E. L. Hudspeth, C. P. Swann and N. P. Heydenburg, *Phys. Rev.* **77** (1950) 736; *ibid.* **80** (1950) 643.

<sup>n</sup> J. B. Nelson, E. L. Hudspeth and E. M. Bernstein, *Phys. Rev.* **136** (1964) 371.

<sup>o</sup> S. Hinds, R. Middleton, A. E. Litherland and D. J. Pullen, *Phys. Rev. Letters*, **6** (1961) 113.

react with oxygen and are present in the earth's atmosphere as  $^{14}\text{CO}_2$ . If several half-lives have elapsed, i.e.  $> 30,000$  years, and, if it is assumed that the nature and intensity of the cosmic radiation has remained constant over this period of time, then a stationary concentration of  $^{14}\text{CO}_2$  will be set up. The activity of living matter is approximately 15.3 disintegrations per gram per minute. However, in dead material  $^{14}\text{C}$  is not replaced by the "carbon cycle" (see p. 1174) and consequently the activity decreases. Since the half-life of  $^{14}\text{C}$  is known, the decrease in activity may be related to the age of the material. Thus the linen covering of the scrolls of the Book of Isaiah found amongst the Dead Sea Scrolls



TABLE 5. PRODUCTS OF THE DISSOLUTION OF NEUTRON-IRRADIATED  $\text{Be}_3\text{N}_2$  in 1 M  $\text{H}_2\text{SO}_4$ 

Product	% activity
Methane	26
Carbon dioxide	14
Guanidine	19
Methyl hydrazine	11
Formic acid	8
Hydrogen cyanide	7
Urea	6
Cyanamide	5
Methylamine	4
Formaldehyde	2

was dated  $35 \text{ B.C.} \pm 200$  years. This relatively large uncertainty arises from the difficulty of the exact measurement of low specific activity of the low energy (0.158 MeV)  $\beta$ -emitter.

There is, of course, considerable health hazard in the use of radioactive carbon compounds. For  $^{14}\text{C}$ , the most widely used radioisotope, the tolerance doses are<sup>57</sup>:

Whole body burden	300 $\mu\text{c}$
Maximum permissible concentration in drinking water	$8 \times 10^{-3} \mu\text{c ml}^{-1}$
Maximum permissible concentration in air	$4 \times 10^{-6} \mu\text{c ml}^{-1}$

#### 1.4. PHYSICAL PROPERTIES

It will be convenient in this section to discuss first the general thermodynamic properties of carbon (as graphite or diamond) and then those physical properties related to the isolated carbon atom. Subsequently those physical properties peculiar to the diamond lattice will be discussed. Properties associated with the diamond-graphite transition have already been covered. Other physical properties of graphite are discussed in section 4.

##### Solid-Vapour Equilibrium

As indicated earlier<sup>33</sup>, at atmospheric pressure carbon sublimes above  $4000^\circ\text{K}$ . Its melting point is  $\sim 4000^\circ\text{K}$  at a pressure of 10 kbar.

The heat of sublimation of graphite has been the subject of extensive investigation<sup>58</sup>. Erroneous values were first obtained because of the failure to recognize the existence of polyatomic species in the vapour. Mass spectrometric analysis of the vapour from a heated graphite filament subsequently<sup>59</sup> indicated that it consisted largely of  $\text{C}_3$  species and a

<sup>57</sup> Radiation Protection, *Recommendations of the International Commission on Radiological Protection*, Pergamon, London (1959).

<sup>58</sup> H. B. Palmer and M. Shelef, in *Chemistry and Physics of Carbon*, vol. 4, p. 85, Ed. P. L. Walker, Arnold, London (1968).

<sup>59</sup> R. E. Honig, *J. Chem. Phys.* **22** (1954) 126.

value of the heat of sublimation to monatomic gas of  $\sim 170$  kcal mole $^{-1}$  was obtained. Heats of sublimation of the  $C_2$  and  $C_3$  species were respectively 210 and 190 kcal mole $^{-1}$  corresponding to values of  $D(C-C)$  of 130 and 160 kcal mole $^{-1}$  in  $C_2$  and  $C_3$  respectively. This would indicate that the bonding in these species is double bond in character. Qualitatively similar conclusions were reached by mass spectrometric analysis of the vapour effusing from a Knudsen cell<sup>60</sup> though the heat of formation of  $C_3$  is still very much in dispute<sup>61</sup>.

The complex nature of carbon vapour is shown by experiments in which graphite was vaporized using a ruby laser. Although the average molecular weight of the vapour was 22, species from  $C_1$ – $C_{10}$  were observed in the mass spectrometer. The order of importance of these species was  $C_2 = C_3 > C_1 > C_5 > C_4 > C_6 = C_7 = C_8 = C_9 = C_{10}$ . Moreover, in the electrical discharge between graphite electrodes, ions up to  $C_{31}^+$  and  $C_{35}^-$  were observed<sup>62</sup>. The properties of carbon vapour have been calculated using molecular orbital theory<sup>63</sup> and indicate the growth of linear polyatomic species at high temperature. Species containing odd numbers of carbon atoms would have closed shell structures and consequently lower energies than even species. Extrapolation of the calculations to liquid carbon show that this should consist of an essentially infinite chain of carbon atoms and that the heats of fusion and vaporization at 4000°K would be  $\sim 10$  and  $\sim 7$  kcal mole $^{-1}$  respectively.

The heat of sublimation of graphite to ideal monatomic gas is best calculated from consideration of the following reactions:



It follows that  $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$ . At 0°K the values of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  are  $-27.1995$ ,  $255.764$  and  $-58.989$  kcal mole $^{-1}$  respectively<sup>64</sup> and hence  $\Delta H_4$  at 0°K is  $169.58 \pm 0.45$  kcal mole $^{-1}$ . Similarly  $\Delta H_4$  at 298.15°K is  $170.89 \pm 0.45$  kcal mole $^{-1}$ . The heat of sublimation is, of course, of some considerable interest in determining the average bond energy in carbon compounds. The relevant energy changes for the determination of the mean C–H bond energy are summarized in Fig. 5.

It is clear from Fig. 5 that  $4D(C-H) = 4\Delta H_f^\circ(H) + \Delta H_4 - \Delta H_f^\circ(CH_4)$ , where  $D(C-H)$  is the mean carbon–hydrogen bond energy in methane.  $\Delta H_f^\circ(H)$  and  $\Delta H_f^\circ(CH_4)$  are<sup>64</sup>  $52.102$  and  $-17.895$  kcal mole $^{-1}$  respectively at 298°K and hence  $D(C-H)$  is 94.8 kcal.

The vapour pressure of graphite<sup>65</sup> is given by the equation

$$\log p = A - \frac{B}{T} + CT + \log T$$

where  $p$  is the vapour pressure in mm Hg. Values of the constants  $A$ ,  $B$ ,  $C$  and  $D$  are given in Table 6. Values of the known heats of formation of the carbon species are summarized in Table 7. The alternation in bond energy values confirms the predicted stability of odd carbon atom species. In Table 8 are given values of the heat capacity, entropy and heat of formation of ideal monatomic carbon gas.

<sup>60</sup> W. C. Chupka and M. G. Inghram, *J. Phys. Chem.* **59** (1955) 100.

<sup>61</sup> P. D. Zavitsanos, *Carbon*, **6** (1968) 731.

<sup>62</sup> E. Dornenburg and H. Hintenberger, *Z. Naturforsch.* **14a** (1959) 756.

<sup>63</sup> K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81** (1959) 4477.

<sup>64</sup> *JANAF Thermochemical Tables*, PB 168,370, U.S. Department of Commerce (1965).

<sup>65</sup> A. N. Nesmeyanov, *Vapour Pressure of the Chemical Elements*, p. 426, Elsevier, Amsterdam (1963).

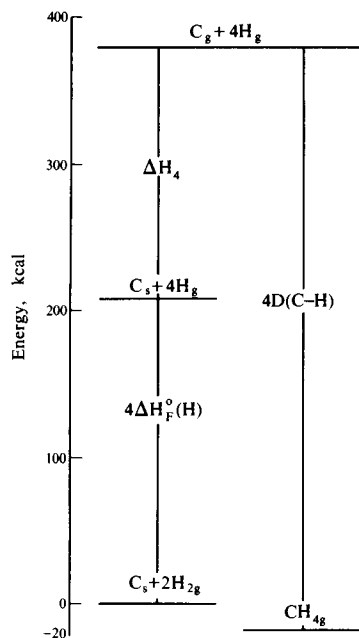


FIG. 5. Formation of methane.

TABLE 6. CONSTANTS IN CARBON VAPOUR PRESSURE EQUATION

Species	<i>A</i>	<i>B</i>	$10^3C$	<i>D</i>
C <sub>1</sub>	44·68828	40986·66	1·55119	−10·59350
C <sub>2</sub>	23·26799	45208·60	0·09799	−3·01924
C <sub>3</sub>	22·118749	42848·50	0·00088	−2·23269
Σ C	−273·33943	379403·72	−96·48412	195·90478

TABLE 7. THERMODYNAMIC DATA FOR CARBON SPECIES<sup>a</sup>

Species	$\Delta H^\circ 0^\circ\text{K}$	Average C-C bond energy kcal mole <sup>−1</sup>
C <sub>1</sub>	169·58	—
C <sub>2</sub>	198·0	141·2
C <sub>3</sub>	188·1	160·4
C <sub>4</sub>	240·5	146·0
C <sub>5</sub>	240·3	151·9
C <sub>6</sub>	≥ 280	≤ 148
C <sub>7</sub>	≥ 270	≤ 152

<sup>a</sup> J. Drowart, R. P. Burns, G. De Marie and M. G. Inghram, *J. Chem. Phys.* **31** (1959) 1131.

TABLE 8. THERMODYNAMIC DATA FOR IDEAL MONATOMIC CARBON GAS<sup>a</sup>

$T, ^\circ\text{K}$	$C_p^\circ, \text{cal mole}^{-1} \text{deg}^{-1}$	$S^\circ, \text{cal mole}^{-1} \text{deg}^{-1}$	$\Delta H_f^\circ, \text{kcal mole}^{-1}$
0	0.000	0.000	169.576
100	5.085	32.283	170.132
200	4.997	35.770	170.557
298	4.981	37.761	170.886
300	4.981	37.792	170.891
500	4.973	40.334	171.321
1000	4.969	43.779	171.552
2000	5.008	47.229	170.913
3000	5.168	49.287	170.024
4000	5.345	50.799	169.149
5000	5.468	52.006	168.261
6000	5.541	53.010	167.272

<sup>a</sup> See ref. 64.

The heat of formation of graphite is, by definition, 0.000 and  $\Delta H_f^\circ$  (diamond) is 0.453 kcal mole<sup>-1</sup> at 298°K.

### The Carbon Atom

The <sup>12</sup>C nucleus consists of 6 protons and 6 neutrons and has zero spin. Equally <sup>14</sup>C has zero spin. The <sup>13</sup>C nucleus, however, has 6 protons and 7 neutrons and its spin is  $\frac{1}{2}$ . Its magnetic moment is 0.70216 nuclear magnetons<sup>66</sup>.

Ionization potentials have been determined spectroscopically and are summarized in Table 9. The ionization potential of an ideal graphite sheet has been calculated<sup>67</sup> to be 4.3 eV and is in good agreement with the experimental value<sup>68</sup>. For this structure, the electron affinity is the same as the ionization potential.

TABLE 9. IONIZATION POTENTIALS OF CARBON

Ion	$I, \text{eV}$
C <sup>+</sup>	11.264 <sup>a</sup>
C <sup>2+</sup>	24.376 <sup>b</sup>
C <sup>3+</sup>	47.871 <sup>b</sup>
C <sup>4+</sup>	64.476 <sup>b</sup>
C <sup>5+</sup>	391.986 <sup>b</sup>
C <sup>6+</sup>	489.84 <sup>b</sup>

<sup>a</sup> S. Stokes and A. B. F. Duncan, *J. Am. Chem. Soc.* **80** (1958) 6177.

<sup>b</sup> C. E. Moore, *National Bureau of Standards, Circular* 647, vol. 3, p. xxxiv (1958).

<sup>66</sup> J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance*, vol. 2, p. 1109, Pergamon, London (1966).

<sup>67</sup> N. S. Hush and J. A. Pople, *Trans. Faraday Soc.* **51** (1955) 600.

<sup>68</sup> R. S. Mulliken, *Phys. Rev.* **74** (1948) 736.

The electron affinities of the  $C_1$ – $C_3$  species have been determined by mass spectrometric studies of the molecular sublimation of graphite and by photodetachment studies and the results are given in Table 10.

TABLE 10. ELECTRON AFFINITIES OF CARBON SPECIES

Species	$E$ , eV
$C_1$	1.25 <sup>a</sup>
$C_2$	3.1 <sup>b</sup>
$C_3$	1.8 <sup>b</sup>

<sup>a</sup> M. L. Seman and L. M. Branscomb, *Phys. Rev.* [2] **125** (1962) 1605.

<sup>b</sup> See ref. 59.

Detailed calculations of the ionization potentials and electron affinities of selected orbitals of the valence states of carbon have been carried out<sup>69</sup> and the electronegativities are given in Table 11.

TABLE 11. ELECTRONEGATIVITIES OF THE CARBON ATOM

State	Hybridization	Electronegativity
Tetrahedral	$sp^3$	2.50
Trigonal	$sp^2$	2.74
Digonal	$sp$	3.20

The electron configurations in and the energies of the ground state and the lowest excited states of carbon are given in Table 12.

TABLE 12. GROUND AND EXCITED STATES OF CARBON

Electron configuration	Symbol	Energy, eV <sup>a</sup>
$2s^22p^2$	$^3P$	0.000
$2s^22p^2$	$^1D$	1.259
$2s^22p^2$	$^1S$	2.676
$2s2p^3$	$^5S^o$	4.170

<sup>a</sup> C. E. Moore, *National Bureau of Standards Circular 647*, vol. 1, p. 21 (1949).

<sup>69</sup> G. Pilcher and H. A. Skinner, *J. Inorg. and Nucl. Chem.* **24** (1962) 937.

In its ground state the carbon atom would be divalent, but in its  $^5S^0$  state tetravalent. The characteristic tetrahedral distribution of groups around a saturated carbon atom is attributable to  $sp^3$  hybridization. The nature of the bonding of carbon to other atoms is affected by the particular valence state of carbon. Data for C-H bonding are given in Table 13.

TABLE 13. EFFECT OF VALENCE STATE OF CARBON ON BONDING

Molecule	Hybridization	$r(\text{C-H})$ , nm	Stretching force constant, $10^5 \text{ dyne cm}^{-1}$	C-H bond dissociation energy, $\text{kcal mole}^{-1}$
$\text{CH}_4$	$sp^3$	0.1090	5.387	103
$\text{C}_2\text{H}_4$	$sp^2$	0.1069	6.126	106
$\text{C}_2\text{H}_2$	$sp$	0.1060	6.397	121
radical CH	$p$	0.1120	4.490	80

The covalent radius of the carbon atom is best determined as one half of the C-C bond distance in diamond, viz. 0.077 nm. The corresponding values for the doubly bonded and triply bonded carbon atoms are 0.067 and 0.060 nm respectively<sup>70</sup>.

Ionic radii are summarized in Table 14.

TABLE 14. RADII OF CARBON IONS

Species	$r$ , nm	Reference
$\text{C}^+$	0.028	a
$\text{C}^{2+}$	0.022	a
$\text{C}^{3+}$	0.017	a
$\text{C}^{4+}$	0.015	a
$\text{C}^-$	0.137	b
$\text{C}^{4-}$	0.260	c

<sup>a</sup> K. Stockar, *Helv. Chim. Acta*, **33** (1950) 1418.

<sup>b</sup> G. Gattow, *Z. anorg. und allgem. Chem.* **294** (1958) 205.

<sup>c</sup> L. Pauling, *J. Am. Chem. Soc.* **49** (1927) 765.

### Diamond<sup>71</sup>

As indicated earlier, because of the strong C-C bonding throughout the lattice, diamonds are extremely hard and involatile with extremely low coefficients of thermal ex-

<sup>70</sup> L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., p. 224, Cornell University Press, Ithaca, N.Y. (1960).

<sup>71</sup> R. Berman (Ed.), *Physical Properties of Diamond*, Clarendon Press, Oxford (1965).

pansion—amongst the lowest of all known materials. Thus at 298·16°K the linear coefficient of expansion is  $1.06 \times 10^{-6}$  and its dependence on temperature is given<sup>72</sup> by

$$\alpha_e = 0.09613 \times 10^{-5} + 3.522 \times 10^{-9}T - 0.0888T^{-2}$$

Diamond dust had a slightly lower coefficient of expansion than the single crystal.

Two types of diamond have been recognized<sup>73</sup>. The main properties in which they show characteristic differences are summarized in Table 15.

TABLE 15. CLASSIFICATION OF DIAMOND TYPE

Property	Type I,	Type II
Occurrence Form	Common Cubic	Rare Cubic but with fine parallel laminations
Isotropy	Considerable anisotropy between crossed nicols	Nearly isotropic
Infrared absorption	3, 4.1, 4.8 and 8 $\mu$	3, 4.1 and 4.8 $\mu$ No band at 8 $\mu$
Ultraviolet	Absorbs < 300 nm	Absorbs < 225 nm
Photoelectric- conductivity	Small, even at high voltages	Markedly photoconductive
X-ray pattern	Normal. Ratio of intensity 111/222 usually small	Normal. Ratio of intensity 111/222 usually large

Although there are characteristic differences, there is a wide range of properties, e.g. density, visible absorption, dielectric constant, etc., which are virtually the same for both types. In Table 16 are summarized data<sup>74</sup> from measurements of the dielectric constant on single crystals using a 1000 Hz source. The compressibility was found to be  $2.22 \times 10^{-7}$  cm<sup>2</sup> kg<sup>-1</sup> for both types. It is interesting that although the dielectric constant is the same for

TABLE 16. DIELECTRIC CHARACTERISTICS OF DIAMONDS

Diamond	% N	Dielectric constant $\epsilon$	$1/\epsilon \left( \frac{\partial \epsilon}{\partial P} \right)_T$ $\times 10^{-7}$ cm <sup>2</sup> kg <sup>-1</sup>	$V/\alpha \left( \frac{\partial \alpha}{\partial V} \right)_T$
Type I	0.05	$5.87 \pm 0.19$	$-2.35 \pm 0.09$	$1.50 \pm 0.10$
Type II	0.02	$5.93 \pm 0.12$	$-1.07 \pm 0.09$	$1.24 \pm 0.06$

both types there is a significant difference in the relative volume coefficient of polarizability (data of the last column). This may be due to the difference in nitrogen content. Silicon and germanium which also have diamond type crystal structures have similar values of this coefficient. As would be expected, the refractive index ( $\mu = 2.41$  at  $\lambda = 546$  nm) is independent of diamond type<sup>73</sup>.

<sup>72</sup> B. J. Skinner, *Am. Mineralogist*, **42** (1957) 53.

<sup>73</sup> R. Robertson, J. J. Fox and A. E. Martin, *Phil. Trans. Roy Soc. (London)*, **232A** (1934) 482.

The magnetic susceptibility varies from  $-0.456 \times 10^{-6}$  to  $-0.411 \times 10^{-6}$  at room temperature according to the diamond specimen<sup>75</sup> but the variation is not related to the diamond type.

The absorption spectra of both types of diamond<sup>76</sup> are shown in Fig. 6. The additional absorption bands between  $6-13 \mu$  and the absorption edge in the ultraviolet in type I diamonds both vary considerably from specimen to specimen. The energy gap<sup>77</sup> in diamond is approximately 6 eV. It seems reasonable, therefore, to attribute the absorption at 225 nm (5.6 eV) as the true absorption edge of the pure diamond lattice. This is consistent

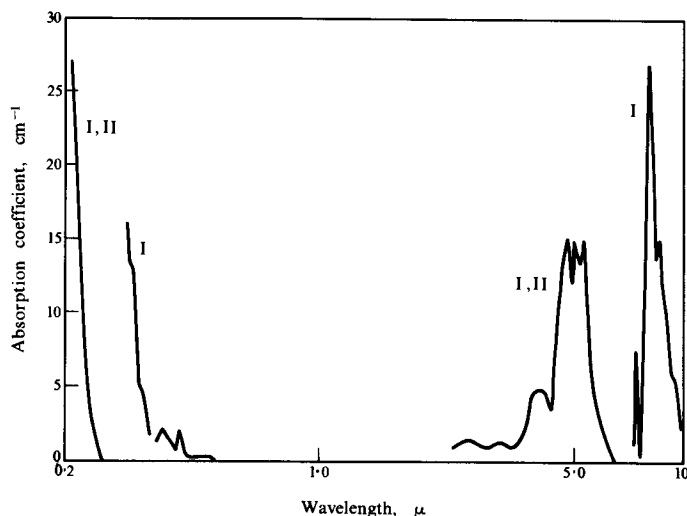


FIG. 6. Absorption spectra of type I and type II diamonds.

with the observation that this absorption is the same intensity in all diamonds and increases uniformly with increasing temperature, similar to the lattice band absorption in Si and Ge. The absorption bands between 2 and  $6 \mu$  are equally characteristic of the true diamond lattice. The additional bands are probably due to nitrogen impurity. Thus the absorption coefficient at  $7.8 \mu$  was shown<sup>76</sup> to be linearly proportional to the nitrogen content in the range 0–0.25% N. Nitrogen was determined by heating the diamond specimen to 2000°K and analysis of the residual gas, which proved to be only nitrogen, set free during graphitization of the crystal.

Slight changes in the lattice constant were observed. Thus in type II crystals,  $a_0$  was 0.356683 nm but increased to 0.356725 nm in type I crystals with the highest nitrogen content (0.25% N). This expansion indicates considerable changes of the normal diamond lattice in the neighbourhood of the nitrogen impurity. The decrease in photoconductivity of type I crystals is probably due to the nitrogen impurity. A small difference in thermal conductivity is also observed<sup>78</sup> as may be seen from Fig. 7.

<sup>74</sup> D. F. Gibbs and G. J. Hill, *Phil. Mag.* [8] **9** (1964) 367.

<sup>75</sup> A. Sigamony, *Proc. Ind. Acad. Sci.* **19A** (1944) 310.

<sup>76</sup> W. Kaiser and W. L. Bond, *Phys. Rev.* **115** (1959) 857.

<sup>77</sup> F. Herman, *Phys. Rev.* **93** (1954) 1214.

<sup>78</sup> R. Berman, E. L. Foster and J. M. Ziman, *Proc. Roy. Soc. (London)*, **237A** (1956) 347.



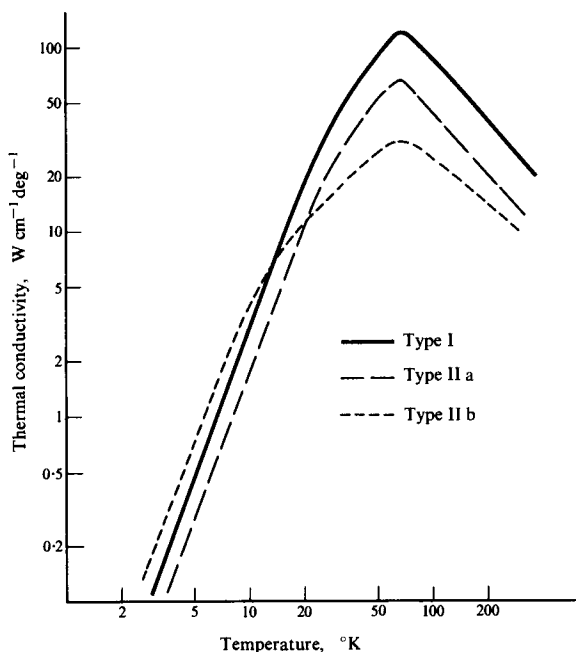


FIG. 7. Thermal conductivity of diamond.

All type I diamonds are insulators with specific resistances in the range  $5 \times 10^4$ – $10^{16}$  ohm cm<sup>79</sup>. However, type II diamonds behave either as insulators (IIA) or *p*-type semiconductors (IIB). Type IIB diamonds are characterized by strong phosphorescence when irradiated with light of 250 nm and by absorption bands at 2.5, 3.7 and 4.2  $\mu$ . The energy of the major temperature-dependent peak (0.34 eV) is similar to that of the acceptor (0.38 eV) and suggests that they are related. Resistivities are typically<sup>80</sup> in the range  $10^8$  ohm cm to 25 ohm cm.

Only a single Raman line with a frequency shift of 1332.0 cm<sup>-1</sup> appears in the first order spectrum of both diamond types<sup>81</sup>. This frequency then represents the fundamental vibration of the diamond structure. The second order spectrum shows a series of sharply defined lines with frequency shifts ranging from 2015 to 2665.4 cm<sup>-1</sup>.

### Small Carbon Molecules

The spectroscopy of the C<sub>2</sub> and C<sub>3</sub> species has been investigated in considerable detail. C<sub>2</sub> has been identified in the green part of the roaring flame of a Bunsen or Meker burner and in an electric discharge through carbon monoxide or hydrocarbon vapours. It is also produced in the thermal decomposition of C<sub>3</sub>O<sub>2</sub><sup>82</sup>. Three strong band systems are associated with this molecule and the details are summarized in Table 17.

<sup>79</sup> J. F. H. Custer, *Physica*, **20** (1954) 183.

<sup>80</sup> J. F. H. Custer, *Nature*, **176** (1955) 173.

<sup>81</sup> R. S. Krishnan and P. S. Narayanan, *J. Ind. Inst. Sci.*, **A39** (1967) 85.

<sup>82</sup> A. Klemenc, R. Wechberg and G. Wagner, *Z. Elektrochem.*, **40** (1934) 488.

TABLE 17. BAND SYSTEMS OF C<sub>2</sub>

Name	Transition	Wavelength range, nm
Swan <sup>a</sup>	$A^3\Pi_g \rightarrow X^3\Pi_u$	668–437
High pressure <sup>b</sup>	$A^3\Pi_g \rightarrow X^3\Pi_u$	785–342
Deslandres– D'Azambuja <sup>c</sup>	$c'\Pi_g \rightarrow b'\Pi_u$	410–340

<sup>a</sup> R. C. Johnson, *Phil. Trans. Roy. Soc. A226* (1927) 157.

<sup>b</sup> G. Herzberg, *Phys. Rev.* **70** (1946) 762.

<sup>c</sup> R. C. Johnson, *Nature*, **125** (1930) 89.

The potential energy curves of ground and excited states of C<sub>2</sub> have been calculated and good correlation has been obtained with the observed spectra<sup>83</sup>.

C<sub>3</sub> is best studied in the discharge between carbon electrodes in a mixture of H<sub>2</sub> and Xe though it is also observed in the discharge through flowing hydrocarbons and in very rich hydrocarbon flames. It is observed in the heads of comets. The absorption is in the range<sup>84</sup> 407–399 nm and was originally erroneously attributed to CH<sub>2</sub>. Experiments using <sup>13</sup>C and deuterium have established that the emitter is C<sub>3</sub>.

The spectrum of C<sub>4</sub> has been measured<sup>85</sup> in an argon matrix at 20°K.

### Surface Properties

As indicated earlier (p. 1177), activated carbon is used extensively as an adsorbent. The surface area may be determined from measurements of the physical adsorption of gases, e.g. N<sub>2</sub>, or of solutes from solution and typical values are in the range 100–1000 m<sup>2</sup> g<sup>-1</sup>. Not all this surface area may be available for adsorption however if the adsorbate is a large molecule.

The pore structure is the most important property of activated carbon. A study of the pore size distribution shows that three types of pore may be distinguished<sup>86</sup>:

- (a) macropores            radius 10<sup>3</sup> nm
- (b) transitional pores   radius 15 nm
- (c) micropores            radius 1 nm

The major part of the surface area arises from transitional pores and micropores and these are the most important in liquid phase and gas phase adsorption respectively. Although the macropores are relatively unimportant as far as adsorption is concerned, they are of considerable importance in that they act as arteries to allow rapid diffusion of adsorbate.

The volumes of macropores and transitional pores in a carbon solid may be determined using a high-pressure mercury porosimeter<sup>87</sup> and that of micropores as indicated above. Results for a typical activated carbon are shown in Fig. 8. In Fig. 8, the area under the

<sup>83</sup> P. F. Fougere and R. K. Nesbet, *J. Chem. Phys.* **44** (1966) 285.

<sup>84</sup> K. Clusius and A. E. Douglas, *Can. J. Phys.* **32** (1954) 319.

<sup>85</sup> W. Weltner and P. N. Walsh, *J. Chem. Phys.* **40** (1964) 1305.

<sup>86</sup> M. M. Dubinin, *Quart. Revs. (London)*, **9** (1955) 101.

<sup>87</sup> A. Cameron and W. O. Stacy, *Australian J. Appl. Sci.* **9** (1958) 283.

curve is a measure of the volume of the pore type. The properties of porous carbon solids have been well reviewed<sup>88</sup>.

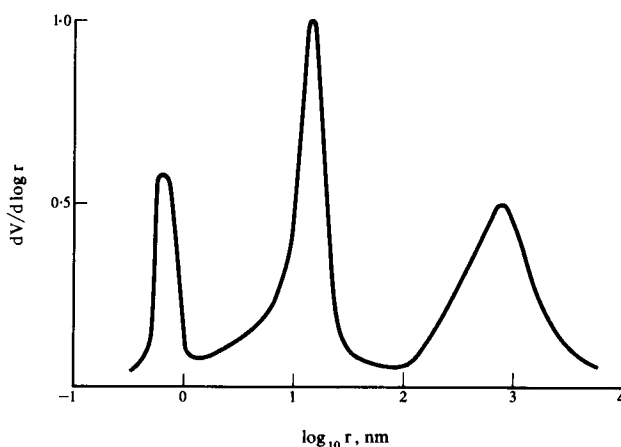


FIG. 8. Differential pore volume distribution curve for a typical activated carbon.

### 1.5. CHEMICAL PROPERTIES

Since carbon is able to form strong chemical bonds with a variety of elements (see p. 1173), it might be expected to be very reactive. However, this reactivity is offset by the high latent heat of sublimation so that at room temperature solid carbon is relatively unreactive. At high temperatures, and particularly in the vapour phase, carbon is extremely reactive. It will be convenient in this section to discuss first the chemistry of solid carbon and then the chemistry of gaseous carbon atoms. Reactions peculiar to the graphite lattice are discussed separately (see section 4). Carbon reacts with a variety of metals at high temperature to give carbides and these are discussed in section 2.

Because of the high energy of the C=O bond ( $D(\text{C}=\text{O}) = 192 \text{ kcal}$ ) carbon reacts with a variety of oxidizing agents to give carbon dioxide. Thus it readily reduces hot concentrated nitric acid or concentrated sulphuric acid.



The reactions are more complex than indicated above since mellitic acid and benzene pentacarboxylic acid have been isolated from the oxidation of carbon by sulphuric acid<sup>89</sup>. Alkali hydroxides, when fused at high temperature, oxidize carbon with the liberation of hydrogen.

The oxidation of carbon by molecular oxygen is of considerable theoretical and practical interest. Commercial interest stems both from the production of carbon monoxide (water gas) and the use of carbon (as coke) as a reducing agent in metallurgical processes.

Oxidation may proceed only to the monoxide when carbon is heated in a limited supply of air.



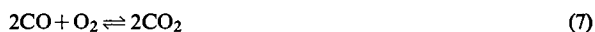
<sup>88</sup> R. L. Bond (Ed.), *Porous Carbon Solids*, Academic Press, New York (1967).

<sup>89</sup> C. L. Mantell, *Carbon and Graphite Handbook*, p. 15, Interscience, New York (1968).

or to the dioxide when heated in a current of air.



Moreover, the equilibrium



is known to exist.

Whereas reaction (5) is accompanied by a large net increase in volume, i.e.  $\Delta S$  is large, there is no increase in volume during reaction (6), i.e.  $\Delta S$  is small. As a consequence, the free energy change of reaction (5) is markedly temperature-dependent, but that of reaction (6) is almost independent of temperature. The data are presented<sup>90</sup> in Fig. 9. Detailed calculations of reaction heats, free energies, etc., have been made<sup>91</sup>.

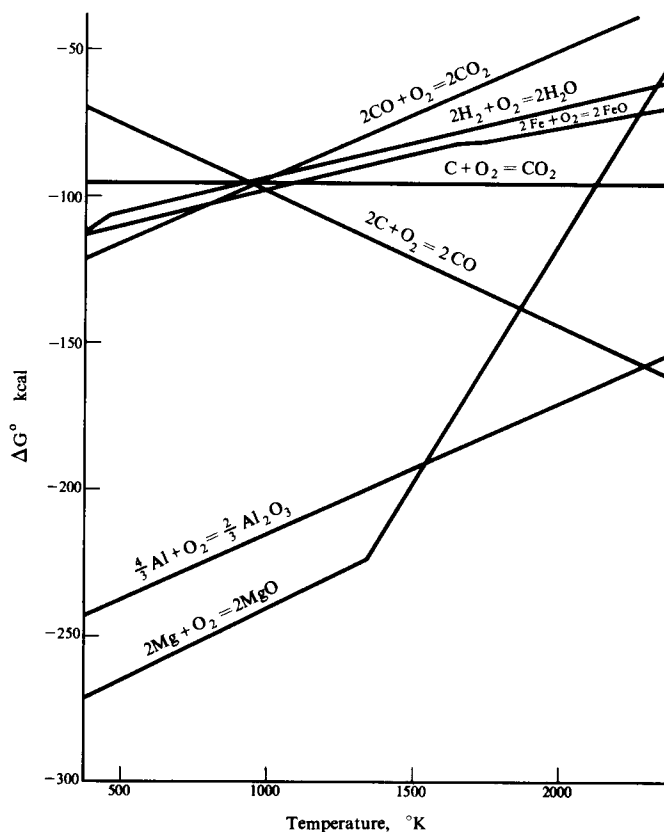
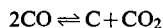


FIG. 9. Standard free energy changes for reactions of carbon.

From Fig. 9 it can be seen that the carbon lines have a common point of intersection at 983°K, i.e. at this temperature the free energies of all three reactions are equal. It follows then that the free energy of the reaction

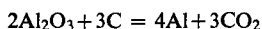


<sup>90</sup> D. J. G. Ives, *Principles of the Extraction of Metals*, R.I.C. Monograph No. 3, p. 17 (1960).

<sup>91</sup> N. V. Lavrov, V. V. Korobov and V. I. Filippova, *The Thermodynamics of Gasification and Gas Synthesis Reactions*, Pergamon, London (1963).

is zero and hence the equilibrium constant is unity at this temperature. Below this temperature CO is the stronger reducing agent and when heated alone should disproportionate, though it has been shown<sup>92</sup> that the rate of disproportionation is slow in the absence of a suitable catalyst, e.g. Fe or Ni, together with the corresponding metal oxide or graphite as a promoter. Above this temperature, carbon is the stronger reducing agent and reduction to carbon monoxide is the preferred reaction.

The marked decrease in free energy of reaction (5) with increasing temperature means that at sufficiently high temperatures carbon should be capable of reducing most metal oxides. In practice, it is difficult to work at temperatures greater than 2300°K. Reduction of metal oxides by carbon is conveniently discussed from the data presented in Fig. 9 as suggested by Ellingham<sup>93</sup>. Thus in Fig. 9 are also presented data for the Mg–MgO, Al–Al<sub>2</sub>O<sub>3</sub>, Fe–FeO and H<sub>2</sub>–H<sub>2</sub>O systems. It is clear that reduction of MgO, FeO and H<sub>2</sub>O will only take place at high temperatures since only under these conditions is the free energy of reduction negative. Reduction of Al<sub>2</sub>O<sub>3</sub> would not be expected to take place though the free energy change at 2300°K is almost zero. Industrially the reaction



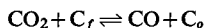
does take place at 1240°K in the Hall–Heroult aluminium process<sup>94</sup>. In this particular case the unfavourable free energy of the reaction is offset by the expenditure of considerable electrical energy. The reduction of steam is, of course, of considerable importance in the production of water gas and has been discussed earlier.

Although carbon is an effective reducing agent, kinetic as well as thermodynamic factors must be considered. Thus diamond will only burn in air above 970–1170°K, the temperature depending on the hardness of the diamond though the free energy change is favourable at low temperatures. Since the rate of reaction between two solids is usually very low, it is probable that metal oxide reductions take place via carbon monoxide as an intermediate and that the reduction occurs at the carbon monoxide–metal oxide interface. The presence of solid carbon keeps the partial pressure of the carbon dioxide formed low via the reaction



so that carbon monoxide is continually being reformed.

The kinetics of the oxidation of carbon by carbon dioxide are consistent with a scheme<sup>95</sup>



where C<sub>f</sub> and C<sub>o</sub> are free and occupied sites respectively at the surface of the carbon. Transfer of carbon from solid to gaseous phase originates from the occupied sites and may be expressed as



where n may have values 0, 1 or 2. A similar reaction scheme is postulated for the oxidation by steam. Studies of both systems in the range 1000–1700°K are consistent with an activation energy for reaction (8) of 59 kcal. The kinetics are, however, complex and are still the subject of considerable investigation.

<sup>92</sup> A. Juliard, R. Rayet and A. Ludé, *Disc. Faraday Soc.* **4** (1948) 193.

<sup>93</sup> C. W. Dannatt and H. J. T. Ellingham, *Disc. Faraday Soc.* **4** (1948) 126.

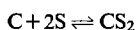
<sup>94</sup> T. G. Pearson, *The Chemical Background of the Aluminium Industry*, R.I.C. Lecture No. 3, p. 87 (1955).

<sup>95</sup> S. Ergun and M. Mentser, in *Chemistry and Physics of Carbon*, vol. 1, p. 203, Ed. P. L. Walker, Arnold, London (1965).

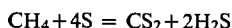
The kinetics of the oxidation of carbon (as graphite) by molecular oxygen have been investigated in some detail<sup>96</sup>. The use of optical microscopy in conjunction with single crystals of graphite has enabled the oxidation rates in the principal crystallographic axes to be measured. The rate of oxidation is extremely sensitive to the presence of impurity. Mn and Ag were found to be particularly effective catalysts of the oxidation.

Carbon does not react with nitrogen though HCN is formed<sup>97</sup> when a mixture of nitrogen and ammonia is passed over heated carbon at 2300°K (see p. 1242).

The reaction of carbon with sulphur has been known for some time. Although an oily liquid was isolated<sup>98</sup> from the reaction of heated iron pyrites with carbon in 1796, it was not recognized<sup>99</sup> as carbon disulphide, CS<sub>2</sub>, until 1814. The action of sulphur vapour with hot coke also gives rise to CS<sub>2</sub>



and was the basis of the early commercial production. Sulphur, at the base of the furnace, was heated and as the vapour rose through the red hot coke, it formed CS<sub>2</sub> which escaped at the top. Other organic sulphur compounds are probably formed and are responsible for the foul smell of the CS<sub>2</sub> produced. The kinetics of the formation of CS<sub>2</sub> have been investigated<sup>100</sup>. The reaction is endothermic,  $\Delta H = -22 \text{ kcal mole}^{-1}$ , and therefore requires heat to keep it going. The reaction is also reversible and at high temperatures CS<sub>2</sub> slowly decomposes. Present-day production<sup>101</sup> is via the action of sulphur vapour on methane



at high temperature in the presence of a catalyst, e.g. silica gel at 900°K or activated bauxite at 1000°K (p. 1237).

The first claim to have prepared a compound of carbon and fluorine was by Moissan who isolated supposedly CF<sub>4</sub> from the ignition of finely divided carbon in fluorine<sup>102</sup>. The material, however, had a b.p. of 258°K compared with the currently accepted value of 145°K. CF<sub>4</sub> was, however, produced from the reaction of fluorine liberated at a carbon anode<sup>103</sup> and was obtained in a pure state from the distillation of the products of the reaction of fluorine with wood charcoal<sup>104</sup>.

The reaction between carbon and fluorine may be explosive and it has been shown<sup>105</sup> that this is due to the formation of a graphite intercalation compound (CF)<sub>n</sub> (see section 4). This is a white, crystalline compound which on heating decomposes violently giving soot, CF<sub>4</sub> and higher fluorocarbons. Subsequently it was found that a controlled reaction between carbon below dull red heat and fluorine could be obtained in the presence of mercury<sup>106</sup>. 1% of mercury(II) or mercury(I) chloride, well mixed with the finely divided carbon, was sufficient to prevent explosion. The products of the reaction are summarized in Table 18.

<sup>96</sup> J. M. Thomas, in *Chemistry and Physics of Carbon*, vol. 1, p. 121, Ed. P. L. Walker, Arnold, London (1965).

<sup>97</sup> T. K. Sherwood, E. R. Gilliland and S. W. Ing, Jr., *Ind. Eng. Chem.* **52** (1960) 607.

<sup>98</sup> W. A. Lampadius, *Ann. Chim. Phys.* (1) **49** (1804) 243.

<sup>99</sup> J. J. Berzelius and A. Marcet, *Ann. Chim. Phys.* (1) **89** (1814) 83.

<sup>100</sup> H. Guerin and J. Adam-Giranne, *Compt. Rend.* **238** (1954) 583.

<sup>101</sup> H. W. Haines, *Ind. Eng. Chem. Int. Ed.* **55** (1963) 44.

<sup>102</sup> H. Moissan, *Compt. Rend.* **110** (1890) 951.

<sup>103</sup> P. Lebeau and A. Damiens, *Compt. Rend.* **182** (1926) 1340.

<sup>104</sup> O. Ruff and R. Keim, *Z. anorg. und allgem. Chem.* **192** (1930) 249.

<sup>105</sup> O. Ruff, O. Bretschneider and F. Ebert, *Z. anorg. und allgem. Chem.* **217** (1934) 1.

<sup>106</sup> J. H. Simons and L. P. Block, *J. Am. Chem. Soc.* **61** (1939) 2962.

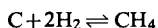
TABLE 18. PRODUCTS OF REACTION OF CARBON AND FLUORINE

	M.p., °K	B.p., °K
CF <sub>4</sub>	89	145
C <sub>2</sub> F <sub>6</sub>	172	195
C <sub>3</sub> F <sub>8</sub>	90	235
C <sub>4</sub> F <sub>10</sub>		268
C <sub>4</sub> F <sub>10</sub>		276
cyclo C <sub>5</sub> F <sub>10</sub>		296
cyclo C <sub>6</sub> F <sub>12</sub>		324
cyclo C <sub>7</sub> F <sub>14</sub>		353

The tendency of carbon to form strong bonds with fluorine,  $D(\text{C-F}) = 116$  kcal, is also evidenced by the observation<sup>107</sup> that carbon grains reacted with incandescence with NF<sub>3</sub> in a nickel tube at 420°K, although no reaction was observed at 370°K. The products were N<sub>2</sub> and CF<sub>4</sub>. The reaction with activated charcoal was explosive<sup>108</sup>.

There is no reaction between pure solid carbon and the other halogens. Evidently the lower bond strength of carbon to these halogens is not sufficient to offset the high latent heat of sublimation. However active carbon will react<sup>109</sup> with carbon tetrachloride at 1600°K, to give dichlorocarbene (CCl<sub>2</sub>) (p. 1216).

Carbon does not react with hydrogen under ordinary conditions at any appreciable rate. When hydrogen, however, is passed over powdered carbon in the presence of a finely divided nickel catalyst, methane is formed.



The reaction is reversible and calculations have been made<sup>91</sup> of the heats, free energies, etc. Thus at 298°K,  $\Delta H = -17.9$  kcal mole<sup>-1</sup> and  $\Delta G = -12.1$  kcal mole<sup>-1</sup>. Above 900°K, the free energy change is positive.

As might be expected carbon is much more reactive towards atomic free radical species. Thus (CN)<sub>2</sub>, HCN and CO<sub>2</sub> were formed during the reaction of microwave activated nitrogen with graphite, in the temperature range 1694–2365°K. The production of HCN and CO<sub>2</sub> was attributed to impurities in the nitrogen and graphite and (CN)<sub>2</sub> is probably the only true product<sup>110</sup>. The products of a microwave discharge in hydrogen at room temperature reacted with carbon to give mainly acetylene and methane but with small amounts of higher molecular weight material, including a yellow hydrocarbon solid<sup>111</sup>. Reaction only proceeded when the carbon sample was located within the discharge. Reaction probably proceeds via vaporization of the carbon and there is some evidence for CH as an intermediate. In an oxygen discharge, carbon reacted readily, either inside or outside the discharge, to give CO and CO<sub>2</sub>. Initially the ratio CO/CO<sub>2</sub> was approximately 1 but increased as oxygen was consumed. The products of an H<sub>2</sub>O discharge were H<sub>2</sub> and CO.

<sup>107</sup> J. Massonne and R. Holst, *Angew. Chem. Int. Ed.* **5** (1966) 317.

<sup>108</sup> H. P. Boehm and W. Scholz, *Ann. Chem. Liebigs*, **691** (1966) 1.

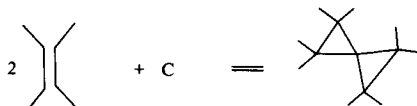
<sup>109</sup> M. Schmeisser and H. Schröter, *Angew. Chem.* **72** (1960) 349.

<sup>110</sup> H. W. Goldstein, *J. Phys. Chem.* **68** (1964) 39.

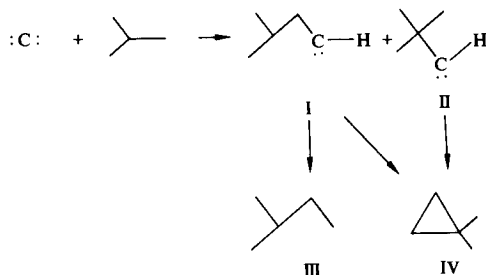
<sup>111</sup> F. J. Vastola, P. L. Walker Jr. and J. P. Wightman, *Carbon*, **1** (1963) 11.

Reactions of atomic carbon have been studied in some detail. Carbon atoms in an electric arc were observed to react with chlorine<sup>112</sup> and ethane hexachloride and hexachlorobenzene were isolated from the products. Although these observations were made at the beginning of the century, it is only in recent years that systematic measurements on the reactivity of carbon atoms have been made. The vapour from a low intensity carbon arc consists of a mixture of ground and excited states of the carbon atom<sup>113</sup>. If the vapour is condensed and allowed to age in an inert matrix at 77°K, all carbon atoms decay to the triplet ground state, <sup>3</sup>P. If, however, the vapour issuing directly from the arc is allowed to impinge on a substrate on a liquid nitrogen cooled wall, then reactions of carbon atoms in the <sup>3</sup>P, <sup>1</sup>D and <sup>1</sup>S states may be observed.

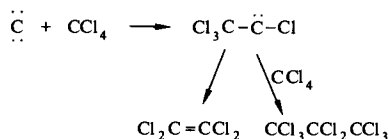
<sup>3</sup>P carbon atoms react readily, even at 77°K, with two molecules of olefin to give a spiropentane<sup>114</sup>.



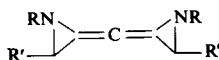
and with benzene to give toluene and cycloheptatriene<sup>115</sup>. Only <sup>1</sup>S carbon atoms, however, reacted with alkanes by insertion into a C-H bond giving a carbene which reacted further<sup>116</sup>.



The biradical I reacted either by abstracting hydrogen from the matrix to give III or by isomerization to give IV. The biradical II isomerized to give IV. Similar insertion reactions are observed with chlorinated hydrocarbons<sup>117</sup>.



With imines compounds of the type



are produced<sup>118</sup>. In general, high energy C<sub>1</sub> species were found to add stereospecifically and the lower energy species non-stereospecifically.

<sup>112</sup> W. von Bolton, *Z. Elektrochem.* **8** (1902) 203.

<sup>113</sup> P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.* **88** (1966) 3749.

<sup>114</sup> P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.* **87** (1965) 1135.

<sup>115</sup> J. L. Sprung, S. Winstein and W. F. Libby, *J. Am. Chem. Soc.* **87** (1965) 1812.

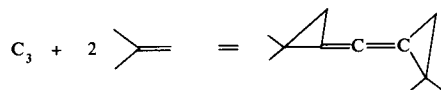
<sup>116</sup> P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.* **88** (1966) 4883.

<sup>117</sup> P. S. Skell and R. F. Harris, *J. Am. Chem. Soc.* **87** (1965) 5807.

<sup>118</sup> I. E. D. Besten and C. W. Wenger, *J. Am. Chem. Soc.* **87** (1965) 5500.



As discussed earlier,  $C_3$  is an important intermediate in carbon vapour and is also present then when the vapour is condensed. Its spectrum in neon, argon and xenon matrices has been measured<sup>119</sup>. It is stable in a paraffin hydrocarbon matrix at 77°K showing that it does not possess insertion properties. However, it adds to olefins giving bisethanoallenes<sup>120</sup>.



It adds stereospecifically to *cis*- and *trans*-2-butene indicating that its ground state is singlet. However, when it is deposited simultaneously with the butenes at 77°K non-stereospecificity is observed indicating that a short-lived triplet state exists.

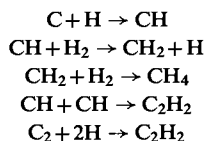
Reaction of condensed carbon vapour with boron compounds has been investigated. With  $B_5H_9$ , products found<sup>121</sup> were  $B_5CH_7$  and possibly  $B_5C_2H_7$ . With  $B_2Cl_4$  the products were  $^{122}C(BCl_2)_4$ ,  $(Cl_2B)_3CCl$  and  $(Cl_2B)_2CCl_2$ .

Thermal carbon atoms in the gas phase have been produced by a microwave discharge in carbon suboxide<sup>123</sup>. Recombination of carbon atoms took place very readily confirming that they were present in the ground electronic state since electronic excitation energy could not be accommodated in the  $C_2$  species. Rate constants for reactions of  $^3P\ C$  with several small molecules were obtained and the data are given in Table 19. Apart from its reaction

TABLE 19. RATE CONSTANTS FOR REACTIONS OF  $^3P\ C$

Substrate	$10^{-7}k$ , l mole <sup>-1</sup> s <sup>-1</sup>
C	1300
O <sub>2</sub>	150
H <sub>2</sub>	< 0.0004
CH <sub>4</sub>	< 0.0038
C <sub>2</sub> H <sub>4</sub>	< 0.0038
C <sub>2</sub> H <sub>2</sub>	< 0.0038

with oxygen, it is relatively unreactive in contrast to the situation in the condensed phase. Presumably in the condensed phase energetic intermediates are more easily able to dissipate their energy and thus be stabilized. However, if hydrogen was simultaneously passed through the discharge, reaction to give acetylene and methane was observed. The carbon atoms are much more reactive towards free radical intermediates. The following sequence of reactions was proposed:



<sup>119</sup> W. Weltner, Jr., P. N. Walsh and C. L. Angell, *J. Chem. Phys.* **40** (1964) 1299.

<sup>120</sup> P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein and R. R. Engel, *J. Am. Chem. Soc.* **87** (1965) 2829.

<sup>121</sup> S. R. Prince and R. Schaeffer, *Chem. Commun.* (1968) 451.

<sup>122</sup> J. E. Dobson, P. M. Tucker, R. Schaeffer and F. G. A. Stone, *Chem. Commun.* (1968) 452.

<sup>123</sup> F. F. Martinotti, M. J. Welch and A. P. Wolf, *Chem. Commun.* (1968) 115.

Carbon atoms may also be produced by the photolysis of cyanogen azide,  $\text{N}_3\text{CN}$ , in suitable matrices, e.g. Ar,  $\text{N}_2$  at cryogenic temperatures with light of wavelength  $< 280$  nm. Photolysis with light of wavelength  $> 280$  nm produces the triplet species  $\text{NCN}^{124}$ . The carbon atoms thus produced react readily with carbon monoxide<sup>125</sup>, fluorine<sup>126</sup>, chlorine and hydrogen chloride<sup>127</sup> to produce the radicals  $\text{CCO}$ ,  $\text{CF}_2$ ,  $\text{CCl}_2$  and  $\text{HCCl}$  respectively.

Reactions of energetic carbon atoms produced via the reaction  $^{14}\text{N}(n, p)^{14}\text{C}$  have been investigated. With ammonia at room temperature, the products are  $\text{CH}_4$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_2\text{NH}_2$ . All the  $\text{CH}_2\text{NH}_2$  and part of the  $\text{CH}_3\text{NH}_2$  are only formed from energetic carbon atoms but the  $\text{CH}_4$  arises entirely from the reaction of carbon atoms that have been first thermalized<sup>128</sup>. Reactions of carbon atoms formed in nuclear processes have been reviewed<sup>129</sup>.

Surface reactions of carbon, especially activated carbon, may be important and have been reviewed<sup>130</sup>. Two types of reaction may be distinguished:

1. Since a pure, clean surface of carbon is only obtainable *in vacuo*, under ordinary conditions interaction with chemical groups on the surface, e.g.  $-\text{COOH}$ ,  $-\text{OH}$ , may occur. The nature of the surface group on active carbon has been studied by infrared internal reflection spectroscopy<sup>131</sup>. Peaks were observed at 1600, 1836 and 2750  $\text{cm}^{-1}$  and attributed to vinyl  $\text{C}=\text{C}$ , phenolic  $\text{O}-\text{H}$  and  $\text{C}-\text{H}$  bonds in close proximity to  $\text{C}=\text{O}$  respectively. Such studies should ultimately be able to relate the functional groups involved to the type of molecule chemisorbed.
2. At the surface of a pure carbon, there will be carbon atoms with free electrons and these will behave as essentially free radical sites. Using 2-2'-azobisisobutyronitrile as a free radical source, it was estimated that carbon black contained  $10^{20}$  surface radicals per gram.

Nitric oxide was found to adsorb normally on carbon at 119°K, though the adsorbed species is probably  $\text{N}_2\text{O}_2$ <sup>132</sup>. However, above 195°K reaction takes place to give  $\text{N}_2$  and carbon-oxygen surface complexes. This was confirmed by e.s.r. studies<sup>133</sup>.

## 1.6. HEALTH HAZARDS

The element carbon is itself relatively non-toxic. The radiological hazards of using radioactive carbon compounds have already been discussed (p.1185). The toxicities of individual carbon compounds will be discussed, if appropriate, with the chemistry of these compounds.

<sup>124</sup> D. E. Milligan, M. E. Jacox and A. M. Bass, *J. Chem. Phys.* **43** (1965) 3149.

<sup>125</sup> M. E. Jacox, D. E. Milligan, N. G. Moll and W. E. Thompson, *J. Chem. Phys.* **43** (1965) 3734.

<sup>126</sup> D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **47** (1967) 703.

<sup>127</sup> M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **47** (1967) 1626.

<sup>128</sup> F. Cacace and A. P. Wolf, *J. Am. Chem. Soc.* **87** (1965) 5301.

<sup>129</sup> A. P. Wolf, *Adv. Phys. Org. Chem.* **2** (1964) 202.

<sup>130</sup> J. B. Donnet, *Carbon*, **6** (1968) 161.

<sup>131</sup> J. S. Mattson, H. B. Mark, Jr. and W. J. Webster, Jr., *Anal. Chem.* **41** (1969) 355.

<sup>132</sup> R. Nelson Smith, D. Lessini and J. Mooi, *J. Phys. Chem.* **60** (1956) 1063.

<sup>133</sup> H. Harker, J. T. Gallagher and A. Parkin, *Carbon*, **4** (1966) 401.

### 1.7. ANALYTICAL CHEMISTRY

The microanalysis of carbon is a standard operation in many organic chemistry laboratories. Basically the method<sup>134</sup> consists in the vaporization of the organic substance in a stream of oxygen. The resulting gas is then passed through a suitable mixture to ensure complete combustion. This mixture may be copper(II) oxide, either alone or with a platinized asbestos catalyst, or catalytic combustion may be achieved by passing over platinum contacts. After removal of interfering elements (N, P, S, halogens) or their compounds the resulting gas is dried over anhydrous magnesium perchlorate and the CO<sub>2</sub> is absorbed either on soda-lime or soda-asbestos. Samples of  $5 \pm 1$  mg can be analysed in this way, the time required being usually 10–20 min. The sensitivity may be increased if the CO<sub>2</sub> is absorbed in barium hydroxide and weighed as BaCO<sub>3</sub> though this latter method is cumbersome for routine use.

The determination of carbon in steels and other alloys is of some industrial importance and may be carried out by modification of the above procedure<sup>135</sup>. The metal or alloy is combusted in oxygen at 1300–1400°K and the CO<sub>2</sub> estimated as outlined above. For refractory alloys, temperatures  $\sim 1700^\circ\text{K}$  are required and may be achieved using electric furnaces heated by silicon carbide rods.

Attempts are being made to provide continuous analysis of the carbon content of steel during its manufacture<sup>136</sup>. In the modern basic oxygen furnace, the carbon content is reduced from 4% to the desired level of about 0.04% in a critical reaction time of about 5 min. Obviously rapid and accurate analysis is desirable. Analysis may be made by using a sampling lance to obtain by remote control a sample which is then vaporized in a plasma jet and analysed spectrographically. Alternatively it may be possible to measure the oxygen potential of the melt and to correlate this with the carbon content. This latter method is the more desirable but there are still technical problems to be overcome.

## 2. CARBIDES

### 2.1. GENERAL

Carbides are formed from combination of the element carbon with other elements of approximately the same or lower electronegativity. On this basis then compounds such as CO<sub>2</sub>, CS<sub>2</sub> and, by convention, CH<sub>4</sub>, are not normally regarded as carbides and their chemistry is dealt with separately in section 3. The term "carbide" was first suggested in 1796 by de Fourcroy<sup>137</sup> as being analogous to sulphide and phosphide.

Carbides may, in general, be prepared by the following methods:

1. Direct combination of the elements at high temperature,  $> 2300^\circ\text{K}$ .
2. Reaction of the metal oxide with carbon at high temperature.
3. Reaction of the heated metal with the vapour of a suitable hydrocarbon. In some special cases, acetylene may be reacted directly with aqueous solutions of the metal salt.

<sup>134</sup> R. Goulden, in *Comprehensive Analytical Chemistry*, p. 412, Ed. C. L. Wilson and D. W. Wilson, Elsevier, Amsterdam (1960).

<sup>135</sup> H. F. Beaghill, in *Standard Methods of Chemical Analysis*, 6th ed., p. 654, Ed. F. J. Welcher, Van Nostrand, New York (1963).

<sup>136</sup> R. V. Williams, *Chemistry in Britain*, **5** (1969) 213.

<sup>137</sup> A. F. de Fourcroy, in *Encyclopédie Methodique*, Ed. L. B. G. de Morveau, Paris (1796).

These methods are discussed in more detail subsequently.

It is difficult to classify carbides simply though the following general categories may be recognized:

1. Ionic carbides.
2. Interstitial carbides.
3. Covalent carbides.

It should be emphasized, however, that several carbides exist with intermediate properties and do not readily fit in with this simple classification. These categories will now be considered in turn.

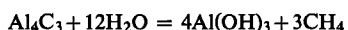
## 2.2. IONIC CARBIDES

Carbides of the more electropositive elements exist as colourless, transparent ionic crystals. They are decomposed by water or dilute acids with the evolution of hydrocarbons, indicating that carbon is present as an anion. The crystal structures have been discussed by von Stackelberg<sup>138</sup> who proposed that they be regarded as close-packed lattices of carbon anions with the cations occupying appropriate holes in the lattice. Thus, since  $r(\text{C}^{4-})$  is<sup>139</sup> 0.26 nm, then cations with  $r < 0.057$  nm may be accommodated in tetrahedral holes giving carbides of limiting formulae  $\text{M}_2\text{C}$ . Alkali metal ions, however, are too big to pack in this way, but could be packed in the larger holes of a close-packed array of  $(\text{C}\equiv\text{C})^{2-}$  ions. Although exceptions are known, it is convenient to classify ionic carbides further according to the number of carbon atoms in the anion.

### Carbides containing only one C atom in the anion

These on hydrolysis give methane, confirming the existence of the  $\text{C}^{4-}$  ion and are sometimes known as methanides.  $\text{Be}_2\text{C}$  and  $\text{Al}_4\text{C}_3$  are known. Diberyllium carbide,  $\text{Be}_2\text{C}$ , is produced<sup>140</sup> by heating carbon with  $\text{BeO}$  at 2200°K *in vacuo*. The reaction does not take place below 1970°K, and above 2370°K  $\text{Be}_2\text{C}$  is decomposed, giving graphite. It occurs as brick-red, regular octahedra having the antiferrofluoride structure, viz. beryllium ions replacing  $\text{F}^-$  and carbon ions replacing  $\text{Ca}^{2+}$  in the calcium fluoride structure.

Aluminium carbide,  $\text{Al}_4\text{C}_3$ , was first prepared<sup>141</sup> by Moissan by heating aluminium and carbon in the electric furnace. Indeed much of the early work on many of the carbides known today was pioneered by Moissan who prepared carbides of thirty-one of the elements. It occurs as pale yellow crystals, m.p. 2470°K, but sublimes *in vacuo* at 2070°K. Its crystal structure is complex<sup>142</sup>, with each carbon atom surrounded by aluminium atoms at distances 0.190–0.222 nm. The shortest C–C distance is 0.316 nm, clearly indicating the existence of discrete carbon atom units. It reacts slowly with cold water but rapidly with hot water or dilute acids giving methane with only a trace of hydrogen.



<sup>138</sup> M. von Stackelberg, *Z. Physik. Chem. (Leipzig)*, **27B** (1934) 53.

<sup>139</sup> L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., p. 514, Cornell University Press, Ithaca, N.Y. (1960).

<sup>140</sup> F. Fichter and E. Brunner, *Z. anorg. und allgem. Chem.* **93** (1915) 91.

<sup>141</sup> H. Moissan, *Compt. Rend.* **119** (1894) 15.

<sup>142</sup> A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., p. 761, Oxford University Press, Oxford (1962).

The reaction is used for the laboratory preparation of methane. With  $\text{HgCl}_2$  in aqueous hydrochloric acid it gives<sup>143</sup>  $\text{Hg}(\text{CH}_3)_2$ .



### Carbides containing 2 C atoms in the anion

This group is by far the most numerous of the ionic carbides. Carbides currently known are shown in Table 20. They are all characterized by the fact that on hydrolysis they yield acetylene and are probably better called acetylides. The existence of  $(\text{C}\equiv\text{C})^{2-}$  as a discrete unit has been confirmed<sup>144</sup> and the metal ions are in their normal oxidation state.

TABLE 20. CARBIDES CONTAINING  $(\text{C}\equiv\text{C})^{2-}$

Gp. I	Gp. II	Gp. III
$\text{Li}_2\text{C}_2$ $\text{Na}_2\text{C}_2$ $\text{K}_2\text{C}_2$ $\text{Rb}_2\text{C}_2$ $\text{Cs}_2\text{C}_2$	$\text{BeC}_2$ $\text{MgC}_2$ $\text{CaC}_2$ $\text{SrC}_2$ $\text{BaC}_2$	$\text{Al}_2\text{C}_6$
$\text{Cu}_2\text{C}_2$ $\text{Ag}_2\text{C}_2$ $\text{Au}_2\text{C}_2$	$\text{ZnC}_2$ $\text{CdC}_2$ $\text{Hg}_2\text{C}_2 \cdot \text{H}_2\text{O}$ $\text{HgC}_2$	

Alkali metal acetylides are best prepared by the action of acetylene on the solution of the metal in liquid ammonia<sup>145</sup>. The hydroacetylide,  $\text{MC}_2\text{H}$ , is first produced, but this may be converted to the acetylide and acetylene by careful heating. They are colourless, crystalline compounds which are decomposed violently by cold water. Although stable at room temperature in the air, they are readily oxidized to the carbonate on warming. There is some disagreement as to the structure of  $\text{Li}_2\text{C}_2$ , both monoclinic<sup>146</sup> and orthorhombic<sup>147</sup> structures having been proposed.  $\text{K}_2\text{C}_2$  has a face-centred tetragonal structure<sup>148</sup>.

$\text{Cu}_2\text{C}_2$ <sup>149</sup>,  $\text{Ag}_2\text{C}_2$ <sup>150</sup> and  $\text{Au}_2\text{C}_2$ <sup>151</sup> are prepared by treating ammoniacal aqueous solutions of the metal salts with acetylene. If copper(II) chloride is used, a red precipitate of  $\text{CuC}_2$  is obtained but this decomposes on drying. They are all explosive, silver acetylide particularly so.

$\text{BeC}_2$ <sup>152</sup> and  $\text{MgC}_2$ <sup>153</sup> are prepared by heating the powdered metal with acetylene at  $\sim 800^\circ\text{K}$ . The carbides of Ca, Sr and Ba may be prepared in the same way but require much higher temperatures.  $\text{CaC}_2$  is of considerable commercial importance as a source of

<sup>143</sup> S. Hilpert and M. Ditmar, *Ber. deut. chem. Ges.* **46** (1913) 3738.

<sup>144</sup> J. Schmidt, *Z. Elektrochem.* **40** (1934) 171.

<sup>145</sup> H. Moissan, *Compt. Rend.* **136** (1903) 1219.

<sup>146</sup> D. R. Secrist and L. G. Wisnyi, *Acta Cryst.* **15** (1962) 1042.

<sup>147</sup> R. Juza and W. Volker, *Naturwissenschaften*, **52** (1965) 537.

<sup>148</sup> M. von Stackelberg, *Z. Physik. Chem. (Leipzig)*, **9B** (1930) 470.

<sup>149</sup> J. Scheiber and W. Reckleben, *Ber. deut. chem. Ges.* **44** (1911) 210.

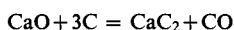
<sup>150</sup> J. Eggert, *Z. Elektrochem.* **24** (1918) 150.

<sup>151</sup> J. A. Mathews and L. L. Watters, *J. Am. Chem. Soc.* **22** (1900) 108.

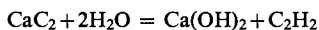
<sup>152</sup> J. F. Durand, *Bull. Soc. Chim. France*, **35** (1924) 1141.

<sup>153</sup> J. Novak, *Z. Physik. Chem. (Leipzig)*, **73** (1910) 513.

acetylene, approximately 80% of the world's supply being produced from it<sup>154</sup>. It is prepared by heating calcium oxide and carbon (coke and anthracite) at 2100–2500°K. The reaction



is endothermic,  $\Delta H = 108 \text{ kcal mole}^{-1}$ , and therefore requires considerable expenditure of energy. This is achieved either by an electric furnace (hence manufacture has been concentrated near hydroelectric power) or more recently by using an excess of coke and using the heat liberated from oxidizing this by injection of oxygen. The hydrolysis



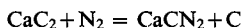
is exothermic,  $\Delta H = -26.54 \text{ kcal mole}^{-1}$ , and needs careful control. Pure  $\text{CaC}_2$  is best prepared by passing acetylene into a solution of calcium in liquid  $\text{NH}_3$  at 193°K. The crystals of  $\text{CaC}_2 \cdot \text{C}_2\text{H}_2$  thus obtained are decomposed at 600°K *in vacuo*. Physical data are summarized in Table 21.

TABLE 21. PHYSICAL CONSTANTS OF  $\text{CaC}_2^a$

Melting point	2570°K
Heat capacity	0.26 cal g <sup>-1</sup>
$\Delta H$ fusion	120 cal g <sup>-1</sup>
Density	2.2 g cm <sup>-3</sup>

<sup>a</sup> See ref. 154.

The alkaline earth carbides are generally stable in air although  $\text{BaC}_2$  absorbs atmospheric nitrogen<sup>155</sup> to give  $\text{Ba(CN)}_2$ .  $\text{CaC}_2$  reacts with nitrogen at 1300°K to give calcium cyanamide<sup>154</sup>.



This is important in the preparation of cyanamide,  $\text{H}_2\text{NC}\equiv\text{N}$  (p. 1244), which is polymerized to give melamine.  $\text{MgC}_2$  is unstable at high temperature and breaks down<sup>156</sup> to give  $\text{Mg}_2\text{C}_3$ .

At least four polymorphs of calcium carbide are known<sup>157</sup>;  $\text{CaC}_2$  IV is cubic and is stable above 720°K,  $\text{CaC}_2$  III occurs only as a metastable phase and  $\text{CaC}_2$  II is found below 298°K. The symmetries of these polymorphs are not definitely established.  $\text{CaC}_2$  I is tetragonal and is stable between 298°K and 720°K. It is the common form, occurring in commercial calcium carbide. Its crystal structure is shown in Fig. 10. The lattice is essentially that of NaCl, but because of the parallel alignment of the  $(\text{C}\equiv\text{C})^{2-}$  anions, the symmetry is reduced from cubic to tetragonal. Other alkaline earth carbides have similar structures. Lattice constants are summarized in Table 22.

A report<sup>158</sup> that  $\text{ZnC}_2$  and  $\text{CdC}_2$  could be prepared by passing acetylene over the finely divided metal at ~800°K has not been subsequently confirmed. Mercury(I) acetylide has been obtained as the hydrate,  $\text{Hg}_2\text{C}_2 \cdot \text{H}_2\text{O}$ , from the action of acetylene on an aqueous suspension of mercury(I) acetate<sup>159</sup>, but attempts to eliminate water only result in decom-

<sup>154</sup> D. W. F. Hardie, *Acetylene—Manufacture and Uses*, Oxford University Press, Oxford (1965).

<sup>155</sup> O. Kuhling and O. Berkold, *Z. angew. Chem.* **22** (1909) 193.

<sup>156</sup> M. A. Bredig, *J. Phys. Chem.* **46** (1942) 801.

<sup>157</sup> M. A. Bredig, *Z. anorg. und allgem. Chem.* **310** (1961) 338.

<sup>158</sup> J. F. Durand, *Bull. Soc. Chim. France* **35** (1924) 161.

<sup>159</sup> R. T. Plimpton and M. W. Travers, *J. Chem. Soc.* **65** (1894) 265.

position.  $\text{HgC}_2$  has been isolated from the reaction of acetylene with  $\text{K}_2\text{HgI}_4$  in aqueous solution but is unstable<sup>160</sup>.

The preparation of an aluminium acetylide,  $\text{Al}_2(\text{C}_2)_3$ , from the reaction of acetylene on finely divided aluminium at  $800^\circ\text{K}$  has been reported<sup>158</sup>, but needs to be confirmed.

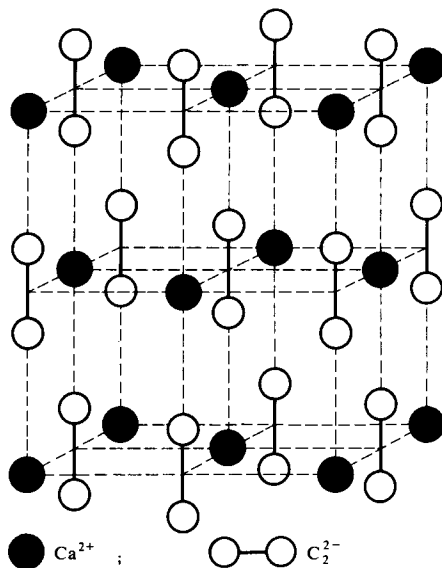


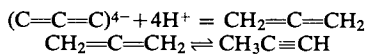
FIG. 10. Structure of  $\text{CaC}_2$  I.

TABLE 22. LATTICE CONSTANTS FOR  
TETRAGONAL ALKALINE EARTH  
CARBIDES

Crystal	$a_0$ , nm	$c_0$ , nm
Mg	0.486	0.576
Ca	0.387	0.637
Sr	0.411	0.668
Ba	0.439	0.704

### Carbides containing 3 C atoms in the anion

The only known compound is  $\text{Mg}_2\text{C}_3$ . This is best prepared by heating magnesium with methane or pentane<sup>161</sup> between  $1000$ – $1100^\circ\text{K}$ . It is also formed, as discussed earlier (see p. 1206), but contaminated with carbon, when  $\text{MgC}_2$  is heated. On hydrolysis, methyl acetylene is produced. This may arise from the interconversion of allene produced by hydrolysis of the anion.



<sup>160</sup> E. H. Keiser, *Am. Chem. J.* **15** (1893) 537.

<sup>161</sup> W. H. Frank, M. A. Bredig and K. H. Kon, *Z. anorg. und allgem. Chem.* **232** (1937) 110.

### Carbides of the lanthanides and actinides

These have the general formulae  $MC_2$  or  $M_2C_3$  (i.e.  $M_4(C_2)_3$ ) and are thus formally similar to the alkaline earth carbides. The differences are, however, sufficiently significant to warrant their being treated as a separate class. Other carbides are formed and will be considered subsequently.

They may, in general, be prepared by heating the oxides with carbon in an electric furnace or by arc melting compressed pellets of the elements in their stoichiometric proportions in an inert atmosphere<sup>162</sup>. They are attacked by water vapour and unlike the alkaline earth carbides react readily with atmospheric oxygen so that care needs to be taken to obtain them in a pure state. It is difficult to obtain  $M_2C_3$  free from  $MC_2$  impurity.

TABLE 23. LATTICE CONSTANTS FOR THE RARE EARTH CARBIDES,  $MC_2^a$

	$a_0$ , nm	$c_0$ , nm
La	0.3934	0.6572
Ce	0.3878	0.6488
Pr	0.3855	0.6434
Nd	0.3823	0.6405
Sm	0.3770	0.6331
Gd	0.3718	0.6275
Tb	0.3690	0.6217
Dy	0.3669	0.6176
Ho	0.3643	0.6139
Er	0.3620	0.6094
Tm	0.3600	0.6047
Yb	0.3637	0.6109
Lu	0.3563	0.5964
Y	0.3664	0.6169

<sup>a</sup> See ref. 162.

All carbides of the 4f and 5f elements of the type  $MC_2$  crystallize with the calcium carbide structure, except that the  $(C\equiv C)^{2-}$  ions lie along the cell axis. Lattice constants are given in Table 23. Apart from  $YbC_2$ , they show the decrease in size associated with the "lanthanide contraction".

There is, however, a significant increase in the  $(C\equiv C)^{2-}$  bond distance when compared with the alkaline earth carbides. The bond distance in  $CaC_2$  is the same as that in acetylene. Data for  $r(C\equiv C)^{2-}$  as determined by neutron diffraction are given in Table 24. Moreover, paramagnetic scattering analyses indicate that the metal atom is essentially trivalent. Presumably an electron from the metal atom is donated to the antibonding orbitals of the  $(C\equiv C)^{2-}$  ion, thus lengthening the bond. Unlike  $CaC_2$ , these carbides conduct electricity, the conductivity of  $LaC_2$  being approximately that of metallic La. Obviously there must be some delocalized interaction between the ions of the crystal<sup>163</sup>.

<sup>162</sup> F. H. Spedding, K. Gschneidner and A. H. Daane, *J. Am. Chem. Soc.* **80** (1958) 4499.

<sup>163</sup> J. Schmidt, *Z. Elektrochem.* **40** (1934) 170.



TABLE 24. VARIATION OF  $r(\text{C}\equiv\text{C})^{2-}$  IN  $\text{MC}_2$  CARBIDES<sup>a</sup>

	$r(\text{C}\equiv\text{C})^{2-}$ , nm
$\text{CaC}_2$	0.1191
$\text{YC}_2$	0.1275
$\text{LaC}_2$	0.1303
$\text{CeC}_2$	0.1283
$\text{TbC}_2$	0.1293
$\text{YbC}_2$	0.1287
$\text{LuC}_2$	0.1276
$\text{UC}_2$	0.1340

<sup>a</sup> M. Atoji, *J. Chem. Phys.* **35** (1961) 1950.

On hydrolysis, acetylene is no longer the major product and hydrogen and a variety of other organic compounds are produced. This is probably to be attributed to the more complex electronic interactions. Typical hydrolysis data for  $\text{ThC}_2$  are shown in Table 25. No hydrogen is liberated from the hydrolysis of  $\text{YbC}_2$ . This fact, together with the abnormal lattice parameters, indicate that it is probably more closely related to the alkaline earth dicarbides and may contain  $\text{Yb(II)}$ .

TABLE 25. HYDROLYSIS PRODUCTS OF  $\text{ThC}_2$  AT 353°K<sup>a</sup>

Product	% product	
	$\text{H}_2\text{O}$	2 M NaOH
$\text{H}_2$	35	36
$\text{CH}_4$	4.0	4.8
$\text{C}_2\text{H}_6$	29	29
$\text{C}_3\text{H}_8$	0.7	0.6
$\text{C}_4\text{H}_{10}$	2.8	3.2
$\text{C}_5\text{--C}_8$ alkanes	0.6	0.4
$\text{C}_2\text{H}_4$	4.5	4.6
$\text{C}_4\text{H}_8$	5.7	5.3
$\text{C}_5\text{--C}_7$ alkanes	1.7	1.3
$\text{C}_2\text{H}_2$	7.5	8.1
$\text{C}_3\text{H}_4$	1.8	1.8
$\text{C}_4\text{H}_6$	4.2	2.8
$\text{C}_6\text{H}_{10}$	0.2	0.2

<sup>a</sup> M. J. Bradley, M. D. Pattengill and L. M. Ferris, *Inorg. Chem.* **4** (1965) 1080.

In carbides of the type  $\text{M}_4(\text{C}_2)_3$ , the metal atom is again trivalent and these compounds might be expected to resemble more closely the alkaline earth carbides. There is however some lengthening of the  $(\text{C}\equiv\text{C})^{2-}$  bond<sup>164</sup>, though the effect is not as marked as for  $\text{MC}_2$  carbides.

<sup>164</sup> M. Atoji and D. E. Williams, *J. Chem. Phys.* **35** (1961) 1960.

Carbides of general formula  $M_3C$  are also formed by some of the rare earth elements<sup>162</sup>. On hydrolysis these give methane and hydrogen indicating some resemblance to the methanides.

Considerable attention has been paid to the carbides of uranium and plutonium because of their possible use in high temperature power reactor technology<sup>165</sup>. Both uranium and plutonium form carbides of formulae  $MC$ ,  $M_2C_3$  and  $MC_2$ <sup>166</sup>. They may in general be prepared by arc-melting the elements in stoichiometric composition in an inert atmosphere. The carbides are grey and metallic in appearance. The plutonium carbides react readily with water vapour and the uranium carbides will react with water under suitable conditions. They react with oxygen, some being pyrophoric. Important physical data for some of the actinide carbides are summarized in Table 26. With  $ThC_2$  the transitions monoclinic ( $\alpha$ )  $\rightarrow$  tetragonal ( $\beta$ )  $\rightarrow$  cubic ( $\gamma$ ) occur at 1700° and 1770°K respectively and for  $UC_2$  the transition tetragonal ( $\alpha$ )  $\rightarrow$  cubic ( $\beta$ ) occurs at 2038°K. The carbides of the type  $MC$  are probably interstitial (see below).

TABLE 26. PHYSICAL PROPERTIES OF THE ACTINIDE CARBIDES<sup>a</sup>

Carbide	M.p., °K	Structure	Lattice constants, nm	$\Delta H^\circ_{298^\circ K}$ , kcal mole <sup>-1</sup>
ThC	~2900	f.c.c.	$a = 0.5346$	-29.6
$\alpha$ -ThC <sub>2</sub>		monoclinic	$a = 1.0555$ $b = 0.8233$ $c = 0.4201$	-31.6
$\beta$ -ThC <sub>2</sub>	~2900 2790 decomp. 2000 2770	tetragonal		
$\gamma$ -ThC <sub>2</sub>		cubic	$a = 0.5808$	
UC		f.c.c	$a = 0.49605$	-21.1
U <sub>2</sub> C <sub>3</sub>		b.c.c.	$a = 0.80889$	-49
UC <sub>2</sub>		tetragonal	$a = 0.35241$ $c = 0.59962$	-20.0
PuC	~2000	f.c.c.	$a = 0.49730$	-12
Pu <sub>2</sub> C <sub>3</sub>	~2300	cubic	$a = 0.81256$	< -1.7
PuC <sub>2</sub>	~2600	tetragonal	$a = 0.363$ $c = 0.6094$	

<sup>a</sup> See ref. 166.

### 2.3. INTERSTITIAL CARBIDES

Interstitial carbides may be regarded formally as arising from the filling of octahedral holes in the close-packed metal atom structure<sup>167</sup>. In order to avoid significant distortion of the lattice, it can be shown that  $r_C/r_M < 0.59$  where  $r_C$  and  $r_M$  are the radii of the carbon and metal atoms respectively. Thus assuming  $r_C = 0.0772$  nm, it follows that  $r_M > 0.13$  nm. For tetrahedral holes  $r_C/r_M < 0.41$  and they would require  $r_M > 0.19$  nm. No carbides of this type are known.

In a cubic close-packed structure, the number of octahedral holes is equal to the number of metal atoms so that if all are filled, the resulting compound has the formula  $MC$  and

<sup>165</sup> L. E. Russell (Ed.), *Carbides in Nuclear Energy*, vols. 1 and 2, Macmillan, New York (1964).

<sup>166</sup> E. K. Storms, *The Refractory Carbides*, Academic Press, New York (1967).

<sup>167</sup> G. Hägg, *Z. physik. Chem. (Leipzig)*, **11B** (1931) 433.

the structure corresponds to the sodium chloride lattice with the metal atoms occupying the chloride ion positions and the carbon atoms the sodium ion positions. Filling of only half the octahedral holes leads to structures of the type  $M_2C$ . The metals Cr, Mn, Fe, Co and Ni all have atomic radii  $<0.13$  nm and the distortion of the lattice arising from the accommodation of carbon atoms leads to greater reactivity. These are best considered separately.

### Carbides of Groups IV–VI

As indicated earlier, Cr is best discussed later. The interstitial carbides formed are shown in Table 27. It is interesting that  $M_2C$  carbides are formed only with Group V and Group VI elements.

TABLE 27. INTERSTITIAL CARBIDES OF GROUPS IV–VI

Group IV	Group V	Group VI
TiC ZrC HfC	VC, $V_2C$ NbC, $Nb_2C$ TaC, $Ta_2C$	MoC, $Mo_2C$ WC, $W_2C$

TABLE 28. PHYSICAL PROPERTIES OF INTERSTITIAL CARBIDES<sup>a</sup>

	M.p., °K	Structure	Lattice constants, nm	$\Delta H^\circ_{298^\circ K}$ , kcal mole <sup>-1</sup>
TiC	3340	f.c.c.	$a = 0.43305$	–44.1
ZrC	3690	f.c.c.	$a = 0.46983$	–47.0
HfC	4220	f.c.c.	$a = 0.46402$	–50.08
VC	2970	f.c.c.	$a = 0.41655$	–24.5
$V_2C$	2440	h.c.p.	$a = 0.29020$ $c = 0.4577$	–16.5
NbC	3870	f.c.c.	$a = 0.44707$	–33.6
$Nb_2C$	3350	h.c.p.	$a = 0.3127$ $c = 0.4972$	–23.3
TaC	4270	f.c.c.	$a = 0.44555$	–34.0
$Ta_2C$	3600	h.c.p.	$a = 0.3106$ $c = 0.4945$	–24.0
MoC	2850	f.c.c.	$a = 0.42810$	–2.4
$Mo_2C$	2760	orthorhombic	$a = 0.47334$ $b = 0.60344$ $c = 0.52056$	–11.0
WC	3050	h.c.p.	$a = 0.29063$ $c = 0.28386$	–9.7
$W_2C$	2050	h.c.p.	$a = 0.29982$ $c = 0.4722$	–6.3

<sup>a</sup> See ref. 166.

In general, interstitial carbides may be prepared by heating the finely divided metal with carbon, in the absence of oxygen, at 2500°K or by heating the metal electrically in acetylene<sup>168</sup>. In this method, the metal is exploded electrically in acetylene. For this purpose, the acetylene is diluted with an inert gas, e.g. Ar, in order to avoid self-pyrolysis to graphite and hydrogen. High degrees of purity may be achieved. Physical constants are summarized in Table 28.

Since both the metal and the carbide are able to dissolve carbon, the phase diagram is usually fairly complex. Results for the Ti-C system<sup>166</sup> are shown in Fig. 11.

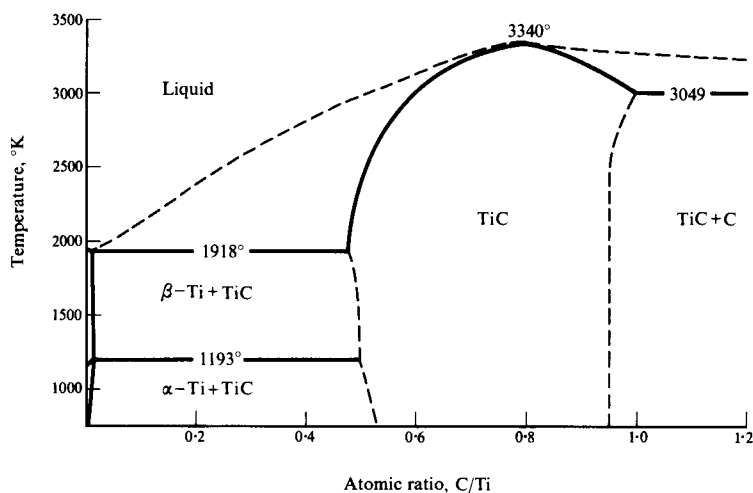


FIG. 11. Phase diagram for Ti-C.

Interstitial carbides have the characteristic properties of metallic alloys, viz. opacity, conductivity, metallic lustre, indicating that the free electron structure of the metal is probably not drastically modified by the presence of carbon. There would appear to be some stabilization of the metal lattice by carbon since the carbides often have higher melting points and are harder than the metals from which they are formed. Thus hardnesses generally lie within the range 8–10 on the Moh scale (cf. diamond 10). It is probable that the concept of a simple interstitial structure is an oversimplification and that, in fact, there exist metal-carbon bonds in the structure. This is consistent with the observation that carbides of the type MC occur with the sodium chloride structure even although the metal M may not possess a close-packed structure<sup>169</sup>. Possible types of bonding in these carbides have been reviewed<sup>170</sup>.

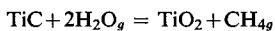
Because of their extreme hardness WC and TaC are used extensively in the production of high-speed cutting tools. The pure carbides are too brittle and are first finely powdered and then mixed with a suitable binder, e.g. powdered Fe, Mn or Co, and the mixture is then pressed into the required shape and sintered. Carbon may be sublimed from a crucible of sintered TaC.

<sup>168</sup> E. Cook and B. Siegel, *J. Inorg. and Nuclear Chem.* **30** (1968) 1699.

<sup>169</sup> R. E. Rundle, *J. Am. Chem. Soc.* **69** (1947) 1327.

<sup>170</sup> W. A. Frad, *Adv. in Inorg. and Radiochem.* **11** (1968) 153.

Unlike the ionic carbides, interstitial carbides are resistant to attack by water and are generally chemically inert. However, they can usually be dissolved in conc.  $\text{HNO}_3$  or  $\text{HF}$ . They are stable in air, but on heating in oxygen will give the oxide at temperatures  $> 800^\circ\text{K}$ .  $\text{TiC}$ ,  $\text{ZrC}$  and  $\text{VC}$  on heating in nitrogen at temperatures  $> 1300^\circ\text{K}$  give the nitride though the others are stable. Heating in hydrogen often leads to loss of carbon.  $\text{TiC}$  reacts with  $\text{CO}_2$  at  $1500^\circ\text{K}$  to give  $\text{TiO}_2$ . The relative inertness of these carbides is probably due to kinetic factors, e.g. the difficulty of attacking the interstitial carbon, since the reactions with oxygen and with water are thermodynamically favourable. Thus for the reaction



$\Delta H = -77.9 \text{ kcal mole}^{-1}$  at  $25^\circ\text{C}$ .

### Carbides of Groups VII and VIII

Chromium is included with this group. The carbides that have been identified are shown in Table 29. They may be prepared by reduction of the metal oxide with carbon at high temperatures or by direct reaction of the metal with carbon.

TABLE 29. CARBIDES OF GROUPS VII AND VIII

$\text{Cr}_{23}\text{C}_6$	$\text{Mn}_{23}\text{C}_6$	$\text{Fe}_3\text{C}$	$\text{Co}_3\text{C}$	$\text{Ni}_3\text{C}$
$\text{Cr}_7\text{C}_3$	$\text{Mn}_3\text{C}$	$\text{Fe}_2\text{C}$	$\text{Co}_2\text{C}$	
$\text{Cr}_3\text{C}_2$	$\text{Mn}_5\text{C}_2$			
	$\text{Mn}_7\text{C}_3$			
	$\text{Mn}_{15}\text{C}_4$			

The metal atom lattice is considerably distorted by the introduction of carbon atoms and, in extreme cases, there may be significant C-C interaction. Thus in  $\text{Fe}_3\text{C}$  it has been shown<sup>171</sup> that each C atom is at the centre of a nearly regular trigonal prism of iron atoms. Fe-Fe bond lengths are 0.249–0.268 nm and Fe-C bond lengths are 0.185–0.215 nm. There is no significant C-C interaction and carbon may be regarded as existing in discrete atoms in this structure. However, in  $\text{Cr}_3\text{C}_2$ , it has been shown<sup>172</sup> that the C-C bond length is only 0.165 nm. This distance is only a little longer than that in normal aliphatic chains and indicates that the carbon atoms may be regarded as existing in chains within the metal lattice. The Cr atoms are inserted between the chains such that each carbon atom is surrounded by six chromium atoms at the corner of an approximately regular trigonal prism. The Cr-C bond length is 0.202–0.207 nm.

Because of their distorted structures, the carbides are very much more reactive than those of Groups IV–VI. They may all be dissolved in dilute acids and in some cases react directly with water to give a mixture of hydrocarbons and hydrogen. Carbides of the type  $\text{M}_3\text{C}$  hydrolyse to give a gaseous mixture consisting of approximately 75%  $\text{H}_2$ , 15%  $\text{CH}_4$  and 8%  $\text{C}_2\text{H}_6$  with traces of higher hydrocarbons<sup>173</sup>. Higher hydrocarbons presumably arise from the C-C interactions in the lattice.

$\text{Fe}_3\text{C}$ , cementite, can be isolated from the smelting of iron ores with carbon. It is an important constituent of steel.

<sup>171</sup> H. Lipson and N. J. Petch, *J. Iron and Steel Inst.* **142** (1940) 95.

<sup>172</sup> K. Hellbom and A. Westgren, *Svensk. Kem. Tidskr.* **45** (1933) 141.

<sup>173</sup> W. R. Myers and W. P. Fishel, *J. Am. Chem. Soc.* **67** (1945) 1962.

## 2.4. COVALENT CARBIDES

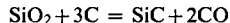
In the covalent carbides, carbon is joined by definite covalent bonds to atoms of other elements of approximately equal electronegativity. The best known examples are boron carbide,  $B_4C$ , and silicon carbide (or carborundum),  $SiC$ , although some of the ionic carbides discussed earlier, e.g.  $Be_2C$ , may have partial covalent character.

Boron carbide is prepared commercially by heating boron oxide (or boron) with carbon in an electric furnace. Currents in the range 4000–6700 A at 120 V are used<sup>174</sup>. Very pure boron carbide may be prepared<sup>175</sup> by thermal decomposition of the vapour of  $BCl_3$  and  $CCl_4$  on the surface of a heated graphite rod in the temperature range 1820–1920°K. It exists as hard, shining, black crystals and finds considerable use as a refractory and as an abrasive<sup>176</sup>. Whiskers of boron carbide may be prepared by condensing boron carbide vapour over a suitable substrate and have considerable tensile strength<sup>177</sup>.

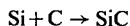
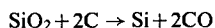
The unit cell of boron carbide contains three  $B_4C$  molecules. The boron atoms exist in icosahedral  $B_{12}$  units (as occur in boron) which are linked at some corners to similar units and at others to a linear chain of three carbon atoms. All carbon atoms exist as  $C_3$  units. Bond distances<sup>178</sup> are B–B, 0.174–0.180 nm; B–C, 0.164 nm; and C–C, 0.139 nm. That the bonding is not pure covalent, however, is indicated by the significant electrical conductivity of the crystals. Chemically it is extremely unreactive. It reacts with molten alkali to give a mixture of carbonate and borate. The carbon atoms may be replaced by atoms of silicon or aluminium<sup>179</sup> giving compounds of the type  $B_{12}C_{3-n}M_n$ .

In the gaseous phase the species  $BC_2$  and  $B_2C$  have been identified mass spectrometrically<sup>180</sup>.

Silicon carbide is produced commercially by heating silica with excess carbon in an electric furnace at 2300°K<sup>181</sup>. The overall reaction is



but it has been shown<sup>182</sup> that the reaction proceeds in the vapour phase via the steps



It can be obtained<sup>183</sup> in a pure condition from the thermal decomposition of  $CH_3SiCl_3$  in hydrogen at 1770°K. The pure compound is colourless but, on surface oxidation, exists as blue-black crystals.

The lattice of  $SiC$  consists essentially of an infinite three-dimensional array of C and Si atoms, each atom being surrounded tetrahedrally by four of the other kind. It is remarkable for the large number of its crystalline forms, over forty different polymorphs having been characterized<sup>184</sup>. Although many of these may be related basically to the structures of diamond, zincblende and wurtzite, not all growth features have been accounted for.

<sup>174</sup> J. J. Scott, U.S. Patent, 3,161,471 (1964).

<sup>175</sup> S. Mierzejewska and T. Niemyski, *J. Less-Common Metals*, **8** (1965) 368.

<sup>176</sup> *Chem. and Eng. News*, **34** (1956) 6369.

<sup>177</sup> A. Gatti, R. Cree, E. Feingold and R. Behan, NASA Contract Rept. CR-59907 (1964).

<sup>178</sup> H. K. Clark and J. L. Hoard, *J. Am. Chem. Soc.* **65** (1943) 2115.

<sup>179</sup> A. Lipp and M. Roder, *Z. anorg. und allgem. Chem.* **343** (1966) 1; *ibid.* **344** (1966) 225.

<sup>180</sup> G. Verhaegen, F. E. Stafford and J. Drowart, *J. Chem. Phys.* **40** (1964) 1622.

<sup>181</sup> *Facts about Silicon Carbide*, The Carborundum Co., Niagara Falls, New York (1963).

<sup>182</sup> H. N. Baumann, Jr., *J. Electrochem. Soc.* **99** (1952) 109.

<sup>183</sup> K. M. Merz and R. P. Adamsky, *J. Am. Chem. Soc.* **81** (1959) 250.

<sup>184</sup> A. J. Verma, *Acta Cryst.* **17** (1964) 51.

As might be expected from its structure, silicon carbide is extremely hard (9·15 on the Moh scale) and finds extensive use as an abrasive<sup>185</sup>. For this purpose, the finely ground powder is bound with clay or sodium silicate, moulded and fired. Chemically it is fairly inert though its inertness is due to kinetic rather than thermodynamic factors. It is stable to concentrated acids even on boiling. It reacts explosively, however, with potassium chromate and lead chromate on heating. At high temperatures it is somewhat more reactive. Thus it is dissolved by fused alkalis and is oxidized by O<sub>2</sub> above 1300°K. It reacts with Cl<sub>2</sub> above 1200°K to give SiCl<sub>4</sub> and C.

### 3. COMPOUNDS

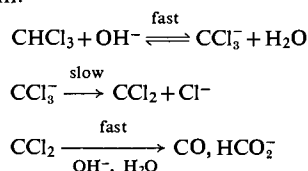
#### 3.1. CARBON-HYDROGEN COMPOUNDS

A discussion of the chemistry of these compounds lies outside the scope of this book. Some data for C-H bonding have been given in Table 13.

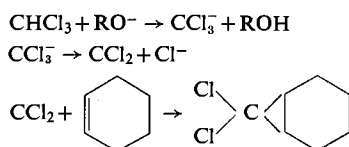
#### 3.2. CARBON-HALOGEN COMPOUNDS

##### The Dihalocarbenes<sup>186, 187</sup>

Dichlorocarbene was first postulated by Geuther in 1862 as an intermediate in the alkaline hydrolysis of chloroform.

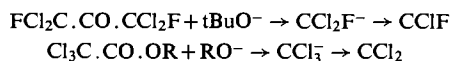


Evidence for this intermediate was given by Doering and Hofmann in 1954; dichlorocarbene was trapped by reaction with an olefin, yielding a cyclopropane derivative:

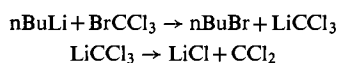


Since then CF<sub>2</sub>, CBr<sub>2</sub>, Cl<sub>2</sub>, CFCl and CClBr have all been identified.

**Preparation.** Reaction of a base with a haloform was the first general method of producing dihalocarbenes; in fact, any compound which produces an ion of the type CX<sub>3</sub><sup>-</sup> is a potential source of dihalocarbene. Thus, reactions of trihaloacetic acids and esters, and trihalomethyl ketones with bases also yield dihalocarbenes.



Dihalocarbenes may be prepared by the action of a strong nucleophile on a tetrahalomethane:

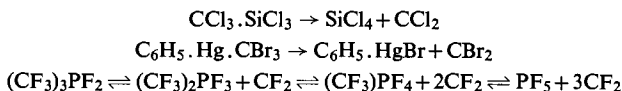


<sup>185</sup> C. M. Parche, in *Encyclopedia of Chemical Technology*, 2nd ed., vol. 4, p. 114, Ed. R. E. Kirk and D. F. Othmer, Wiley, New York (1964).

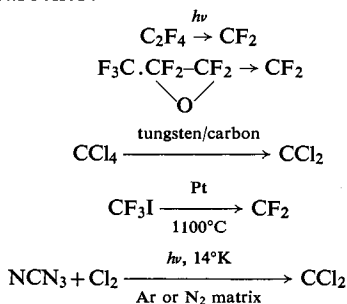
<sup>186</sup> A. Ledwith, *The Chemistry of Carbenes*, R.I.C. Lecture Series No. 5 (1964).

<sup>187</sup> J. Hine, *Divalent Carbon*, Ronald Press (1964).

A widely used preparative method for dihalocarbenes is the thermal decomposition of organometallic compounds containing a trihalomethyl group. Many of these yield dihalocarbenes at easily accessible temperatures, e.g.

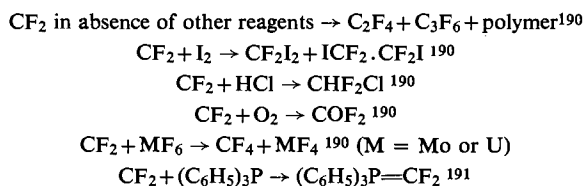


Photolysis or high-temperature pyrolysis of compounds containing CX<sub>2</sub> groups can also be used to generate dihalocarbenes:



*Properties.* The emission spectrum of difluorocarbene in the region 2400–3250 Å was observed by Venkateswarlu who suggested that it indicated that difluorocarbene was a non-linear molecule. Subsequent work confirmed that the vibrational frequencies found were consistent with a bent molecule. This suggests that difluorocarbene is in the singlet state (whereas CH<sub>2</sub> is a triplet). The C–F bond energy in CF<sub>2</sub> has been calculated as 121 kcal/mole<sup>-1</sup> (cf. CF<sub>4</sub> 123 kcal mole<sup>-1</sup>) and Δ*H*<sub>f</sub><sup>o</sup> was estimated as –35 ± 10 kcal mole<sup>-1</sup>. The microwave spectrum of difluorocarbene has been observed and the following parameters calculated: C–F 1.30 Å, <FCF 104.9°, dipole moment 0.46 *D*<sup>188</sup>. Dibromocarbene has been prepared by the co-condensation of lithium atoms and tetrabromomethane in an argon matrix at 15°K. From the observed infrared spectrum the force constants calculated indicated the C–Br was a single bond and that no π-bonding from Br to C existed<sup>189</sup>.

The carbenes are very reactive species and in the study of their reactions the carbenes themselves are generally not isolated but occur only as intermediates. Most of the reactions of dihalocarbenes, which have been studied, have been with organic molecules, in particular the addition to various multiple bonds. Some inorganic reactions of difluorocarbene which have been studied are:



<sup>188</sup> F. X. Powell and D. R. Lide, *J. Chem. Phys.* **45** (1966) 1067.

<sup>189</sup> L. Andrews and F. G. Carver, *J. Chem. Phys.* **49** (1968) 896.

<sup>190</sup> W. Mahler, *Inorg. Chem.* **2** (1963) 230.

<sup>191</sup> V. Franzen, *Angew. Chem.* **72** (1960) 566.



## The Tetrahalomethanes

TABLE 30. PHYSICAL PROPERTIES OF THE BINARY TETRAHALOMETHANES

	CF <sub>4</sub>	CCl <sub>4</sub>	CBr <sub>4</sub>	CI <sub>4</sub>
M.p. (°C)	-183.5	-22.92	90.1	171
B.p. (°C)	-128	76.72	189.5	
Density (g cm <sup>-3</sup> )	1.96	1.60178	2.9609	4.32
	liquid at -184°C	liquid at 15°C	liquid at 100°C	solid at 20°C
-ΔH <sub>f</sub> (25°) (kcal mole <sup>-1</sup> )	223.04 <sup>a</sup>	25.5 <sup>b</sup>	38 <sup>b</sup>	
D(X <sub>3</sub> C-X) (kcal mole <sup>-1</sup> )	123 <sup>c</sup>	68 <sup>c</sup>	49 <sup>d</sup>	
Energy of u.v. absorption (cm <sup>-1</sup> )		42,300 <sup>e</sup>	47,600 <sup>f</sup>	
C-X (Å)	1.317 <sup>g</sup>	1.769 <sup>h</sup>	1.94 <sup>i</sup>	2.15 <sup>i</sup>
<sup>13</sup> C chemical shift (ppm relative to CH <sub>3</sub> COOH)		81	205	

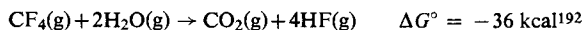
<sup>a</sup> E. Greenberg and W. N. Hubbard, *J. Phys. Chem.* **72** (1968) 222.<sup>b</sup> H. J. Bernstein, *J. Phys. Chem.* **69** (1965) 1550.<sup>c</sup> J. B. Farmer, I. H. S. Henderson, F. P. Lessing and D. G. H. Marsden, *J. Chem. Phys.* **24** (1956) 348.<sup>d</sup> M. Szwarc and A. H. Sehon, *J. Chem. Phys.* **19** (1951) 656.<sup>e</sup> J. R. Lacher, L. E. Hummel, E. F. Bohmfalk and J. D. Park, *J. Am. Chem. Soc.* **72** (1956) 5487.<sup>f</sup> L. I. Katzin, *J. Chem. Phys.* **23** (1955) 2055.<sup>g</sup> W. W. Hoffman and R. L. Livingston, *J. Chem. Phys.* **21** (1953) 565.<sup>h</sup> L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.* **23** (1955) 1854.<sup>i</sup> M. Lister and L. E. Sutton, *Trans. Faraday Soc.* **37** (1941) 393.

TABLE 31. FURTHER PHYSICAL PROPERTIES OF TETRAFLUOROMETHANE AND TETRACHLOROMETHANE

	CF <sub>4</sub>	CCl <sub>4</sub>
Critical temperature (°C)	-47.3 <sup>a</sup>	283.2 <sup>b</sup>
Critical pressure (atm)	37.0 <sup>c</sup>	45.0 <sup>b</sup>
Critical density (g cm <sup>-3</sup> )		0.5576 <sup>b</sup>
Transition point (°C)	-201.9 <sup>a</sup>	-47.41 <sup>b</sup>
ΔH <sub>fus</sub> (cal mole <sup>-1</sup> )	167.4 <sup>a</sup>	782.2 <sup>b</sup>
ΔH <sub>vap</sub> (cal mole <sup>-1</sup> )	3120 <sup>a</sup>	7170 <sup>b</sup>
ΔH <sub>transition</sub> (cal mole <sup>-1</sup> )	353.2 <sup>a</sup>	1424 <sup>b</sup>
Specific heat, 25°C (cal g <sup>-1</sup> )		0.2066 <sup>b</sup>
Vapour pressure relation	<i>B</i> 8.9250 <sup>a</sup>	8.004 <sup>d</sup>
log <sub>10</sub> <i>p</i> (mm) = <i>B</i> - <i>AT</i> <sup>-1</sup>	<i>A</i> 701.73 <sup>a</sup>	1771.3 <sup>d</sup>
		(-19°C to +20°C)
Dielectric constant, 25°C	1.0006 (vapour at 0.5 atm pressure) <sup>c</sup>	2.2270 <sup>b</sup>
Refractive index, <i>n<sub>D</sub></i>	1.151 (-73°C) <sup>c</sup>	1.46044 (20°C) <sup>b</sup>
Solubility in water, 25°C (wt. %)	0.0015 <sup>c</sup>	0.08 <sup>c</sup>
Solubility of water, 25°C (wt. %)		0.013 <sup>a</sup>

<sup>a</sup> R. D. W. Kemmitt and D. W. A. Sharp, *Adv. Fluor. Chem.* **4** (1965) 142.<sup>b</sup> J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds*, vol. 1, p. 224, Elsevier Publishing Co. Inc. (1950).<sup>c</sup> R. C. Downing, *Chemistry and Chemical Technology of Fluorine* (*Encyclopedia of Chemical Technology*, 2nd ed., vol. 9), p. 739, John Wiley and Sons (1966).<sup>d</sup> *International Critical Tables*, Vol. III, p. 215 (1928).<sup>e</sup> S. A. Miller, *Chem. and Process Eng.* (1967) 79.

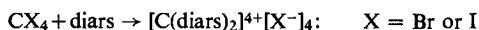
*Properties.* The thermal stability of the binary tetrahalomethanes decreases from CF<sub>4</sub> to CI<sub>4</sub>; thus tetrafluoromethane is decomposed at a tungsten wire at 1000°C, tetrachloromethane is stable up to 400°C while tetraiodomethane decomposes at 171°C without melting. Tetrafluoromethane is chemically very inert, attributed to kinetic rather than thermodynamic stability, since, for example, hydrolysis does not occur to any observable extent despite the energetic favourability.



Tetrachloromethane reacts with steam at 250°C giving carbon dioxide and hydrochloric acid, and tetraiodomethane is hydrolysed by hot water.

Pyrolysis of tetrachloromethane at 1000°C gives chlorine and C<sub>2</sub>Cl<sub>4</sub> with C<sub>2</sub>Cl<sub>6</sub>, and heating in air in the presence of iron yields phosgene. Potassium amalgam and water reduce tetrachloromethane to methane, and the reaction with sodium or sodium potassium alloy can be explosive. The reactions of tetrahalomethanes with active metals (e.g. lithium, magnesium) may be used to prepare tetra-substituted methanes.

The more reactive of the binary tetrahalomethanes have been used as a source of compounds containing unusual carbon ions. Tetrachloromethane reacts with tetrabutyl ammonium chloride to give a yellow solid adduct reported to contain the CCl<sub>5</sub><sup>-</sup> ion<sup>193</sup>. The compound (SbCl<sub>4</sub>N<sub>3</sub>)<sub>2</sub> reacts with boiling tetrachloromethane to give [C(N<sub>3</sub>)<sub>3</sub>]<sup>+</sup>SbCl<sub>6</sub><sup>-</sup><sup>194</sup>. The reaction of chelating molecules with carbon halides has been reported<sup>195</sup>, e.g. *ortho*-phenylenebisdimethylarsine (diars) (p. 1249):



Solutions of iodide ions in tetrachloromethane are reported to give a spectral band due to charge transfer from anion to solvent, the species I<sup>-</sup>.CCl<sub>4</sub> being postulated<sup>196</sup>. Tetrabromomethane forms 1:1 addition products with certain organic compounds, e.g. hexamethylene tetramine<sup>197</sup>.

*Preparation.* Tetrafluoromethane may be prepared from carborundum and fluorine or by the fluorination of carbon dioxide, carbon monoxide or phosgene with sulphur tetrafluoride. It is manufactured industrially by burning fluorine in atmospheres of chlorofluorocarbons, e.g. difluorodichloromethane or trifluorochloromethane, or by the electrolysis of group Ia and IIa fluorides with a carbon anode<sup>198</sup>. Tetrafluoromethane often accompanies other fluorinated products as a result of exhaustive fluorination of organic compounds. Tetrafluoromethane is important as an intermediate in the manufacture of polytetrafluoroethylene.

Tetrachloromethane may be prepared industrially from carbon disulphide and chlorine; in this process no coproduct chlorocarbons are produced. A suggested industrial preparation is the catalytic disproportionation of phosgene at 400°C and 10 atm. However, the most important method now used is the chlorination of methane. Tetrachloromethane has wide use as a laboratory solvent but its use as an industrial solvent has declined due to its toxicity; it is still used as a fire extinguisher but it is oxidized to phosgene under flame conditions and

<sup>192</sup> A. G. Sharpe, *Quart. Revs. (London)*, **11** (1957) 49.

<sup>193</sup> D. H. McDaniel and R. M. Dieters, *J. Am. Chem. Soc.* **88** (1966) 2607.

<sup>194</sup> U. Müller and K. Dehnicke, *Angew. Chem. Int. Ed.* **5** (1966) 841.

<sup>195</sup> R. N. Collinge, R. S. Nyholm and M. L. Tobe, *Nature*, **201** (1964) 1322.

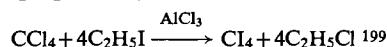
<sup>196</sup> M. J. Blaudamer, T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.* **62** (1966) 361.

<sup>197</sup> T. Dahl and O. Hassel, *Acta Chem. Scand.* **22** (1968) 372.

<sup>198</sup> M. Sittig, *Fluorinated Hydrocarbons and Polymers*, Chemical Process Monograph No. 22 (1966).

difluorodibromomethane and trifluorobromomethane are more suitable compounds. The widest industrial use of tetrachloromethane is as starting material in the manufacture of chlorofluorocarbons.

Tetrabromomethane is prepared by bromination of methane with either hydrogen bromide or bromine, or by reaction of tetrachloromethane and aluminium tribromide at 100°C. Tetraiodomethane is prepared by the reaction



It is a bright red crystalline solid with an odour reminiscent of iodine.

### Mixed Tetrahalomethanes

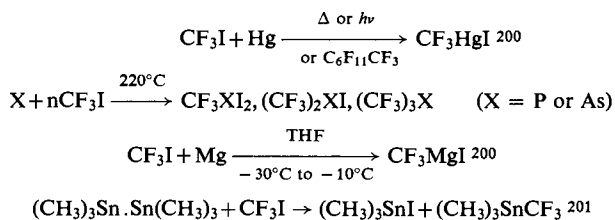
Of the mixed tetrahalomethanes the chlorofluorocarbons have the widest usage, as "freons"; these compounds having convenient physical and chemical properties for use as refrigerants and aerosol propellants. They are non-toxic, non-flammable and non-explosive. These compounds are made by the fluorination of tetrachloromethane.

TABLE 32. PHYSICAL PROPERTIES OF THE "FREONS"<sup>a</sup>

Formula	CF <sub>3</sub> Cl	CF <sub>2</sub> Cl <sub>2</sub>	CFCl <sub>3</sub>
Commercial name	Freon 13	Freon 12	Freon 11
M.p. (°C)	-181.6	-155	-110.7
B.p. (°C)	-81.2	-30	23.77
Critical temperature (°C)	28.8	111.5	198
Initial pressure (atm)	38.1	40.1	432
Δ <i>H</i> <sub>vap</sub> (cal mole <sup>-1</sup> )	3920	4850	5960
-Δ <i>H</i> <sub>f</sub> <sup>o</sup> (kcal mole <sup>-1</sup> ) (25°C)	167	112	66
Dipole moment, <i>D</i>	0.50	0.51	0.49
<sup>19</sup> F chemical shift (ppm relative to CF <sub>4</sub> )	-76.7	-60.4	-36.8

<sup>a</sup> R. D. W. Kemmitt and D. W. A. Sharp, *Adv. Fluor. Chem.* **4** (1965) 142.

Trifluoroiodomethane is a convenient starting material in the preparation of perfluoro-organometallic compounds, e.g.



Trifluoroiodomethane is prepared by the reaction of iodine with silver trifluoroacetate, or by refluxing a mixture of sodium or potassium trifluoroacetate with iodine in dimethylformamide<sup>202</sup>.

<sup>199</sup> R. E. McArthur and J. H. Simons, *Inorganic Syntheses*, **3** (1956) 37.

<sup>200</sup> M. Hudlický, *Chemistry of Organic Fluorine Compounds*, Pergamon Press (1962).

<sup>201</sup> H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.* **82** (1960) 1888.

<sup>202</sup> D. Paskovich, P. Gaspar and G. D. Hammond, *J. Org. Chem.* **32** (1967) 833.

TABLE 33. STRUCTURAL PARAMETERS OF SOME MIXED TETRA-HALOMETHANES

Compound	Bond distances (Å)		Bond angles
CBrCl <sub>3</sub>	C-Br 1.936	C-Cl 1.764	CICCl 111.2°
CBrF <sub>3</sub>	C-Br 1.908	C-F 1.330	FCF 108 ± 1°
CBr <sub>2</sub> Cl <sub>2</sub>	C-Br 1.93	C-Cl 1.75	all angles 109.5°
CBr <sub>3</sub> F	C-Br 1.91	C-F 1.44	BrCBr 114 ± 6°
CClF <sub>3</sub>	C-Cl 1.751	C-F 1.328	FCF 108.6 ± 0.4°
CCl <sub>2</sub> F <sub>2</sub>	C-Cl 1.78	C-F 1.34	{ FCF 109.5 ± 3°
			{ CICCl 108.5 ± 2°
CCl <sub>3</sub> F	C-Cl 1.76	C-F 1.40	CICCl 111.5 ± 1°
CF <sub>3</sub> I	C-F 1.332	C-I 2.126	FCF 107.5 ± 1.5°

### The Carbon Oxohalides

TABLE 34. COMPARATIVE PHYSICAL PROPERTIES OF THE CARBON OXOHALIDES

	COF <sub>2</sub>	COFCl	COFBr	COFI	COCl <sub>2</sub>	COBr <sub>2</sub>
M.p. (°C)	-114	-138	-120	-90	-127.8	
B.p. (°C)	-83.1	-42	-20.6	23.4	7.56	64.5

TABLE 35. STRUCTURAL PARAMETERS OF THE SYMMETRICAL CARBON OXOHALIDES

	COF <sub>2</sub> <sup>a</sup>	COCl <sub>2</sub> <sup>b</sup>	COBr <sub>2</sub> <sup>c</sup>
C-X (Å)	1.312	1.746	2.05
C-O (Å)	1.174	1.166	1.13
<XCX	108.0°	111.3°	110 ± 5°
Dipole moment	0.95D		

<sup>a</sup> V. W. Laurie and D. T. Pence, *J. Chem. Phys.* **37** (1962) 2995.

<sup>b</sup> G. W. Robinson, *J. Chem. Phys.* **27** (1953) 1741.

<sup>c</sup> R. W. Dornte, *J. Am. Chem. Soc.* **55** (1933) 4126.

In addition to these compounds COClBr has also been prepared.

Carbonyl fluoride is prepared by fluorinating carbonyl chloride with sodium fluoride in acetonitrile, or with antimony pentafluoride together with antimony trifluoride; or by the fluorination of carbon monoxide with silver(II) fluoride. It is produced in small amounts during the pyrolysis of polytetrafluoroethylene in air.

Carbonyl chloride, phosgene, is prepared industrially by the chlorination of carbon monoxide. It is formed when tetrachloromethane is pyrolysed in the presence of air. A

TABLE 36. PHYSICAL PROPERTIES OF CARBONYL FLUORIDE AND CARBONYL CHLORIDE

	COF <sub>2</sub> <sup>a</sup>	COCl <sub>2</sub>
Density (g cm <sup>-3</sup> )	1.139 (liquid at -114°C)	1.392 (liquid at 19°C)
Vapour pressure relation $B$ $\log_{10} p \text{ (mm)} = B - AT^{-1}$	$B$ 7.3231 $A$ 841.05	7.460 <sup>b</sup> 1289.2 <sup>b</sup> (-90°C to +25°C)
$\Delta H_{fus}$ (cal mole <sup>-1</sup> )		1371 <sup>c</sup>
$\Delta H_{vap}$ (cal mole <sup>-1</sup> )	3842	5832 <sup>c</sup>
$-\Delta H_f^\circ$ (25°) (kcal mole <sup>-1</sup> )	150.35 ± 0.5	53.30 <sup>d</sup>
Critical temperature (°C)		182 <sup>e</sup>
Critical density (g cm <sup>-3</sup> )		0.52 <sup>e</sup>
Critical pressure (atm)		56 <sup>e</sup>

<sup>a</sup> R. D. W. Kemmitt and D. W. A. Sharp, *Adv. Fluor. Chem.* **4** (1965) 142.

<sup>b</sup> *International Critical Tables*, vol. III, p. 215 (1928).

<sup>c</sup> W. F. Giaque and W. M. Jones, *J. Am. Chem. Soc.* **70** (1948) 120.

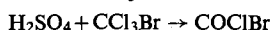
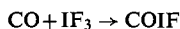
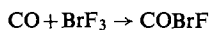
<sup>d</sup> *Selected Values of Chemical Thermodynamic Properties* (Circular of the National Bureau of Standards 500), p. 104.

<sup>e</sup> *International Critical Tables*, vol. III, p. 248 (1928).

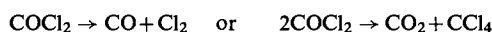
convenient laboratory preparation recently reported is the reaction of formaldehyde with tetrachloromethane in the presence of anhydrous aluminium chloride<sup>203</sup>.

Carbonyl bromide is prepared by the action of sulphuric acid on tetrabromomethane at 150°C.

Some reactions for the preparation of mixed carbon oxohalides are:

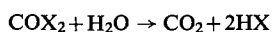


Of the carbon oxohalides carbonyl fluoride is the most thermally stable. Carbonyl chloride dissociates above 300°C by two possible routes:



The photolytic dissociation of carbonyl chloride follows the first course.

The carbon oxohalides are hydrolysed by water:



Carbonyl fluoride is a useful laboratory fluorinating agent, e.g. in the preparation of organic fluorine compounds. It has been used to prepare the perfluoromethoxides of the heavier alkali metals<sup>204</sup>:



<sup>203</sup> N. V. Kheifets, V. A. Leprev and J. N. Aisenshtadt, *J. Appl. Chem. USSR* (Eng. trans.), **41** (1968) 1321.

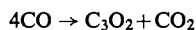
<sup>204</sup> M. E. Redwood and C. J. Willis, *Can. J. Chem.* **43** (1965) 1893.

Carbonyl chloride is a useful laboratory chlorinating agent; it reacts with many metal oxides to yield the corresponding chlorides, often in a very pure state. It reacts with metal sulphides to give carbonyl sulphide and with certain metal phosphates to give carbon dioxide, phosphorus oxychloride and metal chloride. It is reduced to carbon monoxide by hydrogen and reacts with ammonia forming primarily urea, together with other organic nitrogen compounds, e.g. guanidine, biuret  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , and cyanuric acid<sup>205</sup>. Carbonyl chloride can act as a Lewis base forming adducts with  $\text{SnCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{SbCl}_5$  and  $\text{SOCl}_2$ <sup>206</sup>.

### 3.3. CARBON-OXYGEN COMPOUNDS

#### Carbon Suboxides

Tricarbon dioxide,  $\text{C}_3\text{O}_2$ , usually known as "carbon suboxide", has been prepared by the thermal decomposition of either malonic acid  $\text{C}_3\text{H}_4\text{O}_4$  or diacetyl tartaric anhydride. Of the two methods the decomposition of malonic acid using phosphorus pentoxide is generally preferred, since, although yields are poor (20–25%), it is possible to prepare a pure sample, whereas the method from diacetyltartaric anhydride has side reactions which produce impurities such as ketene, which are very difficult to remove from carbon suboxide. Ott<sup>207</sup> has reported the production of carbon suboxide from carbon monoxide in an ozonizer:



Carbon suboxide is an evil-smelling gas, m.p.  $-112.5^\circ\text{C}$ , b.p.  $6.7^\circ\text{C}$ , v.p. at  $0^\circ\text{C}$ , 573.5 mm of Hg.  $\Delta H_f = 47.4 \text{ kcal mole}^{-1}$ . Carbon suboxide polymerizes at room temperature (see below), but can be stored for long periods at  $-78^\circ\text{C}$ .

The structure of carbon suboxide was always assumed to be a linear chain of structure  $\text{O}=\text{C}=\text{C}=\text{O}$ ; a high resolution study of the infrared spectrum by Lafferty *et al.*<sup>208</sup> verified the structure by proving that carbon suboxide has  $D_{\infty h}$  symmetry. The infrared and Raman spectra are reported variously in the literature and have been summarized by Long *et al.*<sup>209</sup>. Bond distances are given as C–C  $1.28 \text{ \AA}$  and C–O  $1.16 \text{ \AA}$ . The C=C bond length is appreciably shorter than that of ethylene and it appears that considerable delocalization is involved in this structure, as would be expected from such a chain of double bonds.

Carbon suboxide reacts with oxygen to give carbon dioxide and with water to give a quantitative yield of malonic acid. It gives malonamide  $\text{CH}_2(\text{CONH}_2)_2$  with ammonia and malonanilide with aniline; the latter reaction can be used in a quantitative estimation of carbon suboxide. Carbon suboxide reacts with hydrogen chloride and bromine to give the halogenated derivatives of malonic acid  $\text{CH}_2(\text{COCl})_2$  and  $\text{CBr}_2(\text{COBr})_2$  respectively. Carbon suboxide has considerable importance in organic synthesis, for instance it forms pyrones from acetylacetone, benzoylacetone and acetone, and forms a small amount of barbituric acid with urea, etc. A review of the uses of carbon suboxide in organic synthesis is given by Dashkevich<sup>210</sup>.

<sup>205</sup> R. Fosse, P. de Graeve and P. É. Thomas, *Compt. Rend.* **201** (1936) 1544.

<sup>206</sup> Z. Iqbal and T. C. Waddington, *J. Chem. Soc. (A)* (1968) 1745.

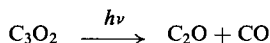
<sup>207</sup> E. Ott, *Ber.* **58** (1925) 772.

<sup>208</sup> W. J. Lafferty, A. G. Maki and E. K. Plyler, *J. Chem. Phys.* **40** (1964) 224.

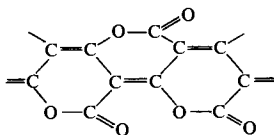
<sup>209</sup> D. A. Long, F. S. Murfin and R. L. Williams, *Proc. Roy. Soc. (London)*, **A223** (1954) 251.

<sup>210</sup> L. B. Dashkevich, *Russ. Chem. Rev.* **35** (1967) 391.

In recent work on the photolysis and polymerization of carbon suboxide, Trotman-Dickenson *et al.*<sup>121</sup> have studied the photolysis of carbon suboxide in ethylene. Products were allene, methyl acetylene and carbon monoxide. The suggested mechanism of photolysis is:



This mechanism was also proposed for thermal decomposition of carbon suboxide, the species  $\text{C}_2\text{O}$  decomposing further to carbon monoxide and solid carbon. Polymerization<sup>212</sup> of carbon suboxide is heterogeneous and dependent in extent on the surface of the vessel. Products vary from a yellow polymer at room temperature, through ruby-red at 100–300°C to violet at 400°C; the polymer turns to carbon above 500°C. The unit structure is the same at all temperatures and is a polycyclic six-membered lactone whose principal resonance form is a pyrilium-like aromatic structure as follows:

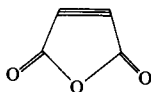


Polymerization by photolysis gives a different molecule.

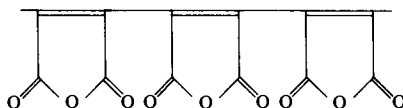
### Other Suboxides

#### Tetracarbon Trioxide, $\text{C}_4\text{O}_3$

This is the anhydride of acetylene dicarboxylic acid. Theoretically the structure expected would be



but this has never been isolated as a monomer. It was thought that this species was an intermediate in the synthesis of carbon suboxide from diacetyltartaric anhydride, but an isotopic study by Crombie *et al.*<sup>213</sup> has shown that this is not correct. Attempts to synthesize  $\text{C}_4\text{O}_3$ <sup>214</sup> have resulted in a polymer of structure



No dimer or trimer has been isolated.

#### Pentacarbon Dioxide, $\text{C}_5\text{O}_2$

This was reported by Wagner<sup>215</sup> as being formed in 3% yield by passing pure carbon suboxide through a glass tube at 200°C. It was reported as relatively stable, melting point

<sup>211</sup> R. T. K. Baker, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)* (1967) 1641.

<sup>212</sup> R. N. Smith, D. A. Young, E. N. Smith and C. C. Carter, *Inorg. Chem.* **2** (1963) 829.

<sup>213</sup> L. Crombie, P. A. Gilbert and R. P. Houghton, *J. Chem. Soc. (C)* (1968) 130.

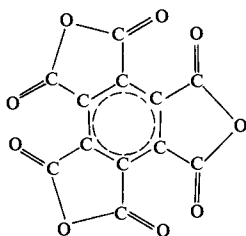
<sup>214</sup> J. Idris Jones, *Chem. Commun.* (1967) 938.

<sup>215</sup> A. Klemenc and G. Wagner, *Ber.* **70** (1937) 1880.

below  $-100^{\circ}\text{C}$  and extrapolated boiling point  $105^{\circ}\text{C}$ . Its existence has since been disputed. The structure of the compound is presumed to be linear and akin to carbon suboxide, i.e.  $\text{O}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{O}$ , and this is possible assuming that the type of resonance shown by carbon dioxide and carbon suboxide is also shown by pentacarbon dioxide. This resonance model would be applicable to all those oxides  $\text{C}_n\text{O}_2$ , where  $n$  is odd.

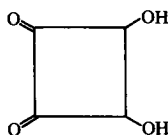
### Mellitic Trianhydride, $\text{C}_{12}\text{O}_9$

When mellitic acid  $\text{C}_6(\text{COOH})_6$  is heated in a sealed tube with acetyl chloride at  $160^{\circ}\text{C}$ , a stable trianhydride is produced. The anhydride is a white solid which sublimes when heated in a sealed tube to  $200^{\circ}\text{C}$  at 3–4 mm pressure. The anhydride has the form:

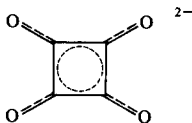


### Anionic Suboxides

When Cohen *et al.*<sup>216</sup> synthesized diketocyclobutenediol ("squaric acid")



they found it to be a strong acid (almost as strong as sulphuric acid) which yields the anion  $\text{C}_4\text{O}_4^{2-}$ . Subsequently croconic and rhodizonic acids yielded the anions  $\text{C}_5\text{O}_5^{2-}$  and  $\text{C}_6\text{O}_6^{2-}$  respectively. These anions form a new class of aromatic substances and Ito and West<sup>217</sup> examined the infrared and Raman spectra to find the  $\text{C}_4\text{O}_4^{2-}$  and  $\text{C}_5\text{O}_5^{2-}$  free ions had  $D_{4h}$  and  $D_{5h}$  symmetry respectively, i.e. both ions were planar. The anions show no absorption in the carbonyl region, implying that all the oxygens were equivalent, having (for example in  $\text{C}_4\text{O}_4^{2-}$ ) the structure



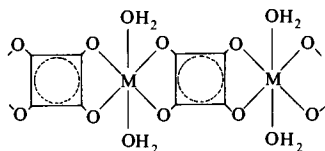
$\text{C}_4\text{O}_4^{2-}$  forms compounds with the divalent metals Cu, Fe, Zn, Ni, Mn, Co, Ca and Mg, of form  $\text{MC}_4\text{O}_4(\text{H}_2\text{O})_2$  and with trivalent metals Al, Fe, Cr of form  $\text{MC}_4\text{O}_4(\text{OH})(\text{H}_2\text{O})_2$ <sup>218</sup>. The structure of these compounds is in polymeric chains with two oxygen bonded to adjacent metals, i.e.

<sup>216</sup> S. Cohen, J. R. Lacher and J. D. Park, *J. Am. Chem. Soc.* **81** (1959) 3480.

<sup>217</sup> M. Ito and R. West, *J. Am. Chem. Soc.* **85** (1963) 2580.

<sup>218</sup> R. West, Hsien-Ying Niu, D. L. Powell and M. Evans, *J. Am. Chem. Soc.* **82** (1960) 6204.





$C_5O_5^{2-}$  forms a similar series of compounds which have been studied by X-ray diffraction<sup>219</sup>. These compounds form one-dimensional coordination polymers resulting from bonding of each metal to the adjacent oxygens of one  $C_5O_5^{2-}$  and to a single oxygen of a second  $C_5O_5^{2-}$  such that two adjacent oxygens per  $C_5O_5$  are not metal coordinated.

### Carbon Monoxide

TABLE 37. PHYSICAL CONSTANTS OF CARBON MONOXIDE

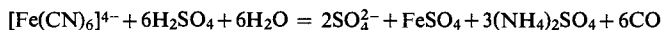
Melting point	$-205.06^\circ\text{C}$ (at 1 atm)
$\Delta H$ fusion	$200 \text{ cal mole}^{-1}$ (at $-205.06^\circ\text{C}$ )
Boiling point	$-191.50^\circ$ (at 1 atm)
$\Delta H$ vaporization	$1444 \text{ cal mole}^{-1}$ (at $-191.50^\circ\text{C}$ )
Critical temperature	$-140.21^\circ\text{C}$
Critical pressure	$34.529 \text{ atm}$
Critical density	$0.3010 \text{ g cm}^{-3}$
Triple point	$205.0^\circ\text{C}/115.4 \text{ mm}$
Auto-ignition temperature	$1204^\circ\text{C}$
$\Delta G^\circ$ formation	$-32.8079 \text{ kcal mole}^{-1}$
$\Delta H^\circ$ formation	$-26.4157 \text{ kcal mole}^{-1}$
$\Delta S^\circ$ formation	$47.301 \text{ cal deg}^{-1} \text{ mole}^{-1}$
$C_p^\circ$ formation	$6.965 \text{ cal deg}^{-1} \text{ mole}^{-1}$
$C_v^\circ$ formation	$4.98 \text{ cal deg}^{-1} \text{ mole}^{-1}$
Vapour pressure relation (solid)	$\log_{10} p = \frac{-0.05223}{T} a + b$ $a = 6.354; b = 6.976$
(liquid)	$\log_{10} p = a - b \log_{10} T - \frac{c}{T}$ $a = 13.7179; b = 2.893;$ $c = 432.8$
Bond length	$1.1282 \text{ \AA}$
Bond energy	$255.8 \text{ kcal mole}^{-1}$
Force constant	$19.02 \times 10^5 \text{ dynes cm}^{-1}$
Dipole moment	$0.12 \times 10^{-19} \text{ e.s.u.}$
Density	$1.2500 \text{ g litre}^{-1}$ (at $0^\circ\text{C}/1 \text{ atm}$ )
Solubility ( $\text{H}_2\text{O}$ )	$3.5 \text{ cm}^3 \text{ per } 100 \text{ cm}^3 \text{ at } 0^\circ\text{C}$
Ionization potential	$14.01 \text{ eV}$

Carbon monoxide is isoelectronic with  $\text{N}_2$ ,  $\text{NO}^+$  and  $\text{CN}^-$ , all of which have the ground state  $^1\Sigma$ . The electronic configuration,  $(\sigma_s^b)^2 (\sigma_s^*)^2 (\pi_{x,y}^b)^4 (\sigma_z^b)^2$  predicts one  $\sigma$ - and two  $\pi$ -bonds, and the calculated bond length  $1.10 \text{ \AA}$  agrees well with the measured value of  $1.13 \text{ \AA}$ . Carbon monoxide (like  $\text{N}_2$ ) crystallizes in a body-centred cubic molecular lattice,  $a = 5.63 \text{ \AA}$ . The cubic form changes into a hexagonal modification at  $-211.6^\circ\text{C}$ , the heat of transformation being  $0.151 \text{ kcal mole}^{-1}$ .

<sup>219</sup> M. D. Glick, G. L. Downs and L. F. Dahl, *Inorg. Chem.* **3** (1964) 1712.

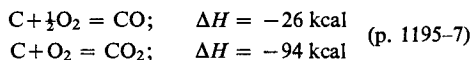
The microwave spectrum<sup>220</sup> shows the first line ( $J = 0$ ) as  $3.84235\text{ cm}^{-1}$ . The infrared spectrum has a fundamental absorption centred at  $2143.2\text{ cm}^{-1}$  and a first overtone at  $4260\text{ cm}^{-1}$ , and the Raman spectrum<sup>222</sup> shows a large displacement of  $2145\text{ cm}^{-1}$ . The electronic spectrum is too complex for brief description<sup>221</sup>.

Carbon monoxide is formed when carbon is burned with a deficiency of oxygen. It is prepared in the laboratory by dropping formic acid on to warm concentrated sulphuric acid, the latter dehydrating the formic acid. Other methods of preparation are by heating an oxalate with concentrated sulphuric acid, and by the action of the latter on a hexacyanoferrate(II):

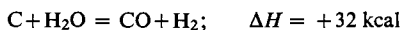


Pure carbon monoxide is obtained by decomposing nickel tetracarbonyl at  $200^\circ\text{C}$ .  $^{14}\text{CO}$  is prepared by the action of  $\text{H}_2\text{SO}_4$  on  $\text{Na}(\text{H}^{14}\text{CO}_2)$ <sup>222</sup>.

Commercially carbon monoxide is produced in the form of producer gas and water gas. Producer gas is obtained by blowing air through incandescent coke. The reactions involved are:

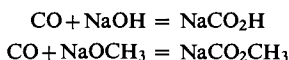


Producer gas consists of about 25%  $\text{CO}$ , 70%  $\text{N}_2$ , 4%  $\text{CO}_2$  and small amounts of  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{O}_2$ . Water gas is made by blowing steam through a bed of incandescent coke; the reaction is endothermic:

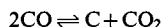


Hence the coke cools down and carbon dioxide is then produced; to avoid this the steam is periodically replaced by a stream of air to reheat the coke. Water gas consists of about 40%  $\text{CO}$ , 50%  $\text{H}_2$ , 5%  $\text{CO}_2$  and 5%  $\text{N}_2$  and  $\text{CH}_4$ .

Carbon monoxide is a toxic, flammable, colourless and odourless gas. Although often considered as an acid anhydride this is not strictly correct. It reacts with alkali hydroxides only at elevated temperatures, combining to give formates. It reacts similarly with alkali methoxides forming acetates—salts where (unlike carbon monoxide) the carbon is formally quadrivalent:



Carbon monoxide is stable in the cold, but at higher temperatures, especially in the presence of catalysts, it undergoes the reversible reaction:



At equilibrium the percentage of carbon monoxide is 10 at  $550^\circ\text{C}$ , and about 99 at  $1000^\circ\text{C}$  (p. 1196). Carbon monoxide reacts with air at elevated temperatures to give carbon dioxide, the presence of trace amounts of water being necessary. Dry carbon monoxide and air do combine, but much less easily, the rate being directly proportional to the concentration of water vapour, when this is small. Consequently at elevated temperatures carbon monoxide acts as a reducing agent, reducing many metal oxides (e.g. those of  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Fe}$ ,  $\text{Pb}$ ,  $\text{Mn}$ ,  $\text{Mo}$ ,  $\text{Ni}$  and  $\text{Ag}$ ) to lower oxidation states, or to the metals or carbides.

<sup>220</sup> T. M. Sugden and C. M. Kenny, *Microwave Spectroscopy of Gases*, p. 281, D. van Nostrand (1965).

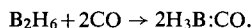
<sup>221</sup> G. Herzberg, *Molecular Spectra and Molecular Structure, 1. Spectra of Diatomic Molecules*, p. 62, D. van Nostrand (1950).

<sup>222</sup> W. Lautsch, H. Rauhut, W. Grimm and W. Broser, *Z. Naturf.* **12b** (1957) 307.

Carbon monoxide reacts with alkali metals in liquid ammonia to give the so-called "alkali metal carbonyls". These white solids contain the  $[\text{OCCO}]^{2-}$  ion, and have been shown<sup>223</sup> to be made up of rod-like  $\text{NaOC}\equiv\text{CONa}$  groups packed in chains. Carbon monoxide also reacts with transition metals giving metal carbonyls.

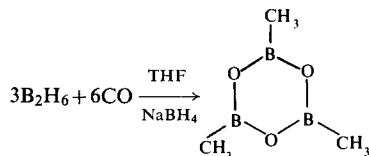
Carbon monoxide reacts with chlorine and bromine under the influence of light or a catalyst to give phosgene and carbonyl bromide respectively (p. 1220). It also reacts slowly with liquid sulphur and rapidly with the vapour to give carbonyl sulphide. Carbon monoxide has been shown recently to react slowly with fluorine and oxygen at  $0-50^\circ\text{C}$  forming a compound  $\text{C}_2\text{F}_2\text{O}_4$  (b.p.  $16^\circ\text{C}$ )<sup>224</sup> for which the structure  $\text{F}\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{F}$  is suggested.

Carbon monoxide acts as a donor molecule in its reaction with diborane at high temperatures and pressure<sup>225</sup>, when it gives carbon monoxide (C-B) borane:

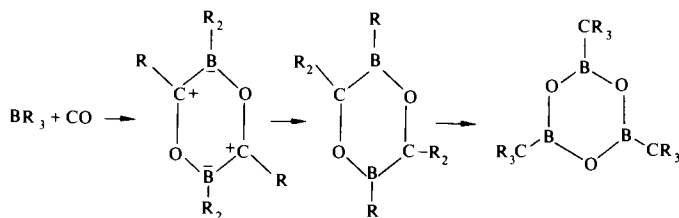


The isoelectronic nature of  $\text{H}_3\text{B}\cdot\text{CO}$  and  $\text{CO}_2$  has been displayed in the successful synthesis of salts of the boranocarbonate ion  $[\text{H}_3\text{B}\cdot\text{CO}_2]^{2-}$ <sup>226</sup>.

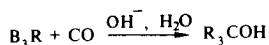
Carbon monoxide also reacts with diborane in tetrahydrofuran in the presence of sodium tetrahydroborate to give trimethyl boroxine<sup>227</sup>:



This is an example of carbon monoxide insertion, which has recently been reviewed<sup>228</sup>. The other reactions reported all involve either boron-carbon or transition metal (Mo, W, Mn, Fe, Co, Ni, Pd and Pt)-carbon bond cleavage. Similarly to the previous reaction carbon monoxide inserts into  $\text{BR}_3$  via successive steps:



The reaction of  $\text{BR}_3$  and carbon monoxide can also give different products depending upon the conditions<sup>229</sup>; in the presence of water and alkali the trialkyl carboxylic acid is obtained,



<sup>223</sup> E. Weiss and W. Buchner, *Chem. Ber.* **98** (1965) 126.

<sup>224</sup> A. J. Arvia, P. J. Aymonino, C. H. Waldow and H. J. Schumacher, *Angew. Chem.* **72** (1960) 169.

<sup>225</sup> A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.* **59** (1947) 780.

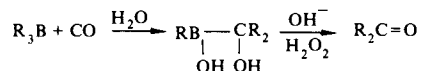
<sup>226</sup> L. J. Malone and R. W. Parry, *Inorg. Chem.* **6** (1967) 817.

<sup>227</sup> H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.* **88** (1966) 2606.

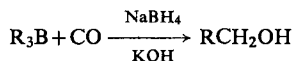
<sup>228</sup> M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.* **5** (1967) 254, 302.

<sup>229</sup> H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.* **89** (1967) 2737.

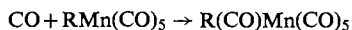
in the presence of water, followed by alkaline peroxide, the corresponding ketone is produced,



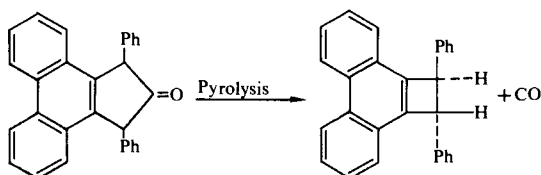
and in the presence of alkali and sodium tetrahydroborate the primary alcohol is obtained:



An example of carbon monoxide insertion into a metal-carbon bond is:



As opposed to "insertion reactions", carbon monoxide is also important in "extrusion reactions"<sup>230</sup>, i.e. those in which a small inorganic fragment (CO) is totally eliminated from a cyclic organic compound to form a product which either has a ring smaller than that present in the starting material (ring contraction) or has a smaller number of fused rings (bridge expulsion)<sup>231</sup>, e.g.



The toxic action of carbon monoxide is due to its combination with the haemoglobin of the red cells of the blood to form a relatively stable compound, carbon monoxide haemoglobin. It thus prevents the haemoglobin from taking up the oxygen to form oxyhaemoglobin and deprives the body of its needed oxygen. The affinity of carbon monoxide for haemoglobin is about 300 times that of oxygen, therefore only small amounts of carbon monoxide present in the air will cause toxic reactions to occur.

Carbon monoxide reacts with Grignard reagents giving a variety of products, acyloins, alpha-ketones and olefins being isolated. It also reacts with sodium alkyls, producing ketones and tertiary alcohols.

Carbon monoxide is extremely important commercially in the production of organic compounds. It reacts in the presence of catalysts with hydrogen, water, acetylenes, olefins, acetylenes and active hydrogen-containing compounds, olefins and water, olefins and hydrogen, and organic halides to name but a few. These have become associated with names such as the Fischer-Tropsch, the Kölbel-Englehardt, the Oxo Process, etc.

Hydrogenation of carbon monoxide (Fischer-Tropsch synthesis) gives a variety of products, depending on the catalyst and the conditions used, methane, benzene, paraffins, olefins, paraffin waxes, hydrocarbon high polymers, methanol, higher alcohols, ethylene glycol, glycol and other suggested compounds being obtained.

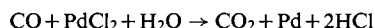
Carbon monoxide adds to alcohols and, depending on the catalyst and conditions used, gives either formate esters or carboxylic acids and their esters. It adds to organic halides in the presence of hydrogen fluoride, boron trifluoride and nickel carbonyl as catalysts giving carboxylic acids.

<sup>230</sup> B. P. Stark and A. J. Duke, *Extrusion Reactions*, p. 16, Pergamon (1967).

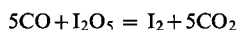
<sup>231</sup> M. P. Cava and D. Mangold, *Tetrahedron Letters* (1964) 1751.

Aldehydes and alcohols are preparable in high yields by the Oxo Process (a reaction of olefines, carbon monoxide and hydrogen in the presence of cobalt catalysts). In the presence of acidic catalysts or metal carbonyls, olefins, carbon monoxide and compounds containing active hydrogen (e.g. water, alcohols, phenols, carboxylic acids, and ammonia) yield carboxylic acid esters, aryl esters, carboxylic anhydrides and amides. Compounds containing active hydrogen with carbon monoxide can be added to acetylene to yield acrylic acid and derivatives.

Carbon monoxide can be detected by its reaction with aqueous palladium(II) chloride when a grey precipitate of palladium is obtained:



It can be estimated, in the absence of acetylene, by absorption, in a hydrochloric acid solution of copper(I) chloride, from a gas mixture. An addition compound  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$  is formed. The reaction with diiodine pentoxide is suitable for determinations of small amounts ( $< 1\%$ ) where the liberated iodine can be titrated:



### Carbon Dioxide

Carbon dioxide is present in the atmosphere at a concentration of 300 ppm; it issues from the earth in volcanic regions, and from supersaturated solution in some mineral springs. The main source is, however, carbonate rocks (especially the carbonates of calcium and magnesium) which constitute whole mountain ranges. As a product of human respiration it occurs to the extent of about 4% in exhaled air; exhaust gases from petrol engines contain up to 13% carbon dioxide and it is also present in appreciable concentration in water gas, producer gas and blast furnace gas.

Most carbon dioxide, and especially that used in the manufacture of sodium carbonate by the ammonia-soda process, is obtained from limestone heated by burning producer gas; the carbon dioxide (about 30%) is removed by absorption in potassium carbonate (or, less commonly, by ethanolamine), from which it is liberated on warming. Some carbon dioxide is also prepared by the passage of air over red hot coke; secondary oxidation by air is usually necessary to convert the carbon monoxide produced to the dioxide and simultaneously any hydrogen and hydrogen sulphide produced are oxidized to water and sulphur dioxide. The latter can be removed by a preliminary scrubbing with water. Other sources of carbon dioxide include the liquefaction of air and fermentation processes; in the latter case adsorption on silica gel is used to separate the carbon dioxide from the less volatile organic impurities.

Solid carbon dioxide (dry ice) is made either by rapid expansion of carbon dioxide under pressure, or by a slower expansion, cooled by rapidly evaporating liquid ammonia at  $-60^\circ$ . Its use as a cooling agent and as a source of carbon dioxide gas is now familiar. Sublimation of solid carbon dioxide produces gas which is sufficiently pure for most purposes; any further purification which may be necessary can be effected by adsorption and desorption on potassium carbonate followed by solidification *in vacuo* with liquid nitrogen and then repeated sublimation.

The formation of carbon-14 by slow neutron capture in the upper atmosphere ( ${}^{14}_7\text{N}(n,p){}^{14}_6\text{C}$ , p. 1183) produced (before nuclear explosions complicated the situation) a

steady-state concentration of  $^{14}\text{CO}_2$  in the atmosphere; absorption of this by plants permitted the use of radiocarbon dating (p. 1183). The most important method of incorporating carbon-14 into the plants is by photosynthesis. The alga *Chlorella vulgaris*, which grows vigorously on a wholly inorganic medium with carbon dioxide as the sole carbon source, is the most generally useful means of obtaining uniformly labelled carbon-14 compounds<sup>232</sup>.

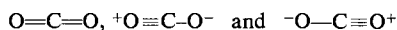
Carbon dioxide is the only primary chemical form of carbon-14 which is available in substantial quantities. This is usually stored and distributed as a metal carbonate. The reaction  $^{14}_7\text{N}(n, p)^{14}_6\text{C}$  (p. 1183) is used to produce the carbon-14 and the carbon is extracted by complete oxidation to carbon dioxide. Alternatively if nitrates are used as target materials instead of nitrides, then the carbon-14 is produced directly as carbon dioxide.

As carbon dioxide is the major source of carbon-14 its conversion to other carbon compounds is therefore important. Some of the more useful syntheses are listed below.

1. The reaction of Grignard reagents with  $^{14}\text{CO}_2$  to give carboxyl-labelled acids.
2. The reduction of  $^{14}\text{CO}_2$  with lithium aluminium hydride in tetrahydrofurfuryl alcohol to give methanol  $^{14}\text{C}$ .
3. Heating barium carbonate- $^{14}\text{C}$  with barium to give the carbide, which is the best intermediate for acetylene-1,2- $^{14}\text{C}$ .
4. The reaction of a carbonate- $^{14}\text{C}$  with an azide to produce the labelled cyanide.
5. The reduction of sodium or potassium bicarbonate- $^{14}\text{C}$  by hydrogen using a palladium charcoal catalyst to give formic acid- $^{14}\text{C}$ .
6. Barium cyanamide, formed by heating the carbonate at  $850^\circ$  for 3 hr in a stream of ammonia, is useful for labelled carbon-nitrogen compounds.

### Physical Properties

The physical properties of carbon dioxide are given in Table 38. The absence of a dipole moment and a slightly shorter bond length than the usual  $\text{C}=\text{O}$  value ( $1.22 \text{ \AA}$ ) are consistent with the formulation of a linear molecule. A resonance hybrid model, to which the structures



contribute significantly, may be postulated; the two latter forms are identical and contribute equally, presumably to a much lesser extent than the first. The infrared and Raman spectra of carbon dioxide have been extensively studied; the earlier observations are summarized by Herzberg<sup>233</sup>. The more recent investigations do not cover the complete infrared frequency range, but the fine structures of the so-called 2.7, 10 and 15 micron bands have been studied separately, under various conditions, in great detail<sup>234-236</sup>. Somewhat wider frequency ranges have been studied by C. P. Courtoy<sup>237</sup> ( $8100\text{--}3500 \text{ cm}^{-1}$ ) and C. V. Berney and D. F. Eggers<sup>238</sup> ( $5400\text{--}1620 \text{ cm}^{-1}$ ).

<sup>232</sup> J. R. Catch, *Carbon-14 Compounds*, Butterworths (1961).

<sup>233</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, p. 272, van Nostrand, New York (1945).

<sup>234</sup> H. R. Gordon and T. K. McCubbin, Jr., *J. Mol. Spec.* **19** (1966) 137.

<sup>235</sup> W. Malkmus, C. B. Ludwig and C. C. Ferriss, *J. Chem. Phys.* **45** (1966) 3953.

<sup>236</sup> H. R. Gordon and T. K. McCubbin, Jr., *J. Mol. Spec.* **18** (1965) 73.

<sup>237</sup> C. P. Courtoy, *Ann. Soc. Sci. Bruxelles*, **73** (1959) 5.

<sup>238</sup> C. V. Berney and D. F. Eggers, *J. Chem. Phys.* **40** (1964) 990.

TABLE 38. PHYSICAL PROPERTIES OF CARBON DIOXIDE

Melting point 56.6° (5.2 atm)				
Boiling point -78.5° sublimes				
Critical temperature 31.00° ± 0.01				
Critical pressure 75.282 ± 1 atm				
Density 1.977 g l <sup>-1</sup> gas				
1.101 g cm <sup>-3</sup> liq (-37°)				
1.56 g cm <sup>-3</sup> solid (-79°)				
Solubility (100 cm <sup>3</sup> ) water, 0.385 g at 0°				
0.097 g at 40°				
0.058 g at 60°				
C=O bond length, 1.1632 Å				
Bond dissociation energy, 127 kcal mole <sup>-1</sup>				
$\Delta H_f^\circ$ , 94.0518 kcal mole <sup>-1</sup>				
$\Delta G_f^\circ$ , 94.2598 kcal mole <sup>-1</sup>				
$S^\circ$ , 1.061 cal deg <sup>-1</sup> mole <sup>-1</sup>				
Ionization potentials, 13.79, 17.59, 18.07 and 19.38 eV				
Dielectric constant, $10^4(\epsilon-1) = 9.88$ at 0°				
Vapour point equation (liq.), $p = a\left(\frac{T}{100} - b\right)^n$				
$p$ (kg cm <sup>-2</sup> ): $a = 7.856$ , $b = 1.261$ , $n = 3.917$				
% dissociation				
°K	0.1 atm	1	10	100
2000	4.35	2.05	0.96	4.09
4000	97.9	93.9	83.4	63.8

$$\text{Specific heat } C_v = 0.691 + 0.889p + 1.42p^2$$

The four ionization potentials of carbon dioxide were measured by photoelectron spectroscopy<sup>239</sup> and Frank-Condon factors were shown to be in good agreement with the experimental results.

Liquid carbon dioxide is a poor solvent. Phosphorus and iodine are slightly soluble as are PCl<sub>3</sub>, AsBr<sub>3</sub> and SbBr<sub>3</sub>. Water is soluble only to an extent of 0.02% at -29° and 0.10% at 22.6°.

### Chemical Properties

The equilibria governing the dissociation of carbon dioxide to carbon monoxide and oxygen are fully considered elsewhere (pp. 1195-7).

Carbon dioxide unites with the more electropositive metals to give, according to conditions, the metal carbonate, oxalate or oxide with concomitant formation of carbon. Less electropositive metals yield carbides (p. 1203) and oxygen.

Insertion of carbon dioxide into M-N bonds in compounds of type X<sub>n</sub>'M-N≡ (M = B, Si, As, Ti etc.) occurs; with M=Sn, M-O cleavage takes place. The subject has been reviewed<sup>240</sup>.

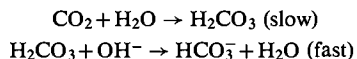
<sup>239</sup> D. W. Turner and D. P. May, *J. Chem. Phys.* **46** (1967) 1156.

<sup>240</sup> M. F. Lappert and B. Prokai, *Adv. Organometall. Chem.* **5** (1967) 247.

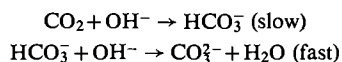
Small amounts of carbon dioxide may be estimated by absorption in barium hydroxide solution protected by a layer of pentane. Near infrared analysis may be used to determine carbon dioxide in presence of water and ammonia at elevated temperatures and pressures<sup>241</sup>.

The more important chemical properties of carbon dioxide are those relating to the carbon dioxide-water system.

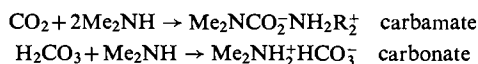
The reaction of an aqueous solution of carbon dioxide with a base is slow; the reason is (1) that only a small amount of the aqueous carbon dioxide exists in the hydrated form, and (2) that the interconversion carbon dioxide  $\rightleftharpoons$  hydrated species is slow. The nature of the hydrated species depends on pH; at pH < 8, the important reactions are



and at pH > 10 the predominant reactions are



Both mechanisms are important in the pH range 8–10. A <sup>13</sup>C n.m.r. study of <sup>13</sup>C-enriched CO<sub>2</sub> in water<sup>242</sup> has confirmed the existence of the various species, but has not provided an explanation for the slowness of hydration. Analytically, unhydrated and hydrated carbon dioxide may be distinguished by the (rapid) reactions with dimethylamine,



and the carbonate is precipitated out by addition of barium chloride. These reactions were used in early kinetic investigations of the CO<sub>2</sub>/H<sub>2</sub>O reaction; other aspects of the kinetics are well reviewed<sup>243</sup>. The true ionization constant  $K_a$  of carbonic acid ( $K_a = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ ) has the value *circa*  $2.5 \times 10^{-4}$  at 25°C; the apparent dissociation constant ( $K = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2 + \text{H}_2\text{CO}_3]$ ) has the value  $4.45 \times 10^{-7}$  at 25°C, and hence  $[\text{CO}_2]/[\text{H}_2\text{CO}_3] = \textit{circa} 600. The  $\text{p}K_a$  value for carbonic acid is of the order expected (2–3) for an acid (HO)X<sub>a</sub>O<sub>b-a</sub> with  $b-a = 1$ ; as a dibasic acid with constants  $K_1$  and  $K_2$ , the difference  $\text{p}K_2 - \text{p}K_1 = 6.6$  is also of the order for an acid containing the group >X(OH)<sub>2</sub>.$

Addition of hydrogen chloride to a suspension of sodium carbonate in ether at –30°C gives crystals of the etherate of carbonic acid H<sub>2</sub>CO<sub>3</sub>.Et<sub>2</sub>O; these decompose at –10°C. A similar reaction in dimethyl ether yields the etherate H<sub>2</sub>CO<sub>3</sub>.Me<sub>2</sub>O, and this melts at –47°C to give a viscous liquid; infrared and <sup>1</sup>H nuclear magnetic resonance spectra support formulation as OC(OH)<sub>2</sub>.OMe<sub>2</sub>, and  $\Delta H_f$  is given as  $-153 \pm 10$  kcal mole<sup>244</sup>.

A hydrate CO<sub>2</sub>.8H<sub>2</sub>O is formed by carbon dioxide at 45 atm and water at 0°C.

Suspensions of calcium silicate or phosphate show some solubility in water saturated with carbon dioxide at 60 atm; the formation of the more soluble hydrogen phosphates CaHPO<sub>4</sub> and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> is implied.

## The Carbonates

### Preparation

In general, metal carbonates are prepared by reaction of carbon dioxide with a soluble base (e.g. NaOH) or by metathetic reaction of a soluble carbonate with a soluble salt of

<sup>241</sup> J. G. Koren and A. J. Andreatch, *Anal. Chem.* **37** (1965) 256.

<sup>242</sup> A. Patterson and R. Ettinger, *Z. Electrochem.* **64** (1960) 98.

<sup>243</sup> D. M. Kem, *J. Chem. Educ.* **37** (1960) 14.

<sup>244</sup> G. Gattow and U. Gerwarth, *Z. anorg. und allgem. Chem.* **357** (1968) 78.

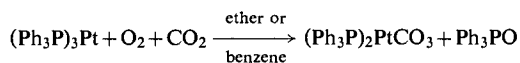


the metal. Since the great majority of metal carbonates are insoluble in water, this second method is theoretically of wide applicability, but is limited in practice by the possibility of precipitation of hydroxides or basic salts, and by the formation of complex carbonates in presence of excess carbonate ion.

Saturation of a solution of sodium carbonate with carbon dioxide leads to the (relatively) slow formation of bicarbonate, in which the solution is effectively buffered at a pH around 8 (p. 1232). Since bicarbonates other than those of the alkali metals can exist only in solution, use of bicarbonate rather than carbonate ion in a preparation can sometimes avoid the concomitant precipitation of hydroxides or basic salts when a heavy metal is used. However, multipositive cations such as those of iron(III), aluminium, zirconium and titanium yield either hydroxides (or oxides), or basic salts, rather than pure carbonates, even with bicarbonate. In other cases, e.g. with magnesium, zinc, and cobalt(II), the initially-precipitated basic carbonate is slowly converted by standing with bicarbonate to the normal carbonate. Copper(II) does not form a pure carbonate even under these conditions.

Increase of solubility of a metal carbonate when carbon dioxide is passed through the solution is attributable to bicarbonate formation, but since a wide variety of insoluble carbonates show increased solubility in presence of excess (dissolved) carbon dioxide, complex formation may also occur. From such solutions, or from those containing merely an excess of carbonate ion, many double or complex salts have been obtained; the formulation of these compounds is discussed below.

Methods of preparing carbonates not involving aqueous solutions are of very limited applicability. Metal oxide (solid)/carbon dioxide (gas) reactions, which might in theory yield the carbonate, are often too slow in practice, possibly because of inactivity of the oxide surface; displacement reactions of the type carbon dioxide (gas)/metal salt (melt) are precluded by the low Lux-Flood acid strength of carbon dioxide (see below). A recent reaction<sup>245</sup> for the preparation of a carbonato-platinum complex may be of more general application; the reaction is



## Structure

In the free carbonate ion, the C–O distances are expected to be equivalent, the ion having  $D_{3h}$  symmetry. Crystallographic and spectroscopic data indicate that lower symmetry can arise from (1) site effects, (2) perturbations by hydrogen bonding arising from the presence of water, hydroxide ion or hydrogen-carbonate ion in solid carbonates, and (3) coordination to a metal, i.e. formation of carbonato-complexes. There are three possible structures for simple carbonates, those of calcite, aragonite and vaterite. In calcite,  $D_{3h}$  symmetry is retained, with the three C–O distances equal at 1.294 Å, and a similar situation exists in lithium carbonate and (generally) in the carbonates of small cations. In aragonite, the site symmetry is lowered to  $C_s$ , and this structure is generally adopted in the carbonates of larger cations, with 6 oxygen atoms around each cation. The site symmetry of the carbonate ion in vaterite is not known; the crystal has a hexagonal structure with 6+2 nearest neighbours at 2.4 and 2.9 Å respectively.

Distortion of the carbonate anion by hydrogen bonding is found in, for example, sodium bicarbonate (with C–O distances 1.346, 1.263 and 1.264 Å); in basic carbonates,

<sup>245</sup> C. J. Nyman, C. E. Wymore and G. Wilkinson, *Chem. Commun.* (1967) 407.

the effect of the hydroxyl ion may be observed as producing either abnormal C–O distances (with symmetry retained) (e.g. in basic lead carbonate  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ , all C–O distances 1.45 Å) or in distortion (e.g. in azurite  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  with C–O distances 1.30, 1.27 and 1.24 Å)<sup>246</sup>. With complex formation, there appear to be no crystallographic data for monodentate carbonato-complexes; the crystal structure of carbonato-tetrammine cobalt(III) bromide shows the carbonate ligand to be bidentate to the cobalt, with two long (1.34 Å) C–O(Co) bonds and the C–O (terminal) remaining at 1.25 Å<sup>247</sup>.

Attempts have been made to correlate changes in the vibrational spectrum of the carbonate ion with its environment in carbonates of various kinds<sup>248</sup>. Of the four ( $\nu_1 \dots \nu_4$ ) modes of vibration of the planar  $\text{CO}_3^{2-}$  ion,  $\nu_1$  becomes infrared active for symmetries  $C_5$  and  $C_{2v}$ , and the degeneracy of the  $\nu_3$  vibration is also lost. A normal coordinate analysis of unidentate carbonato complexes suggested  $C_s$  symmetry for the carbonate ion, and this has been confirmed experimentally<sup>245</sup>. However, studies of the infrared spectra of complex, basic, acid and normal carbonates do not permit a close correlation between the observed frequencies and the bonding of the carbonate ion<sup>249</sup>. Studies of the intensities of the  $\nu_1$  symmetrical C–O stretching mode in complex carbonates indicate that the intensity is chiefly determined by site symmetry, not by the mechanism responsible for lowering this (see Table 39); there is a marked decrease in  $\gamma$ , intensity in going from mono- to bidentate carbonato-cobalt(II) complexes.

TABLE 39. MEAN EXTINCTION COEFFICIENT FOR CARBONATES OF VARIOUS SYMMETRY CLASSES<sup>250</sup>

Type of compound	Symmetry class	$\epsilon_{av}$
Calcite type carbonate	$C_3$	2.8
Vaterite	$< C_3$ (unknown)	14.7
Bidentate complex	$C_{2v}$	21.5
Dialkyl carbonate	$C_{2v}$	25
Aragonite type carbonate	$C_s$	35.9
Basic carbonate	$C_s$	40.0
Unidentate complex	$C_s$	58.3

### Chemical Reactions of Carbonates

(a) *Thermal decomposition.* For the decomposition metal carbonate (solid)  $\rightleftharpoons$  metal oxide (solid) + carbon dioxide (gas) the equilibrium constant  $K_p$  can be equated with the partial pressure of carbon dioxide  $p_{\text{CO}_2}$  provided the oxide and carbonate do not form solid solutions (or interact in any way, e.g. to form a basic carbonate), and provided any solid oxide and carbonate remain. Values of  $\log K_p$  for a number of carbonates are given in Table 40<sup>251</sup>, together with the radii of the appropriate cations. The  $\log K_p$  values run roughly parallel with decomposition temperatures, i.e. those at which the equilibrium pressure of carbon dioxide is 1 atm; these temperatures are rather sensitive experimentally to traces of water.

<sup>246</sup> R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Vol. 2, p. 459, Interscience (1964).

<sup>247</sup> G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.* (1962) 586.

<sup>248</sup> K. Nakamoto, *Infrared Spectrum of Inorganic and Coordination Compounds*, p. 92, Wiley (1963).

<sup>249</sup> B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.* (1958) 3137.

<sup>250</sup> J. A. Goldsmith and S. D. Ross, *Spectrochim. Acta*, **22** (1966) 1069.

<sup>251</sup> M. W. Lister, *Oxyacids*, p. 101, Oldbourne (1965).

TABLE 40. EQUILIBRIUM CONSTANTS ( $K$ ), FOR DECOMPOSITION OF CARBONATES AT 25°C

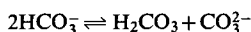
Ion	$\log K_p$	Radius	Ion	$\log K_p$	Radius
Li <sup>+</sup>	-31.2	0.68 Å	Ag <sup>+</sup>	-5.6	1.26 Å
Na <sup>+</sup>	-48.5	0.97			
K <sup>+</sup>	-62.4	1.33	Zn <sup>2+</sup>	-3.3	0.74
Rb <sup>+</sup>	-62.7	1.47	Cd <sup>2+</sup>	-8.9	0.97
Cs <sup>+</sup>	-61.4	1.67	Hg <sup>2+</sup>	-24.0	1.10
			Pb <sup>2+</sup>	-7.5	1.20
Mg <sup>2+</sup>	-11.5	0.66			
Ca <sup>2+</sup>	-22.8	0.99	Mn <sup>2+</sup>	-10.5	0.80
Sr <sup>2+</sup>	-32.2	1.12	Fe <sup>2+</sup>	-6.2	0.75
Ba <sup>2+</sup>	-37.9	1.34	Co <sup>2+</sup>	-7.4	0.72
			Ni <sup>2+</sup>	-0.6	0.69
			Cu <sup>2+</sup>	(0.6)	0.72

Since the entropy changes are all approximately the same, the  $\log K_p$  values of Table 40 are determined primarily by the heats of reaction  $\Delta H$ , and these can be understood in terms of an ionic crystal model for the oxides and carbonates.

(b) *Reactions in aqueous solution.* Normal carbonates, other than those of the alkali metals and ammonium, are insoluble in water. The hydrogen carbonates of calcium, strontium and barium exist in aqueous solution and are formed by, for example, the reaction



The equilibrium constant for the reaction



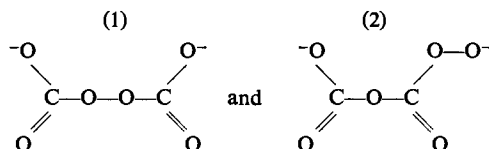
is of the order  $10^{-4}$  corresponding to  $\sim 0.01$  M  $\text{CO}_3^{2-}$  and 0.01 M  $\text{H}_2\text{CO}_3$  in molar sodium hydrogen carbonate.

The weakness of carbonic acid results in appreciable hydrolysis of alkali carbonate solutions; the hydroxide ion concentration in 0.5 M  $\text{Na}_2\text{CO}_3$  is about 0.01 M. Hence weakly acidic substances cause evolution of carbon dioxide from carbonate solutions.

Addition of a soluble carbonate to a neutral or weakly alkaline solution of almost any metal cation produces precipitation of either the carbonate, basic carbonate or hydroxide. Silver(I) carbonate, produced in this way, is soluble in ammonia and decomposes on boiling to the brown oxide  $\text{Ag}_2\text{O}$ , and these reactions provide a test for the carbonate ion. In some cases, addition of excess carbonate ion causes the precipitated carbonate to redissolve, although the process may be slow; the formation of carbonato-complexes, e.g.  $[\text{Sn}(\text{CO}_3)_3]^{2-}$ ,  $[\text{Fe}(\text{CO}_3)_2]^{2-}$ , can be assumed, but few of these have been unambiguously characterized. Oxidation of cobalt(II) in presence of excess carbonate ion yields the well-characterized carbonato tetrammine cobalt(III) ion,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$  (p. 1234).

The formation of the peroxomonocarbonate ion  $\text{CO}_4^{2-}$  occurs when solutions of hydrogen peroxide and alkali metal carbonates are mixed; the sparingly soluble salts obtained may contain hydrogen peroxide, e.g.  $\text{K}_2\text{CO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ . Reaction of carbon dioxide with sodium hydroperoxide perhydrate gives the peroxo-hydrogen carbonate  $\text{NaHCO}_4 \cdot \text{H}_2\text{O}$ . With sodium peroxide, carbon dioxide gives the peroxomonocarbonate and also, at low temperatures, the pale orange or white peroxydicarbonate  $\text{Na}_2\text{C}_2\text{O}_6^{2-}$ . A pale blue salt  $\text{K}_2\text{C}_2\text{O}_6$  is obtained when potassium carbonate is oxidized anodically at low temperature

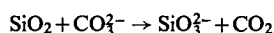
and high current density. It is possible that the peroxodicarbonate ion exists in two isomeric forms



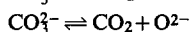
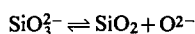
but infrared spectroscopy and X-diffraction analysis<sup>252</sup> supports only (1); the different colours (dependent on the method of preparation) are ascribed to impurities.

Peroxydicarbonates decompose on heating to give oxygen and carbon dioxide; peroxy-carbonates give oxygen only.

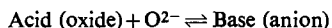
(c) *Reactions of fused carbonates.* The use of fused alkali carbonates to convert insoluble oxides or salts of metals to soluble alkali metal salts is a familiar procedure in analysis, e.g.



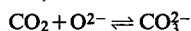
This reaction is governed by the equilibria



Equilibria of this type have been considered as acid/base reactions, with the oxide ion as the transferable species:



e.g.



On this basis, carbon dioxide is a weaker acid than silica and hence the oxide ion is transferred from  $\text{CO}_3^{2-}$  to  $\text{SiO}_2$  to give silicate. The "acidity" of a carbonate melt can be expressed in terms of  $\text{pO}^{2-}$  ( $= -\log_{10} \text{O}^{2-}$ ), or, more practically, as  $\text{pCO}_2$ . Ingram and Janz<sup>253</sup> have used  $E_{\text{redox}}/\text{pCO}_2$  plots (analogous to  $E_0/\text{pH}$  plots in aqueous solution) to explain the diversity of corrosion behaviour shown by metals in fused alkali carbonate melts; thus gold, which forms no oxide film, remains unattacked whereas nickel, which does form an oxide film, is severely attacked.

Cryoscopic studies of solutions of sodium salts in molten sodium carbonate indicate formation of ions  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{O}^{2-}$ ; the ion  $\text{O}_2^{2-}$  yields oxygen and  $\text{O}^{2-}$ <sup>254</sup>. There is a short review of reactions in alkali carbonate melts<sup>255</sup>.

### Other Carbon Oxides and Oxyanions

The anion  $\text{CO}_3^-$  has been detected as one product of the gamma irradiation of single crystals of potassium hydrogen carbonate by the  $^{13}\text{C}$  hyperfine structure in the e.s.r. spectrum of the  $^{13}\text{C}$ -enriched hydrogen carbonate; further identification of  $\text{CO}_3^-$  was provided by the similarity of the optical spectrum to that of  $\text{NO}_3$  in urea nitrate. It is possible that the observed distortion of  $\text{CO}_3^-$  from  $D_{3h}$  symmetry is due to strong hydrogen bonding (cf. p. 1233).

<sup>252</sup> G. S. Karetnikov and M. F. Sorokima, *Khur. Fiz. Khim.* **39** (1965) 364; V. I. Sokol, V. M. Bakulina, E. Ya. Filatov and T. P. Firsova, *Zhur. Neorg. Khim.* **9** (1968) 2347.

<sup>253</sup> M. D. Ingram and G. J. Janz, *Electrochim. Acta*, **10** (1965) 783.

<sup>254</sup> M. Rolin and J. M. Recapet, *Bull. Soc. Chim. France*, (1964) 2511.

<sup>255</sup> G. Charlot and B. Tremillon, *Chemical Reactions in Solvents and Melts*, pp. 495-497, Pergamon (1969).

Another product of  $\gamma$ -irradiation of potassium hydrogen carbonate has hyperfine and g-tensors closely similar to those of the radical  $\text{CO}_2^-$ , which has been identified as a product of irradiation of sodium formate or of calcite. The different reactivity of  $\text{CO}_2^-$  compared with the isoelectronic  $\text{NO}_2$  (ready dimerization of  $\text{CO}_2^-$ , and reaction with hydrogen to give formate ion, cf.  $\text{NO}_2$  giving nitrous acid) is ascribed to differences in electron distribution<sup>256</sup>.

$\text{CO}_3$  has been obtained in a matrix by reaction of oxygen atoms with carbon dioxide<sup>257</sup>.

### 3.4. CARBON-SULPHUR COMPOUNDS

#### Carbon Disulphide

Carbon disulphide was first discovered by Lampadius in 1796. A review of the preparation and industrial uses is given by Budrell<sup>258</sup>; and a general review is given by Reid<sup>259</sup>. The two main preparations are: (1) from a mix of sulphur and charcoal in a cast iron retort at 900°C, (2) passing a mixture of sulphur and methane through a silica gel or alumina catalyst at 600°C. (1) is the older, traditional method; (2) is becoming more prevalent where a ready cheap supply of methane is available. Carbon disulphide prepared by either method is readily purified.

Carbon disulphide is a colourless, highly refractive, volatile, liquid having an unpleasant odour depending on purity. A list of physical properties has been published by the Stauffer Chemical Company<sup>260</sup>.

TABLE 41. PHYSICAL PROPERTIES OF CARBON DISULPHIDE

Boiling point	46.25°C
Melting point	-111.6°C
Critical temperature	273°C
Critical pressure	75 atm
$\Delta H$ fusion	1.049 kcal mole <sup>-1</sup>
$\Delta H$ vaporization	6.60 kcal mole <sup>-1</sup>
$\Delta H_f$ (25°C)	27.55 kcal mole <sup>-1</sup> (gas)
	21.0 kcal mole <sup>-1</sup> (liquid)
$\Delta G_f$ (25°C)	15.55 kcal mole <sup>-1</sup> (gas)
	15.2 kcal mole <sup>-1</sup> (liquid)
Vapour pressure	$\ln p_{\text{mm}} = 4.67948 - 1578.8/T$
Conductivity (liquid, 18°C)	$78 \times 10^{-19}$ ohm <sup>-1</sup> cm <sup>-1</sup>

The ultraviolet spectrum shows carbon disulphide to have a linear structure  $\text{S}=\text{C}=\text{S}$ ; bond distances are C-S 1.55 Å, S-S 3.18 Å. The near ultraviolet spectrum<sup>261</sup> has shown the first excited state to be bent with an apex angle of 135°. The transition involved is  $^1\Sigma_g^+ \rightarrow$

<sup>256</sup> P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals*, pp. 132, 168, Elsevier (1967).

<sup>257</sup> N. G. Moll, D. R. Clutter and W. E. Thompson, *J. Chem. Phys.* **45** (1966) 4469.

<sup>258</sup> W. J. Budrell, *Chem. and Ind.* (1961) 1465.

<sup>259</sup> E. E. Reid, *Organic Chemistry of Bivalent Sulphur*, **5** (1963) 422.

<sup>260</sup> Stauffer Chemicals Co. (1964).

<sup>261</sup> B. Kleman, *Canad. J. Chem.* **41** (1963) 2034.

$^1B_2$ , the  $^1B_2$  state being a component of a  $^3A_2$  state with large splitting. Ultraviolet and infrared spectral data are given by Treiber *et al.*<sup>262</sup>.

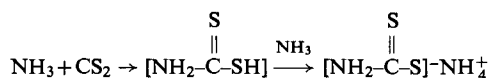
Carbon disulphide is decomposed by sunlight and strong irradiation gives CS radicals even at  $-196^\circ\text{C}$  (see below). At high pressure and above  $175^\circ\text{C}$  carbon disulphide polymerizes to give a black solid, denser than graphite or sulphur, having the structure

S  
||  
(-C-S)<sub>n</sub>

<sup>263</sup>. From reaction of CS<sub>2</sub> with sodium or potassium at  $-196^\circ\text{C}$  there is e.s.r. spectral evidence for the formation of CS<sub>2</sub><sup>-</sup> with a probable bond angle of about  $140^\circ$ <sup>264</sup>.

With halogens carbon disulphide gives a variety of products depending on conditions. Chlorination in the presence of iodine gives perchloromethanethiol, Cl<sub>3</sub>CSCl. More drastic chlorination using AlCl<sub>3</sub>, MoCl<sub>5</sub> or SbCl<sub>5</sub> as a catalyst gives carbon tetrachloride and S<sub>2</sub>Cl<sub>2</sub> which in turn chlorinates more carbon disulphide. This is an important commercial route to CCl<sub>4</sub>. Bromine reacts similarly, but iodine does not react. Fluorine gives a variety of products depending on conditions, including SF<sub>4</sub>, F<sub>3</sub>CSF<sub>5</sub>, SF<sub>6</sub>, F<sub>2</sub>C(SF<sub>3</sub>)<sub>2</sub>, F<sub>2</sub>C(SF<sub>5</sub>)<sub>2</sub>, F<sub>3</sub>SCF<sub>2</sub>SF<sub>5</sub> and S<sub>2</sub>F<sub>10</sub>.

With aqueous sodium hydroxide carbon disulphide gives the trithiocarbonate, Na<sub>2</sub>CS<sub>3</sub> (see below). Ammonia gives ammonium dithiocarbonate, an important intermediate for many organo-sulphur compounds, by a two-stage reaction:

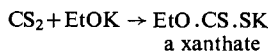


Hydrogenation of carbon gives products dependent on conditions:

- (a) CS<sub>2</sub> + 2H<sub>2</sub> → SH—CH<sub>2</sub>—SH ( $180^\circ$ , reduced nickel catalyst)  
 (b) CS<sub>2</sub> + 3H<sub>2</sub> → CH<sub>3</sub>SH + H<sub>2</sub>S ( $250^\circ$ , cobalt catalyst).

There is no reaction with water at ambient temperatures, but at higher temperatures up to  $200^\circ\text{C}$  carbon oxysulphide is formed, and catalysed reaction between  $200^\circ$  and  $500^\circ\text{C}$  gives hydrogen sulphide and carbon dioxide.

Carbon disulphide is used extensively in the synthesis of organo-sulphur compounds. The preparation of xanthates has great industrial importance to the production of rayon and cellophane. This involves the reaction of carbon disulphide with alcohols in the presence of alkali hydroxide:



The reaction is general for alcohols, best for primary alcohols but giving poor results for tertiary alcohols and diols in which the OH groups are separated by less than 3 carbon atoms.

Carbon disulphide undergoes insertion reactions; a review is given by Lappert and Prokai<sup>265</sup>. The most common insertion is with M—N bonds (M = B, Si, P, As, S and Ti), for example with phenylbis(diethylamino)borane, PhB(NEt<sub>2</sub>)<sub>2</sub>, the product is PhB(NEt<sub>2</sub>)SCSNEt<sub>2</sub>. Insertion also occurs with some M—O bonds, e.g. Bu<sub>3</sub>SnOME gives Bu<sub>3</sub>SnSCSOMe, and with some M—S bonds, e.g. CuSR → CuSCSSR.

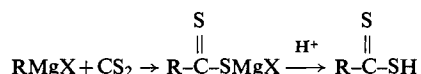
<sup>262</sup> E. Treiber, J. Gieter, J. Rehnstrom and K. E. Almin, *Acta Chem. Scand.* **11** (1957) 752.

<sup>263</sup> E. Whalley, *Canad. J. Chem.* **38** (1960) 2105.

<sup>264</sup> J. E. Bennett, B. Mile and A. Thomas, *Trans. Faraday Soc.* **63** (1967) 262.

<sup>265</sup> M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.* **5** (1967) 247.

Carbon disulphide reacts with many organo-metallic compounds, notably with Grignard reagents to give dithiocarboxylic acids



It also reacts with aluminium alkyls to give  $\text{R}_2\text{Al}-\text{S}-\text{AlR}_2$ ,  $\text{R}_2\text{Al}-\text{S}-\text{CR}_3$  and  $\text{RAl}(\text{SCR}_3)_2$ ,

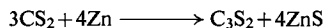
with diethyl zinc to give  $\text{C}_2\text{H}_5-\overset{\overset{\text{S}}{\parallel}}{\text{C}}-\text{S}-\text{ZnC}_2\text{H}_5$  and with triethylphosphine to give the addition compound  $(\text{C}_2\text{H}_5)_3\text{P} \cdot \text{CS}_2$ .

Recent work<sup>266</sup> has shown that carbon disulphide acts as a ligand. Carbon disulphide with tris(triphenylphosphine)platinum(0) gives the stable adduct  $(\text{Ph}_3\text{P})_2\text{PtCS}_2$  in which  $\text{CS}_2$  retains a planar configuration. The bonding of  $\text{CS}_2$  may be considered to involve one electron transfer via the intermediacy of Pt from the highest-lying  $\pi$  molecular orbital of the ligand to its lowest antibonding molecular orbital. The compounds  $\text{Pd}(\text{CS}_2)(\text{PPh}_3)_2$  and  $\text{Ni}(\text{CS}_2)(\text{PPh}_3)$  are also reported; the latter is probably dimeric with  $\text{CS}_2$  bridges.  $\text{CS}_2$  complexes of vanadium, iron, cobalt, ruthenium and iridium have also been prepared<sup>267</sup>; the interaction of tris(triphenylphosphine)dichlororuthenium(II) with  $\text{CS}_2$ <sup>268</sup> leads to two complexes,  $[\text{RuCl}(\text{CS}_2)(\text{PPh}_3)_3]\text{Cl}$  and  $[\text{RuCl}(\text{CS})(\text{PPh}_3)_2]_2$ , containing the thiocarbonyl group. Iridium and rhodium also form both thiocarbonyl and  $\text{CS}_2$  complexes<sup>269</sup>.

The major industrial use of carbon disulphide is in the production of rayon and cellophane. Raw cellulose is treated with dilute caustic soda and carbon disulphide to produce the cellulose xanthate which is extruded in filaments or sheets into acid solution to give rayon or cellophane respectively. Carbon disulphide is regenerated. Other uses are in carbon tetrachloride production, as a solvent and in fumigation and pest control materials.

*Carbon monosulphide.* The entity CS has been isolated<sup>270</sup> at  $-196^\circ\text{C}$  from  $\text{CS}_2$  in a high-frequency discharge. It was detected by low-temperature infrared analysis. With selenium or tellurium deposited in a thin layer on the walls of the tube CS forms  $\text{SCTe}$  and  $\text{SCSe}$ . With chlorine, bromine or iodine CS forms compounds  $\text{SCX}_2$ .

*Carbon subsulphide,*  $\text{C}_3\text{S}_2$ , can be prepared by passing an electric discharge through  $\text{CS}_2$  vapour between carbon and antimony electrodes, or with  $\text{CS}_2$  liquid passed through a zinc arc:



$\text{C}_3\text{S}_2$  is a red liquid, m.p.  $-5^\circ\text{C}$ . It is soluble in  $\text{CS}_2$  and benzene and stable to water,  $\text{OH}^-$  or  $\text{H}^+$ . It is decomposed by heating *in vacuo* to  $\text{CS}_2$  and carbon, polymerizes slowly at ambient temperatures, rapidly at  $100^\circ\text{C}$  and forms  $\text{C}_3\text{S}_2\text{Br}_6$  with bromine.

Other subsulphides of formula  $(\text{CS}_x)_n$  ( $x = 2.5$  or  $3$ ) have been formed<sup>271</sup> as polymeric species by the reaction of trithiocarbonates and thiophosgene under various conditions or by reaction of carbon sulphide di-hydrogen sulphide with bromine.

<sup>266</sup> M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)* (1967) 865.

<sup>267</sup> M. C. Baird, G. Hartwell and G. Wilkinson, *J. Chem. Soc. (A)* (1967) 2037.

<sup>268</sup> M. C. Baird, G. Hartwell and G. Wilkinson, *J. Chem. Soc. (A)* (1968) 2198.

<sup>269</sup> M. C. Baird, G. Hartwell and G. Wilkinson, *J. Chem. Soc. (A)* (1968) 2660.

<sup>270</sup> R. Steudel, *Angew. Chem. (Int.)*, **6** (1967) 635.

<sup>271</sup> B. Krebs and G. Gattow, *Z. anorg. Chem.* **338** (1965) 225.

## Carbon-Sulphur Anions

Trithiocarbonates  $\text{CS}_3^{2-}$ 

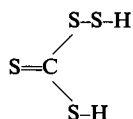
For the sulphur analogues of carbonates, several methods of synthesis are available. Carbon disulphide in aqueous sodium hydroxide gives sodium trithiocarbonate (see above); other methods are listed below.

*Ammonium trithiocarbonate.* Prepared by refluxing ammonium sulphide  $(\text{NH}_4)_2\text{S}_x$  with carbon disulphide. This yields pale yellow crystals of ammonium trithiocarbonate which are hygroscopic, soluble in water, alcohol and ether, and decompose on heating to carbon disulphide and ammonium sulphide.

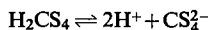
*Barium trithiocarbonate.* Prepared by reaction of hydrogen sulphide with barium hydroxide to give barium di-hydrogen sulphide  $\text{Ba}(\text{HS})_2$ . Carbon disulphide is passed over this in a stream of nitrogen and the addition of ether gives a yellow precipitate of the trithiocarbonate. Its solubility in water is 1.5 g/100 g  $\text{H}_2\text{O}$  at  $200^\circ\text{C}$ .  $\Delta H_f = -130.1$  kcal mole $^{-1}$ . Krebs, Gattow and Muller<sup>272</sup> found by X-ray diffraction and infrared spectroscopy that the crystals were isomorphous with both calcite and aragonite.

*Trithiocarbonic acid*,  $\text{H}_2\text{CS}_3$ , is a highly refractive red oil prepared when solid  $\text{BaCS}_3$  is treated with ice-cold 5 M hydrochloric acid. Physical properties quoted by Krebs and Gattow<sup>273</sup> are m.p.  $-26.9^\circ\text{C}$ , b.p. (extrapolated)  $57.8^\circ\text{C}$ ,  $\Delta H_f^{298} + 5.6$  kcal mole $^{-1}$ ,  $d_4^{20}$  1.483 g cm $^{-3}$ . Krebs and Gattow<sup>274</sup> also report the structure of yellow monoclinic crystals of the acid at  $-110^\circ\text{C}$ ; individual molecules  $\text{SC}(\text{SH})_2$  form double spirals parallel to the  $c$ -axis. Within the molecule the  $\text{CS}_3$  groups are planar, with C-S bond distances 1.69 to 1.77 Å,  $\angle(\text{SCS}) = 120^\circ$ . Trithiocarbonic acid decomposes to gaseous hydrogen sulphide and carbon disulphide; sulphur is soluble in the acid but does not form  $\text{H}_2\text{CS}_4$ . The di-etherate  $\text{H}_2\text{CS}_3\text{Et}_2\text{O}$  is formed by decomposing an ethereal solution of barium trithiocarbonate with gaseous HCl. Krebs and Gattow<sup>275</sup> further report the addition compound  $\text{H}_2\text{S} \cdot \text{CS}_2$  from low temperature reaction of the components. The addition compound melts at  $-120^\circ\text{C}$  and  $\Delta H_f^{153} = 10.2$  kcal mole $^{-1}$ . A full comparison of this addition compound with trithiocarbonic acid is given.

*Perthiocarbonic acid*,  $\text{H}_2\text{CS}_4$ <sup>276</sup>, has been prepared by treating a suspension of ammonium perthiocarbonate in dimethyl ether with the stoichiometric amount of gaseous hydrogen chloride at  $-78^\circ\text{C}$ ; the product has m.p.  $-36^\circ\text{C}$ ,  $\Delta H_f^{298} = 9.7$  kcal mole $^{-1}$ . The structure



has been verified by infrared and chromatographic methods. In aqueous solution perthiocarbonic acid ionizes:



*Carbon oxosulphide*, COS, is prepared in the laboratory by the addition of powdered potassium or ammonium thiocyanate to dilute sulphuric acid. It can also be prepared by oxidation of carbon disulphide by sulphur trioxide or by reaction of  $\text{CS}_2$  with urea. A good

<sup>272</sup> B. Krebs, G. Gattow and A. Muller, *Z. anorg. Chem.* **337** (1965) 279.

<sup>273</sup> B. Krebs and G. Gattow, *Angew. Chem. (Int.)*, **1** (1962) 47.

<sup>274</sup> B. Krebs and G. Gattow, *Naturwiss.* **51** (1964) 544.

<sup>275</sup> B. Krebs and G. Gattow, *Z. anorg. Chem.* **325** (1963) 15.

<sup>276</sup> B. Krebs and G. Gattow, *Z. anorg. Chem.* **345** (1966) 137, 172.



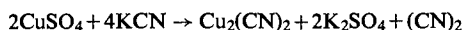
review on carbon oxysulphide is given by Reid<sup>277</sup>. Physical properties are: m.p.  $-138.5^{\circ}\text{C}$ , b.p.  $-50.2^{\circ}\text{C}$ ,  $\Delta H_f = 1.129 \text{ kcal mole}^{-1}$ ,  $\Delta H_v = 4.450 \text{ kcal mole}^{-1}$ . Solid COS is rhombohedral with one molecule per unit cell; in the gaseous state the molecule is linear; from electron diffraction,  $\text{C-O} = 1.13 \text{ \AA}$ ,  $\text{C-S} = 1.58 \text{ \AA}$ ; the dipole moment is  $0.72 \text{ D}$ . Spectroscopic data suggests that both the C-S and C-O bonds have double bond character. In its reactions carbon oxosulphide is intermediate between carbon dioxide and carbon disulphide.

### 3.5. CARBON-NITROGEN COMPOUNDS

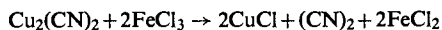
#### Cyanogen

##### Preparation

Early syntheses of cyanogen, involving the pyrolyses of heavy metal cyanides, were complicated by the formation of paracyanogen and were also occasionally hazardous. On the laboratory scale the most extensively used method has been the reaction of copper(II) sulphate with potassium cyanide in aqueous medium at  $60^{\circ}\text{C}$ <sup>278</sup>:



The gases evolved consist of a mixture of cyanogen (78%),  $\text{CO}_2$  (20%) and  $\text{HCN}$  (2%). Passage through solid  $\text{NaOH}$  removes  $\text{CO}_2$ , and through  $\text{AgNO}_3$  solution removes  $\text{HCN}$ , before drying the cyanogen using  $\text{CaCl}_2$  or  $\text{CaSO}_4$ . Cyanogen can also be obtained from the copper(I) cyanide produced in this reaction by heating an aqueous solution with iron(III) chloride:



An alternative method of preparation of cyanogen is by direct oxidation of hydrogen cyanide gas, using either air over a silver catalyst, chlorine over activated carbon or nitrogen dioxide over calcium oxide-glass<sup>279</sup>. Various other reactions which have been used to prepare cyanogen are described by Brotherton and Lynn<sup>278</sup>.

##### Properties

$(\text{CN})_2$  is a colourless, poisonous gas with an odour reminiscent of bitter almonds. The maximum tolerable vapour concentration of 10 ppm indicates a toxicity similar to that of hydrogen cyanide. The bond lengths and angles quoted in Table 42 derive from electron diffraction measurements at  $-95^{\circ}\text{C}$ <sup>280</sup> which also indicate that solid cyanogen has a fairly simple orthorhombic structure, the four molecules per unit cell being so arranged that all the nitrogen atoms lie in a hexagonal close-packed array. This is possible since the distance between the two nitrogen atoms in the molecule approximates closely to the van der Waals' distance for nitrogen. This crystal structure gives rise to three antisymmetric CN stretching modes in the infrared spectra of polycrystalline films of  $(\text{CN})_2$  at  $-190^{\circ}\text{C}$ <sup>281</sup>. High-resolution infrared spectra of the vapour have also been recorded<sup>282</sup>. These physical studies indicate that the single canonical form  $:\text{N}\equiv\text{C}-\text{C}\equiv\text{N}:$  may be used to represent the structure,

<sup>277</sup> E. E. Reid, *Organic Chem. of Bivalent Sulphur*, **4** (1962) 386.

<sup>278</sup> T. K. Brotherton and J. W. Lynn, *Chem. Rev.* **59** (1959) 841.

<sup>279</sup> W. F. Fierce and W. J. Saudner, *Ind. Eng. Chem.* **53** (1961) 985.

<sup>280</sup> A. S. Parkes and R. E. Hughes, *Acta Cryst.* **16** (1963) 734.

<sup>281</sup> F. D. Verderame and E. R. Nixon, *J. Chem. Phys.* **42** (1965) 3337.

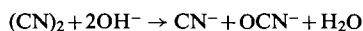
<sup>282</sup> A. G. Maki, *J. Chem. Phys.* **43** (1965) 3193.

TABLE 42. PHYSICAL PROPERTIES OF CYANOGEN<sup>278</sup>

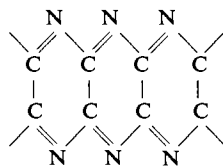
Boiling point	-21.17°C
Melting point	-27.9°C
Density of gas	2.321 g l <sup>-1</sup>
Density of liquid at b.p.	0.9537 g cm <sup>-3</sup>
Critical pressure	59.6 atm
Critical temperature	123.3°C
$\Delta H_f$	73.8 kcal mole <sup>-1</sup>
Bond lengths <sup>280</sup> :	
C-C	1.37 ± 0.02 Å
C-N	1.13 ± 0.015 Å
C-CN angle	180°
Solubility g (CN) <sub>2</sub> /100 g solvent:	
water	1.1-1.3
ethanol	26
ether	5

although the C-C bond length is less than that expected for a single bond indicating that there is some resonance with a C=C form.

Although cyanogen is fairly soluble in water, alcohol and ether, its solutions in these solvents soon decompose giving a variety of compounds including oxamide, HCN, HOCN and urea. In basic solution the cyanide and cyanate ions are formed:



Despite the very high enthalpy of formation cyanogen is stable when pure up to 850°C, although when impure it polymerizes at 300-500° to a brown, black mass known as paracyanogen, the structure of which has been inferred from infrared spectroscopy to be

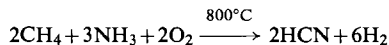


The polymer reverts to (CN)<sub>2</sub> above 800° and above 850° CN radicals are produced. A stoichiometric mixture of oxygen and cyanogen burns producing a temperature in the order of 4640°K<sup>283</sup> which is one of the hottest flames known from a chemical reaction.

### Hydrogen Cyanide

#### Preparation

Industrial preparations of hydrogen cyanide employ a catalytic oxidation of a mixture of methane and ammonia in a highly exothermic reaction (113.3 kcal mole<sup>-1</sup>)<sup>284</sup>.



The reaction of ammonia with carbon monoxide on the surface of a catalyst such as Al<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> at 500-700°C also yields hydrogen cyanide but direct union of the elements H<sub>2</sub>, N<sub>2</sub> and C to form HCN will only take place at temperatures greater than 1800°C. Hydrogen cyanide has also been obtained by recovery from crude "coal gas" in which it is present in

<sup>283</sup> J. B. Conway and A. V. Grosse, *J. Am. Chem. Soc.* **80** (1958) 2972.

<sup>284</sup> P. W. Sherwood, *Petroleum Processing*, **9** (1954) 384.

amounts varying from 0.1 to 0.3% by volume. In the laboratory hydrogen cyanide can be prepared by treating sodium cyanide with dilute sulphuric acid, and can be purified by repeated distilling and condensing over phosphorus(V) oxide.

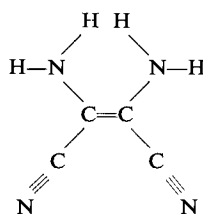
TABLE 43. PHYSICAL PROPERTIES OF HCN<sup>285</sup>

Melting point	-13.4°C
Boiling point	25.6°C
Density	0.681 g cm <sup>-3</sup>
Critical pressure	55 atm
Critical temperature	183.5°C
Equiv. cond. (0°C)	4.5 × 10 <sup>-7</sup> ohm <sup>-1</sup>
Viscosity (20°C)	0.00201 dyne sec cm <sup>-2</sup>
Dielectric constant	123 (15.6°C)
Dipole moment	2.8D
Trouton constant	20.2
C-N bond length <sup>286</sup>	1.156 Å
C-H bond length	1.065 Å

### Properties

Hydrogen cyanide is extremely poisonous, the maximum tolerable vapour concentration being 10 ppm; it is recommended that water containing more than 0.01 ppm of cyanide (as CN<sup>-</sup>) should be rejected as unfit for public use. Bark and Higson have reviewed the methods available for detection of small amounts of cyanide<sup>287</sup>.

Although it gives rise to the isomeric series R-N≡C and RC≡N hydrogen cyanide is known only in one form, all efforts to isolate HNC having failed. The frequencies of the vibration-rotation absorption bands of HCN in the infrared region from 2000 to 3600 cm<sup>-1</sup> are accurately known<sup>288</sup> and hence HCN may be used as a calibrant for spectrometers in this region. In the liquid the high dielectric constant is due to the association of the polar molecules, by hydrogen bonding (cf. H<sub>2</sub>O). In the absence of stabilizers liquid hydrogen cyanide can polymerize violently. One solid polymer has been shown to be tetrameric, existing as diaminomaleonitrile<sup>289</sup>:



The addition of hydrogen cyanide to acetylene using an aqueous copper(I) chloride-ammonium chloride catalyst can be used to produce both acrylonitrile and succinonitrile and is important industrially. Another important usage is in the preparation of adiponitrile.

<sup>285</sup> T. Moeller, *Inorganic Chemistry*, p. 341, Wiley (1952).

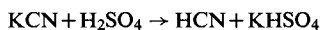
<sup>286</sup> A. H. Nethercot *et al.*, *Phys. Rev.* **86** (1952) 798.

<sup>287</sup> L. S. Bark and H. G. Higson, *Analyst*, **88** (1963) 751.

<sup>288</sup> A. G. Maki and L. R. Blaine, *J. Mol. Spec.* **12** (1964) 45.

<sup>289</sup> B. R. Penfold and W. N. Lipscomb, *Tetrahedron Letters*, **6** (1960) 17.

Hydrogen cyanide is miscible with water, ether and alcohols. In aqueous solution it is only very slightly dissociated ( $K_a = 2.1 \times 10^{-9}$ ), being an even weaker acid than HF, hence in aqueous solution soluble cyanides hydrolyse. Although its high dielectric constant makes liquid hydrogen cyanide an interesting protonic solvent, its poisonous nature has deterred extensive investigation of its characteristics. Nevertheless, sufficient data are available to show that its solvent power is less than that of water and that ionic mobilities in hydrogen cyanide are 3–4 times greater than the mobilities of the corresponding ions in water. This very high mobility in liquid hydrogen cyanide indicates that the ions are less solvated than in water since the lower viscosity of hydrogen cyanide (Table 43) cannot account for such a marked increase in mobility. A number of reactions in liquid hydrogen cyanide which can be regarded as typical neutralizations have been studied. An example is the equimolar reaction of KCN with  $\text{H}_2\text{SO}_4$  in which no apparent reaction takes place but on removal of the HCN the calculated amount of  $\text{KHSO}_4$  is recovered, i.e.



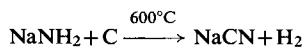
A summary of the solubilities and reactions of many inorganic and organic compounds in liquid hydrogen cyanide is given by Audrieth and Kleinberg<sup>290</sup>.

### Cyanides

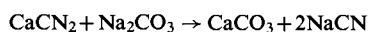
Numerous cyanides, both ionic and covalent, are known; the preparations and properties of some of the more important compounds are given below. The many complexes in which the cyanide acts as a ligand are discussed elsewhere.

#### Ionic Cyanides

Early industrial preparations of sodium cyanide, NaCN, employed the Castner–Kellner process from sodium amide,



but it is now manufactured from calcium cyanamide,  $\text{CaCN}_2^*$ . The cyanamide is fused with carbon and sodium carbonate and the product is leached out with water.



Calcium cyanamide is prepared by the reaction of finely ground calcium carbide with nitrogen. This is an exothermic reaction so that heating ( $1100^\circ\text{C}$ ) the reaction mixture at one point is sufficient to initiate the reaction which is then self-propagating. Acidification of calcium cyanamide gives cyanamide,  $\text{H}_2\text{N} \cdot \text{CN}$ , but the product commercially available is the dimer  $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NHCN}$  which contains the tautomer  $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{N}=\text{C}=\text{NH}$  (a substituted carbodi-imide). The carbodi-imides are reviewed by Kurzer and Douraghi-Zadeh<sup>291</sup>.

Sodium cyanide forms colourless crystals soluble in water and alcohol, but due to hydrolysis, the solutions of the alkali and alkaline earth metal cyanides in water have a strongly basic reaction. The cyanides NaCN, KCN and RbCN have crystal structures similar to

<sup>290</sup> L. F. Audrieth and J. Kleinberg, *Non-Aqueous Solvents*, p. 135, Wiley (1953).

<sup>291</sup> F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.* **67** (1967) 107.

\* More correctly described as a salt of carbodi-imide, i.e.  $\text{Ca}^{2+}[\text{N}=\text{C}=\text{N}]^-$ .

that of NaCl; the cyanides of Cs and Tl(I) both have the CsCl crystal structure. This similarity to the halide structures is due to the  $\text{CN}^-$  ion being freely rotating with an effective radius of 1.92 Å which is intermediate between that of the chloride and bromide ions<sup>292</sup>.

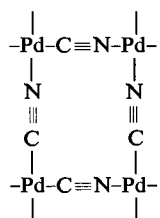
Sodium cyanide is used in the preparation of plating baths for electroplating, especially with the noble metals, and also for the extraction of silver and gold. Potassium cyanide is hygroscopic, very soluble in water but less so in alcohols, and has similar uses to NaCN; the sodium salt is generally preferred because of its higher cyanide content.

Lithium cyanide, best prepared by reacting lithium with silver cyanide in tetrahydrofuran, in the presence of naphthalene<sup>293</sup>, differs from the other alkali cyanides in that it has a much lower m.p. (160°C; cf. 550° and 620° for NaCN and KCN) and density, and in the crystal each ion is only four-coordinate<sup>292</sup>.

The cyanide ion is easily characterized by relatively sharp and weak absorptions in its infrared spectrum in the region 2250–2050  $\text{cm}^{-1}$ .

### Covalent Cyanides

Most of the covalent cyanides are insoluble in water, a notable exception being  $\text{Hg}(\text{CN})_2$ , which is made by treating mercury(II) sulphate with sodium cyanide and extracting the product with ethanol. This compound forms a molecular crystal composed of almost linear  $\text{NC-Hg-CN}$  molecules<sup>294</sup>. X-ray and neutron diffraction studies have shown that there are two weak Hg–N bonds in a plane perpendicular to the Hg–C bonds. Most of the other cyanides are built of chains of metal atoms linked by CN groups ( $\text{M-CN-M-CN-M-}$ ). In AgCN and AuCN the chains are linear and pyramidal.  $\text{As}(\text{CN})_3$ <sup>295</sup> also forms nearly linear chains, as a result of the weak bonds formed between one of the cyanide groups and the arsenic atom of an adjacent molecule. In other cyanides such as  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$  the linking of the metal atoms leads to a three-dimensional network whereas a simple layer structure is suggested for the PdII, PtII and NiII cyanides which form four co-planar bonds:



Selenium dicyanide is a V-shaped molecule with a C–Se–C angle of 120° and there is a short distance between the selenium atom and a nitrogen atom of a neighbouring molecule<sup>296</sup>. Most of the covalent cyanides which are insoluble in water will dissolve in excess alkali cyanide due to complex formation.

<sup>292</sup> A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., p. 733, O.U.P. (1962).

<sup>293</sup> K. Rossmanith, *Monatsch. Chem.* **96** (1965) 1690.

<sup>294</sup> J. Hvoslef, *Acta Chem. Scand.* **12** (1958) 1568.

<sup>295</sup> K. Emerson and D. Bretton, *Acta Cryst.* **16** (1963) 113.

<sup>296</sup> F. Feher, D. Hirschfeld and K. H. Lunke, *Acta Cryst.* **16** (1963) 154.

### Cyanogen Halides

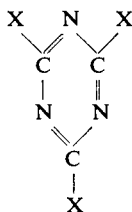
Cyanogen fluoride<sup>297</sup> is best prepared by the pyrolysis of cyanuric fluoride in a stream of nitrogen, at 1300° and about 50 mm pressure. It can also be obtained by fluorination of cyanogen and from the pyrolysis of  $\text{CF}_2=\text{NH}_2$ . The halides  $\text{CNCl}$  and  $\text{CNBr}$  can be prepared by treating a cyanide with chloride or bromide in aqueous solution or in an inert medium such as carbon tetrachloride. The iodide  $\text{CNI}$  is prepared from a dry cyanide such as  $\text{Hg}(\text{CN})_2$  by treating with iodine. Some of the physical constants of the cyanogen halides are tabulated below.

TABLE 44. PHYSICAL PROPERTIES OF THE CYANOGEN HALIDES<sup>297, 298</sup>

	CNF	CNCl	CNBr	CNI
Boiling point	-46°	13.0	61.3	sublimes (1 atm) at 146°
Melting point	-82°	-6.9	51.3	146°
C-X, Å	1.26	1.63	1.79	1.99
C-N, Å	1.16	1.16	1.16	1.16
Dipole moment, D	—	2.5	2.94	2.71

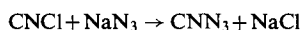
The molecules are linear, the important canonical forms being  $\text{X}-\text{C}\equiv\text{N}$  and  $\text{X}^+=\text{C}=\text{N}^-$ , and the contribution of the charged form increasing with the electropositivity of the halogen. Thus the infrared spectrum of  $\text{CNF}$  suggests that the  $\text{X}-\text{C}\equiv\text{N}$  structure predominates<sup>297</sup>. The infrared spectra of  $\text{CNCl}$ ,  $\text{CNBr}$  and  $\text{CNI}$  have also been recorded<sup>299</sup>.

Like hydrogen cyanide the cyanogen halides tend to polymerize, forming the trimeric cyanuric halides which have the cyclic structure shown below



This polymerization is favoured by the presence of the corresponding hydrogen halide ( $\text{HX}$ ) and hence by moisture since this produces  $\text{HX}$  by hydrolysis. Thus although cyanogen fluoride is stable indefinitely at  $-76^\circ\text{C}$ , at room temperature it polymerizes rapidly and in the presence of hydrogen fluoride it explodes.

Alkaline hydrolysis of the cyanogen halides yields the cyanate ion  $\text{OCN}^-$  and reaction with  $\text{NaN}_3$  produces the highly explosive cyanogen azide



<sup>297</sup> *Advances in Fluorine Chemistry*, p. 163, Ed. Stacey, Tatlow and Sharp, Butterworths (1965).

<sup>298</sup> Ref. 292, p. 721.

<sup>299</sup> W. S. Freitag and E. R. Nixon, *J. Chem. Phys.* **24** (1956) 109.

Cyanogen chloride and silver cyanate react quantitatively to yield the involatile compound  $(C_2N_2O)_x$  the infrared spectrum of this compound indicates the presence of  $C\equiv N$  and  $C=O$  bonds, and mass spectrometric evidence favours the cyanogen isocyanate  $N\equiv C-N=C=O$  structure rather than dicyanogen oxide  $N\equiv C-O-C\equiv N$ <sup>300</sup>.

### Cyanates and the Related Ions, $SCN^-$ , $SeCN^-$ , $TeCN^-$ , $HOCN$ and $OCN^-$

There is little evidence for the existence of the cyanogen analogue  $(OCN)_2$ , but cyanic acid can be obtained by thermal decomposition of its trimer cyanuric acid. It is a fairly strong acid ( $K_a = 12 \times 10^{-5}$  at  $0^\circ C$ ), freezing at  $-86.8^\circ C$  and boiling at  $+23.5^\circ C$ . Although most evidence is consistent with the acid existing mainly in the *iso* form  $HN=C=O$  the possibility of there being a small amount of cyanic acid  $HO-C\equiv N$  in tautomeric equilibrium with the *iso* form has not been ruled out and it has recently been shown<sup>301</sup> that the freshly prepared acid, obtained by reaction of finely powdered sodium cyanate with  $HCl$ , does contain some  $HOC\equiv N$  ( $\sim 3\%$ ). In solution the acid decomposes to give ammonia, water and carbon dioxide.

The cyanates are stable compounds prepared by oxidation of aqueous cyanide using lead(II) or lead(IV) oxides. Sodium cyanate has been obtained in 90% yield by the reaction of sodium dispersions with urea<sup>302</sup> and commercially potassium and sodium cyanates are manufactured by reaction of urea with sodium carbonate<sup>303</sup>. The infrared spectra of the cyanate ion in a state of matrix isolation in alkali halides have been recorded<sup>304</sup> and interpreted on the basis of a linear cyanate ion. The ion is isoelectronic with  $CO_2$  and with the azide ion and the alkali cyanates resemble the corresponding azides in many of their physical properties. Covalent compounds such as  $P(NCO)_3$  and some complexes are also known<sup>305</sup>. The covalent compounds are generally prepared by the reaction of their halides with  $AgOCN$  in benzene. In the majority of these compounds the cyanate is in the *iso* form, i.e. the nitrogen of the cyanate group is linked to the metal atom.

### HNCS and NCS<sup>-</sup>

Thiocyanogen  $(SCN)_2$  can be prepared by oxidation of an ethereal suspension of silver thiocyanate with iodine or bromine or by a similar reaction performed in liquid sulphur dioxide<sup>306</sup>. In this reaction after filtering off the silver bromide the sulphur dioxide is removed under reduced pressure at  $-50^\circ$  leaving white crystals of  $(SCN)_2$ . These crystals melt to produce an orange suspension at about  $-7^\circ C$  although some preparations have produced samples with m.p.  $-2^\circ$  to  $-3^\circ C$ . In the liquid form thiocyanogen is unstable and polymerizes rapidly to give the brick red solid parathiocyanogen. Recent studies<sup>307</sup> give  $\Delta H_f = 74.3 \text{ kcal mole}^{-1}$  and spectroscopic data obtained in this study are in accord with the structure  $N\equiv C-S-S-C\equiv N$ .

<sup>300</sup> E. Mayer and K. Kleboth, *Angew. Chem. (Int.)*, **8** (1969) 444.

<sup>301</sup> N. Goring and A. Holm, *Acta Chem. Scand.* **19** (1965) 1768.

<sup>302</sup> D. O. Depree, E. B. Oldenburg and J. A. Burns, Jr., *J. Inorg. Nucl. Chem.* **15** (1960) 287.

<sup>303</sup> A. Scattergood, *Inorg. Syntheses*, **2** (1946) 88.

<sup>304</sup> J. C. Decius and D. J. Gordon, *J. Chem. Phys.* **47** (1967) 1286.

<sup>305</sup> Ref. 285, p. 476.

<sup>306</sup> F. Seel and E. Müller, *Chem. Ber.* **88** (1955) 1747.

<sup>307</sup> C. E. Vanderzee and A. S. Quist, *Inorg. Chem.* **5** (1966) 1238.

Thiocyanic acid is best prepared by treating potassium hydrogen sulphate with potassium thiocyanate. The reactants are dried *in vacuo*, mixed and then heated gently to speed the reaction. Below 0° thiocyanic acid is a crystalline stable solid, but at normal temperatures it decomposes rapidly to give hydrogen cyanide and a solid yellow compound isoperthiocyanic acid  $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$ .

Microwave studies<sup>308</sup> give the following values for the bond lengths:  $\text{H}-\text{N} = 1.00 \text{ \AA}$ ,  $\text{N}-\text{C} = 1.21 \text{ \AA}$  and  $\text{C}-\text{S} = 1.56 \text{ \AA}$ . The HNC angle is 132°, although earlier studies reported slightly larger values.

As with cyanic acid there is the possibility of the acid being a tautomeric mixture of  $\text{HSC}\equiv\text{N}$  and  $\text{NH}=\text{C}=\text{S}$ , but only the *iso* form  $\text{HN}=\text{C}=\text{S}$  is present in the vapour phase and in solution in carbon tetrachloride. However, HNCS does differ from HNCO in that the two series of esters  $\text{RSC}\equiv\text{N}$  and  $\text{RN}=\text{C}=\text{S}$  are known and in general it does behave more like a tautomeric mixture of the two forms.

The thiocyanates are readily formed from cyanides by the addition of sulphur, for example, potassium thiocyanate is formed by melting potassium cyanide with sulphur. For the non-metallic thiocyanates the reaction of the corresponding non-metal chloride with silver cyanate in a benzene suspension has been extensively used<sup>309</sup>. Numerous thiocyanate complexes have been prepared and examples of both N and S bonding of the thiocyanate ligand to the metal ion are known<sup>310</sup>.

Like the cyanate the thiocyanate ion is linear ( $\text{N}-\text{C} = 1.17 \text{ \AA}$  and  $\text{C}-\text{S} = 1.61 \text{ \AA}$ ) and many thiocyanates are water-soluble, the most notable exceptions being those of copper(I), silver, gold(III) and mercury(II) which are insoluble, and the lead salt which is only slightly soluble. In crystalline silver thiocyanate the crystal is built up of infinite chains of silver atoms linked by SCN groups, the chains being bent at both the S and Ag atoms<sup>311</sup>. In other thiocyanates such as  $\text{Mg}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Ca}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  infrared and Raman spectral studies<sup>312</sup> indicate that the crystal is built of metal ions linked by SCN bridges. The phosphorus, silicon and arsenic thiocyanates<sup>313</sup> have also been studied and their infrared spectra are consistent with the compounds being isothiocyanates rather than normal thiocyanates.

Thiocyanogen will react with the halogens to form thiocyanogen halides and cyanogen thiocyanate,  $\text{CN}(\text{SCN})$  is also known (cf. cyanogen isocyanate, p. 1247).

### SeCN<sup>-</sup>

Selenocyanogen  $(\text{SeCN})_2$  is obtained by oxidation of silver selenocyanide with iodine in ether below 10° or by the reaction of lead tetra-acetate in chloroform with potassium selenocyanide in acetone. It is a stable yellow powder *in vacuo* when dry, but normally polymerizes to a red material. A linear structure similar to that of thiocyanogen is probable for selenocyanogen. Hydrolysis converts selenocyanogen into a mixture of the three acids  $\text{H}_2\text{SeO}_3$ , HCN and  $\text{HSeCN}$ . The selenocyanate ion is linear with bond lengths  $\text{N}-\text{C} = 1.22 \text{ \AA}$  and  $\text{C}-\text{Se} = 1.83 \text{ \AA}$ . The potassium and sodium salts can be obtained by fusing the corresponding cyanides with selenium at temperatures of 150° and 250°C

<sup>308</sup> G. C. Dousmann *et al.*, *J. Chem. Phys.* **21** (1953) 1416.

<sup>309</sup> H. H. Anderson, *Silicon, Sulphur and Phosphates*, pp. 37-235. Colloquium for the Section for Inorganic Chemistry, I.U.P.A.C., Münster (1954).

<sup>310</sup> J. O. Burmeister, *Coord. Chem. Rev.* **1** (1966) 205.

<sup>311</sup> I. Lindqvist, *Acta Cryst.* **10** (1957) 29.

<sup>312</sup> A. Tramer, *Compt. Rend.* **253** (1961) 1780.

<sup>313</sup> D. B. Sowerby, *J. Inorg. Nucl. Chem.* **22** (1961) 205.



respectively<sup>314</sup>, and many other selenocyanates can be obtained by precipitation from aqueous solution using potassium selenocyanate. Selenocyanates prepared in this way include those of Ag<sup>I</sup>, Cu<sup>I</sup>, Pb<sup>II</sup>, Te<sup>I</sup> and Hg<sup>II</sup>.

#### TeCN<sup>-</sup>

No evidence for the existence of TeCN<sup>-</sup> has been found<sup>315</sup> although Te(CN)<sub>2</sub> has been prepared by heating TeBr<sub>4</sub> with AgCN in benzene.

### 3.6. CARBON COMPLEXES

Carbon forms a few carbonium, neutral and carbanionic species which may be regarded as complexes in those cases where the groups attached to carbon function as polyatomic ligands in conventional complex compounds.

#### Carbonium Ions

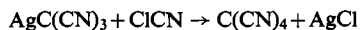
Reference has been made (p. 1218) to the triazidomethylum ion (CN<sub>3</sub>)<sub>3</sub><sup>+</sup>, formed by reaction of the compound (SbCl<sub>4</sub>N<sub>3</sub>)<sub>2</sub> with tetrachloromethane; the infrared spectrum of [C(N<sub>3</sub>)<sub>3</sub>]SbCl<sub>6</sub> indicates C<sub>3v</sub> symmetry with the three nitrogen atoms coplanar with the central carbon atom<sup>316</sup>.

The guanidinium cation C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup> and alkyl derivatives C(NR<sub>2</sub>)<sub>3</sub><sup>+</sup> are well known and need no further description.

Reaction of *o*-phenylenebisdimethylarsine (diars) with halomethanes CH<sub>2</sub>X<sub>2</sub> or CX<sub>4</sub> gives carbonium ions [H<sub>2</sub>C diars]<sup>2+</sup> and [C(diars)<sub>2</sub>]<sup>4+</sup> which appear as stable white crystalline salts of the halide X<sup>317</sup>.

#### Neutral Complexes

Some neutral species CX<sub>4</sub> corresponding to carbonium ions CX<sub>3</sub><sup>+</sup> or carbonions CX<sub>3</sub><sup>-</sup> have only recently been synthesized. Thus although tetranitromethane C(NO<sub>2</sub>)<sub>4</sub> has been known for many years and is the starting-point for nitrocarbanions (see below), the corresponding C(CN)<sub>4</sub> and C(NMe<sub>2</sub>)<sub>4</sub> have only recently been obtained. Tetracyanomethane is obtained as a readily sublimed solid by reaction of silver tricyanomethide with cyanogen chloride<sup>318</sup>



and the solid tetrakisdimethylaminomethane by reaction of tetramethylchloroformamidium chloride [(Me<sub>2</sub>N)<sub>2</sub>CCl]<sup>+</sup>Cl<sup>-</sup> with lithium dimethylamide; the proton nmr spectrum shows a sharp singlet at  $\tau$  7.39 (TMS as internal standard)<sup>319</sup>.

The reaction of tetrahalomethanes with active metals has also been used to synthesize neutral complexes CX<sub>4</sub>. Tetrabromomethane reacts visibly with magnesium in tetrahydrofuran, but gives no identifiable products; however addition of a trialkylchlorosilane R<sub>3</sub>SiCl gives good yields of the tetrasilylmethane (R<sub>3</sub>Si)<sub>4</sub>C as well as (R<sub>3</sub>Si)<sub>3</sub>CH and (R<sub>3</sub>Si)<sub>2</sub>CH<sub>2</sub><sup>320</sup>.

<sup>314</sup> G. R. Watkins and R. Shutt, ref. 303, p. 186.

<sup>315</sup> N. N. Greenwood, R. Little and M. J. Sprague, *J. Chem. Soc.* (1964) 1292.

<sup>316</sup> U. Müller and K. Dehnicke, *Angew. Chem. (Int.)*, **5** (1966) 841.

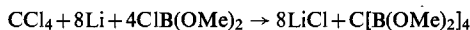
<sup>317</sup> R. N. Collinge, R. S. Nyholm and M. L. Tobe, *Nature*, **201** (1964) 1322.

<sup>318</sup> E. Mayer, *Monatsh.* **100** (1969) 462.

<sup>319</sup> H. Weingarten and W. A. White, *J. Am. Chem. Soc.* **88** (1966) 2885.

<sup>320</sup> R. L. Merker and M. J. Scott, *J. Org. Chem.* **29** (1964) 953.

Similarly reaction of tetrachloromethane with lithium in presence of dimethoxychloroborane gives the tetrakis(dimethoxyboryl)methane<sup>321</sup>:



The preparation of  $\text{C(BCl}_2\text{)}_4$  has been described in a previous section (p. 1201).

### Anionic Complexes

Salts containing the anion  $\text{C(NO}_2\text{)}_3^-$  may be prepared safely by the reaction of tetranitromethane with potassium hexacyanoferrate(II):



The parent acid, nitroform, is a strong acid and, as obtained by acidification of the potassium salt, exists as the *aci*- form  $\text{C(NO}_2\text{)}_2\text{.NO.OH}$ . Crystal structure determinations indicate a propeller-shaped anion in  $\text{N}_2\text{H}_5^+[\text{C(NO}_2\text{)}_3]^-$  but in  $\text{K[C(NO}_2\text{)}_3]$  one  $\text{NO}_2$  is perpendicular to the rest of the anion<sup>322</sup>.

Derivatives of cyanoforn,  $\text{HC(CN)}_3$ , have been known for some years, and the structures of several compounds containing the  $\text{C(CN)}_3^-$  ion have been determined. The parent salt  $\text{KC(CN)}_3$  is prepared by reaction of potassium cyanide with bromomalonitrile. The  $\text{C(CN)}_3^-$  ion forms salts with a number of first row transition metal ions in oxidation state +2; in the potassium and copper(II) salts the  $\text{C(CN)}_3^-$  ion is reported to be almost planar, with  $\text{C-N} = 1.15 \text{ \AA}$  in the copper(II) salt<sup>323</sup>. A M.O. treatment of the ion suggests that the nitrogen atoms, rather than the central carbon, are the likely sites for electrophilic attachment (e.g. the proton)<sup>324</sup>.

The substance  $\text{C[B(OMe)}_2\text{]}_4$  described above, on treatment with a Grignard reagent yields the anion  $\{\text{C[B(OMe)}_2\text{]}_3\}^-$ <sup>320</sup>.

## 4. GRAPHITE<sup>325-332</sup>

### 4.1. NATURAL GRAPHITE

Natural graphite is very widely distributed throughout the world, occurring occasionally in large masses but generally found as nodules in eruptive rocks and in veins through cracks in sedimentary deposits. Large well-developed crystals have been discovered in meteorites where graphite is a common constituent. Current commercially operated deposits are found in Ceylon, Korea, Austria, Siberia, Madagascar and North America. In 1955 the world production was 290,000 tons, of which 90,000 tons came from Korea alone.

<sup>321</sup> R. B. Castle and D. S. Matteson, *J. Am. Chem. Soc.* **90** (1968) 2194.

<sup>322</sup> B. Dickens, *Chem. Commun.* (1967) 246; N. I. Golovina and L. O. Atovyman, *Zhur. strukt. Khim.* **8** (1967) 307.

<sup>323</sup> C. Biondi, M. Bonamico, L. Torelli and A. Vacciago, *Chem. Commun.* (1955) 191.

<sup>324</sup> J. H. Enemark and R. H. Holm, *Inorg. Chem.* **3** (1964) 1516.

<sup>325</sup> A. R. Ubbelohde and F. A. Lewis, *Graphite and its Crystal Compounds*, Oxford (1960).

<sup>326</sup> A. Pacault, *Les Carbones*, Paris (1965).

<sup>327</sup> R. E. Nightingale, *Nuclear Graphite*, New York (1962).

<sup>328</sup> H. W. Davidson, P. K. C. Wiggs, A. H. Churchouse, F. A. P. Maggs and R. S. Bradley, *Manufactured Carbon*, Pergamon (1968).

<sup>329</sup> W. N. Reynolds, *Physical Properties of Graphite*, Elsevier (1968).

<sup>330</sup> R. C. Croft, Lamellar compounds of graphite, *Quart. Rev.* **14** (1960) 1.

<sup>331</sup> G. R. Hennig, Interstitial compounds of graphite, *Prog. in Inorg. Chem.* **1** (1959) 125.

<sup>332</sup> W. Rüdorff, Graphite intercalation compounds, *Adv. in Inorg. Chem. and Radiochem.* **1** (1959) 224.

Natural graphite is separated from the grosser impurities by flotation and then refluxed alternately with hydrofluoric and hydrochloric acids. Final purification is achieved by heating to 1500°C *in vacuo*, or at 3000°C in a stream of chlorine.

Graphite has traditionally found its main uses as electrode material<sup>333</sup> and as a refractory<sup>334</sup>, but is now finding increasing use as a high-strength material<sup>335</sup> and moderator for nuclear reactors<sup>336</sup>. It is also commonly used as a lubricant<sup>337</sup> and as part of a high temperature thermocouple<sup>338</sup>.

#### 4.2. SYNTHETIC GRAPHITE

Despite the large commercial exploitation of natural graphite deposits the bulk of the world's supply comes from synthetic forms, of which 1,230,000 tons were manufactured in 1960. Methods of preparation vary depending on the ultimate use and form of the material, but nearly all use coal or petroleum products as the starting material and generate the graphite by progressive pyrolysis.

##### Pyrolytic Graphite

Pure graphite is normally manufactured by the Acheson process<sup>339</sup> starting from petroleum coke. After calcining at 1400°C to remove gross impurities and improve the crystal structure, the coke is mixed with coal pitch binder at 165°C. This can be extruded into the desired shape before firing at 800° to 1000°C to stabilize the binder. After impregnation with further pitch to achieve the required density graphitization is produced by heating in an electrical oven *in vacuo* at 2600° to 3000°C.

The final product can show wide variations in density, porosity, etc., but for general purpose use this is no great disadvantage. Subsequent treatment and purification depends on the ultimate use of the material.

The pyrolysis of simple organic compounds<sup>326</sup> leads to more highly ordered graphites whose degree of structural imperfection depends on the deposition temperature<sup>340</sup>. The production of carbon films for resistors by this technique requires very careful control of the pyrolysis. Incomplete combustion in petrol engines yields graphite particles by the condensation of polycyclic aromatic molecules, simultaneously excluding foreign atoms from the matrix.

##### Kish Graphite

In the manufacture of cast iron, carbon flakes known as Kish graphite separate from the melt. This material is very similar to natural graphite as shown by its X-ray structure<sup>341</sup>.

<sup>333</sup> M. M. Angelevich, *Carbon Electrodes and Graphitised Articles*, Moscow (1961).

<sup>334</sup> ASTM Standards part 13, *Refractories* (1966).

<sup>335</sup> P. Brenner, *Metall.* **20** (1966) 926.

<sup>336</sup> L. S. Kothair and U. P. Duggal, *Adv. Nucl. Sci. Technol.* **2** (1964) 185.

<sup>337</sup> E. M. Klemgard, *Lubrication Eng.* **16** (1960) 468.

<sup>338</sup> A. R. Ubbelohde, L. C. F. Blackman and P. H. Dundas, *Chem. and Ind.* (1959) 595.

<sup>339</sup> F. Jeitner, E. Nedopil and O. Vohler, *Ber. deut. keram. Ges.* **41** (1964) 135.

<sup>340</sup> A. R. G. Brown, W. Watt, R. W. Powell and R. R. Tye, *Industrial Carbon and Graphite*, Soc. Chem. Ind., London (1958).

<sup>341</sup> E. Matuyama, *Nature*, **183** (1959) 670.

### Electrolytic Graphite

Graphite has been produced by the electrolysis of graphite oxide sols<sup>342</sup> (see section 4.8). Again the species is very similar to natural graphite and is composed of long dendritic crystals.

### Carbon Whiskers

The whisker, a form of highly purified artificial graphite<sup>343</sup>, is finding increasing use as a strengthening filler for plastics and in other composites<sup>344</sup>. Unlike metal whiskers these are not dislocation-free single crystals, but scroll-like formations continuous along the whisker length and possessing remarkable mechanical strength.

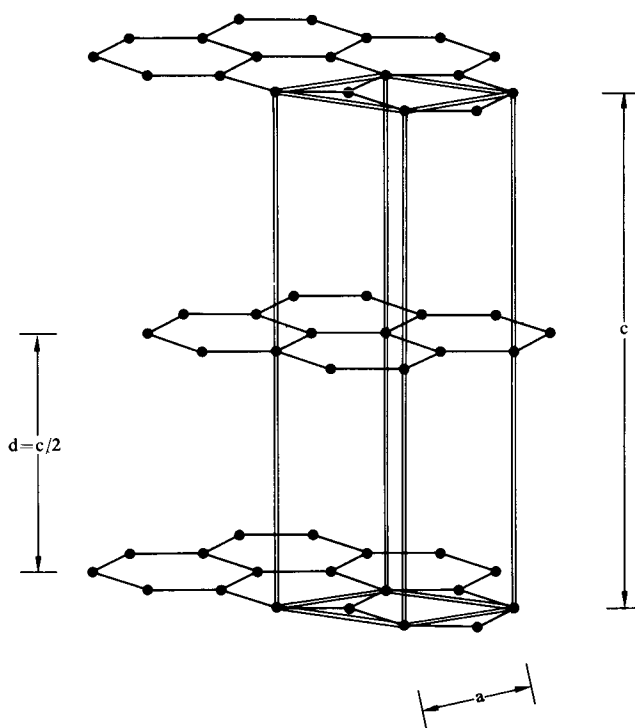


FIG. 12. The lattice structure of hexagonal ( $\alpha$ ) graphite.

Two principal commercial preparations are in use. A carbon arc operated at 3600°C in 90 atm of argon forms whiskers by the deposition of carbon from the vapour at the basal plane edges, eventually acquiring a tubular form. The maximum whisker length is about 5 cm and an average diameter of 5000 nm is usually reached. Recently, the pyrolysis of long-chain carbon macromolecules such as polyvinylchloride has been shown to produce a more or less continuous graphite whisker with well-regulated mechanical properties<sup>345</sup> (see also p. 1176).

<sup>342</sup> H. Thiele, *Tech. Ind. Schweiz. Chem. Z.* **18** (1935) 47.

<sup>343</sup> R. Bacon, *J. Appl. Phys.* **31** (1960) 283.

<sup>344</sup> A. P. Levitt, *Mech. Eng.* **89** (1967) 36.

<sup>345</sup> S. Otani, *Carbon*, **3** (1965) 31.

## 4.3. CRYSTALLOGRAPHY

In the perfect crystalline form graphite shows a planar morphology with a brilliant silver surface. In polycrystalline forms it is dark grey but may be readily distinguished from ungraphitized carbons by its ability to mark paper.

The ideal crystal lattice shown in Fig. 12 is the hexagonal  $\alpha$ -form, space group  $D_{6h}^4-C6/mmc$ . The basal planes consist of open hexagons (interatomic spacing = 0.1415 nm) stacked in an alternating sequence with a lattice spacing of 0.33539 nm<sup>346</sup>. In practice the lattice constant depends on the graphite source and is also a function of temperature (Fig. 13). The dependence follows the law

$$d = d_0 + \alpha T + \beta T^2$$

with the constants  $\alpha$  and  $\beta$  depending on the type of graphite. For a single crystal of Ceylon graphite<sup>347</sup>  $\alpha = 90.54 \times 10^{-6}$  and  $\beta = 6.33 \times 10^{-6}$ .

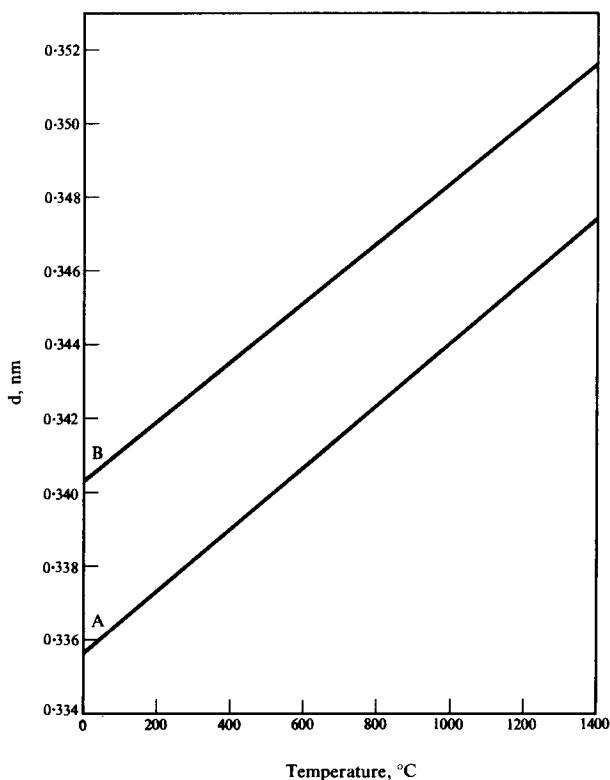


FIG. 13. Temperature dependence of the lattice constant of graphite. Curve A: Perfect crystal of natural graphite. Curve B: Highly disordered synthetic graphite.

Pulverized graphite often shows a second rhombohedral or  $\beta$ -crystalline form (Fig. 14) with a space group  $D_{3d}^5-R\bar{3}m$ . The same hexagonal networks are found but a regular network is formed from three repeating layers rather than the two in the  $\alpha$ -form. The lattice constant is consequently  $\frac{2}{3}$  of that of the  $\alpha$ -modification.

<sup>346</sup> J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. (London)*, **57** (1945) 477.

<sup>347</sup> E. G. Steward and B. P. Cooke, *Nature*, **185** (1960) 78.

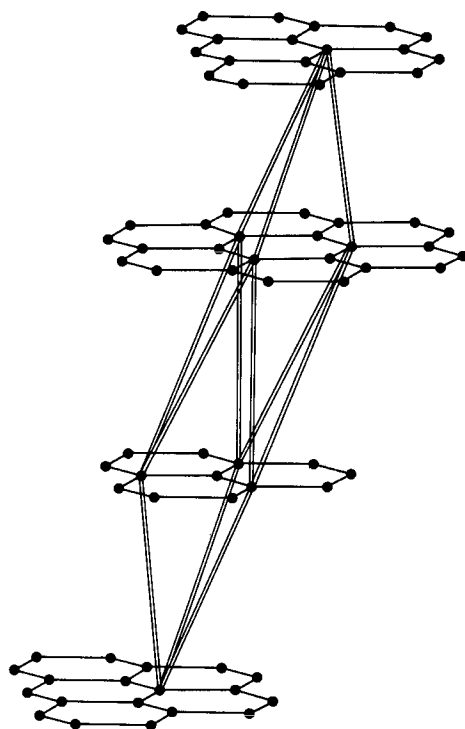


FIG. 14. The lattice structure of rhombohedral ( $\beta$ ) graphite.

Each of the structural characteristics of these ideal lattices are subject to modification by defects occurring either in the stacking sequences or in the carbon bond networks. In layer-stacking defects the hexagonal nets may be substantially perfect, but there is no ordered stacking sequence, leading to a “turbostratic” structure. Perhaps surprisingly, the interlayer separation is not very dependent on the degree of stacking order. Bacon<sup>348</sup> has proposed the empirical relation,  $d$  (Å) =  $3.440 - 0.086(p - 1) - 0.064p(1 - p)$  for the dependence of the interlayer spacing on stacking order  $p$  ( $p = 0$  for an ideal crystal). It is often assumed, when discussing turbostratic structures, that the carbon hexagon networks are infinitely large. For network sizes of less than 5 nm it is claimed that the spacing  $d$  increases more or less smoothly<sup>349</sup>. In practice layer disorder often accompanies break-up of the hexagonal networks and results primarily from edge type defects. When a C–C bond cannot be formed due to a disturbance of the planar sequence the “spare” carbon valencies may be satisfied in a number of ways. Often foreign atoms can bond to the edge defects<sup>350</sup> or weaker spin-paired bonds can be formed with neighbouring atoms<sup>351</sup>. The broken bonds can also lead to holes or ruptures in the structure—the so-called “hole and claw” defects<sup>352</sup>. Bond isomerism defects, i.e. carbon atoms with  $sp^3$  hybridization, would lead to a buckling of the carbon planes similar to the graphite oxide case (see Fig. 20).

<sup>348</sup> G. E. Bacon, *Acta Cryst.* **4** (1951) 558.

<sup>349</sup> U. Hofmann and D. Wilm, *Z. Electrochem.* **42** (1936) 504.

<sup>350</sup> H.-P. Boehm, *Adv. Catalysis*, **16** (1966) 179.

<sup>351</sup> C. A. Coulson, *Proc. 4th Carbon Conf.* (1959) 215.

<sup>352</sup> A. R. Ubbelohde, *Nature*, **180** (1957) 380.

In addition, dislocations in the structures can be detected, often associated with the defects. Screw dislocations for example may originate from claw defects, leading to steps in the structure. Four major dislocations have been detected, the principal one being defined when both the line and Burgers vectors lie in the basal plane arising from stacking faults<sup>353</sup>. All combinations of edge and coupled edge and screw dislocations have been observed, with an average energy of formation of  $0.5 \text{ erg cm}^{-2}$ . When the line and Burgers vectors both lie in non-basal directions only screw dislocations have been observed. In a pyrolytic graphite  $10^6$  to  $10^9$  screws per  $\text{cm}^2$  were observed with a pitch equal to the thickness of the atomic plane<sup>354</sup>. Edge dislocations have also been inferred from Moiré fringes, with the line vector in a non-basal plane and the Burgers vector lying in the plane. Dislocation loops in the basal plane have also been reported. The total density of dislocations can range between  $10^9$  and  $10^{13}$  per  $\text{cm}^2$  for even ultra-pure samples<sup>355</sup>.

Neutron irradiation produces a large amount of disorder in graphite which manifests itself as changes in the interlayer spacing, mechanical and electrical properties. A comprehensive review of this subject has been given by Simmons<sup>356</sup>.

#### 4.4. PHYSICAL PROPERTIES

##### Density

The density of an ideal hexagonal graphite is calculated to be  $2.266 \text{ g cm}^{-3}$  from X-ray measurements<sup>357</sup>, but in practice due to defects and dislocations values greater than  $2.15 \text{ g cm}^{-3}$  are seldom realized. Experimental values range from  $1.46 \text{ g cm}^{-3}$  for activated carbon to  $2.23 \text{ g cm}^{-3}$  for petroleum cokes. The use of fluid immersion techniques for density measurements is often a good guide to the size of pores in the material. Table 45 shows that even with helium the values are far below the theoretical limit, pointing to pore sizes less than 3 nm in radius.

TABLE 45. DENSITY OF GRAPHITE

Material	Immersion fluid	Density ( $\text{g cm}^{-3}$ )
Single crystal (X-ray)	—	2.266
Bulk	—	1.75
Bulk	helium	2.154
Bulk	benzene	2.163
Bulk	methanol	2.161

##### Mechanical Properties

The mechanical behaviour of graphite illustrates the anisotropy exhibited by graphite in most of its properties. This reaches a maximum for a perfect single crystal as shown by the data in Table 46.

<sup>353</sup> S. Amelinckx, P. Delavignette and M. Heerschap, *The Chemistry and Physics of Carbon*, Ed. P. L. Walker, Vol. 1, Dekker (1965).

<sup>354</sup> G. R. Hennig, *Science*, **147** (1965) 733.

<sup>355</sup> H. M. Otte and I. D. Blucher, *Phys. Status Solidi*, **9** (1965) 395.

<sup>356</sup> J. H. W. Simmons, *Radiation Damage in Graphite*, Pergamon (1965).

<sup>357</sup> U. Hofmann, D. Wilm and E. Csalan, *Z. Elektrochem.* **42** (1936) 506.

TABLE 46. THE ELASTIC CONSTANTS OF GRAPHITE<sup>329</sup>

Parameter	Value (10 <sup>11</sup> dyne cm <sup>-2</sup> )	Parameter	Value (10 <sup>-14</sup> dyne cm <sup>2</sup> )
$C_{11}$	106	$S_{11}$	9.85
$C_{12}$	18	$S_{12}$	-1.5
$C_{13}$	2.72	$S_{13}$	-6.3
$C_{33}$	3.65	$S_{33}$	275
$C_{44}^a$	0.018	$S_{44}^a$	56,000

<sup>a</sup> Variable due to stacking faults.

Young's modulus =  $1/S_{11}$  in the basal plane =  $9 \times 10^{12}$  dyne cm<sup>-2</sup>  
 =  $1/S_{33}$  along the *c*-axis

Bulk compressibility =  $2S_{11} + 2S_{12} + 4S_{13} + S_{33}$

Poisson ratios =  $-S_{12}/S_{11}$ ;  $-S_{13}/S_{11}$ ;  $-S_{13}/S_{33}$

For polycrystalline graphites and moulded or extruded samples these values depend on the method of preparation. The value for Young's modulus in the basal plane is exceptionally high, indicating that in this direction at least graphite is one of the strongest materials in nature. For whiskers the axial modulus has been reported as high as  $10^{13}$  dyne cm<sup>-2</sup><sup>343</sup>, which explains its use as a strengthening agent. The crystals are not perfectly elastic with some residual strain well below the breaking point at low stress levels.

Graphite crystals show good cleavage parallel to the basal plane with a very low hardness. Associated with this behaviour graphite has the property of being a very useful lubricating agent attributed to the formation of surface coatings of hexagon networks on the sliding surfaces. The controlling factor appears to be the low bonding forces between planes, although layer movement is probably a defect mechanism. Support for this is obtained from experiments showing that strong heating *in vacuo* until the evolution of gas ceases markedly increases the friction coefficient. Furthermore, the addition of a small proportion of high molecular weight hydrocarbons reduces the friction<sup>358</sup>.

#### 4.5. THERMAL PROPERTIES

##### Specific Heat

The specific heat of graphite has been obtained over a wide range of temperatures and for a variety of materials (Fig. 15)<sup>359</sup>. The excellent agreement obtained between workers having widely different samples implies that the specific heat is insensitive to minor crystal defects, except possibly at very low temperatures. Spencer<sup>360</sup> has empirically formulated the behaviour as,  $C_p = -1.265 + 14.008 \times 10^{-3}T - 103.31 \times 10^{-3}T^2 + 2.75 \times 10^{-9}T^3$ . The disagreement between workers at very low temperatures has been attributed to differences in the crystallite size and crystal defects<sup>361</sup>.

<sup>358</sup> R. H. Savage and D. L. Schaefer, *J. Appl. Phys.* **27** (1956) 136.

<sup>359</sup> A. Goldsmith, T. E. Waterman and H. J. Hirshhorn, *Handbook of Thermophysical Properties of Solid Materials*, Vol. 1, New York (1961).

<sup>360</sup> H. Spencer, *Ind. Eng. Chem.* **40** (1948) 2152.

<sup>361</sup> K. Komatsu, *J. Phys. Chem. Solids*, **6** (1958) 380.



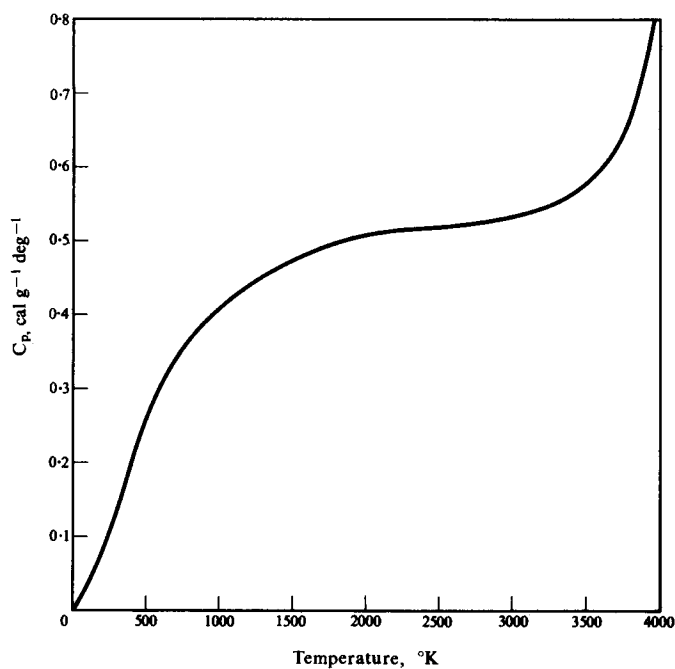


FIG. 15. The specific heat of graphite as a function of temperature.

Measurements of the entropy and enthalpy are less subject to controversy; the values are given in Table 47 <sup>327</sup>.

TABLE 47. THE ENTROPY AND ENTHALPY OF GRAPHITE

$T$ (°K)	$H_T^\circ - H_0^\circ$ (cal mole <sup>-1</sup> )	$S^\circ$ (cal mole <sup>-1</sup> °K <sup>-1</sup> )
13	0.0421	0.0041
25	0.2478	0.0154
50	2.0226	0.0629
100	14.674	0.2275
200	92.46	0.7384
298.16	251.183	1.3718
500	820.9	2.7988
1000	3075.7	5.8585
2000	8748.5	9.7561
4000	21,372.7	14.1129

### Expansion

For single crystals the thermal expansion of graphite again shows marked anisotropy, with most expansion occurring perpendicular to the basal plane. This reflects the weaker forces existing in this direction between the hexagon networks. Figures 16 and 17 illustrate

the behaviour<sup>362</sup>. The shrinkage in the  $a$ -dimension up to 400°C has been attributed to a Poisson effect, although it could also be due to changes in the charge transfer forces with increasing separation of the networks. The absolute values of the expansion coefficients vary widely as a function of the structure of the graphite, but the change in mean coefficient with temperature is almost identical.

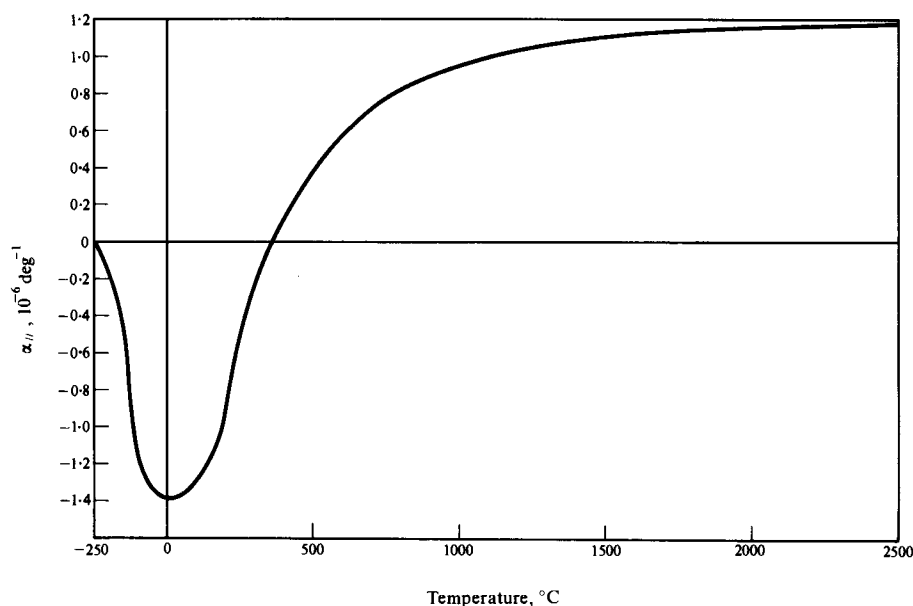


FIG. 16. Temperature dependence of the expansion coefficient  $\alpha_{||}$ .

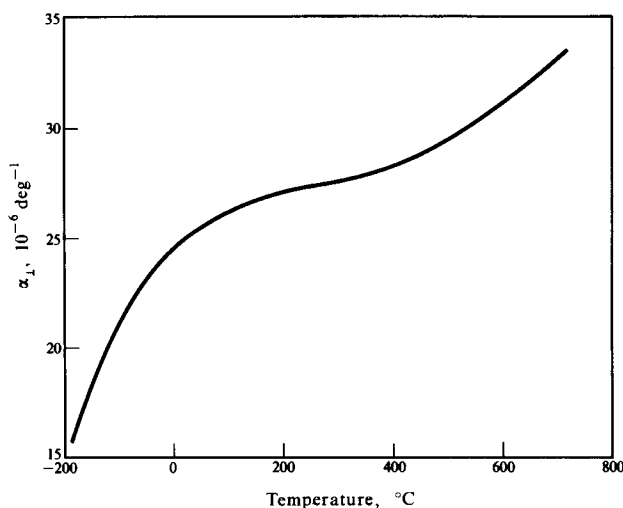


FIG. 17. Temperature dependence of the expansion coefficient  $\alpha_{\perp}$ .

<sup>362</sup> E. A. Kellet and B. P. Richards, *J. Nucl. Mater.* **12** (1964) 184.

### Thermal Conductivity

The thermal conductivity of graphite is of major importance in view of its use as a refractory material. Most recent measurements indicate a maximum in the value for the basal plane at about 100°K. The values range from 0.01 W cm<sup>-1</sup> °K<sup>-1</sup> at 3°K through 40 W cm<sup>-1</sup> °K<sup>-1</sup> at 100°K to 15 W cm<sup>-1</sup> °K<sup>-1</sup> at room temperature. In the increasing region the dependence on temperature has a power 2.7. Along the *c*-axis the graph is linear with a 2.3 power dependence, a typical figure being 1 W cm<sup>-1</sup> °K<sup>-1</sup> at 100°K<sup>363</sup>.

Current evidence suggests that carbon melts at 3800°K and boils at 4200°K at atmospheric pressure<sup>364</sup>.

### 4.6. BOND STRUCTURE

The electrical conductivity of graphite in the basal plane is 2 μohm cm at 10°K and 40 μohm cm at room temperature<sup>365</sup>. The resistivity thus corresponds to that of a semi-metal. In contrast the values are 0.3 to 0.5 ohm cm at 50°K and 0.15 to 0.25 ohm cm at room temperature along the *c*-axis. In this direction graphite possesses the characteristic resistivity of a semiconductor. It is plain that a theoretical understanding of the band structure is of prime importance. Since graphite may be thought of as a large aromatic molecule, such studies could provide much insight into aromatic molecules and vice versa.

There have been numerous calculations of the graphite band structure using molecular orbital (tight binding) theory<sup>366</sup> centred on two types of model—two- and three-dimensional. In the simple two-dimensional case of a single layer, three σ-bonds are presumed to be formed from the 2*s*, 2*p<sub>x</sub>* and 2*p<sub>y</sub>* orbitals with one π-bond from the 2*p<sub>z</sub>*. The several calculations disagree on some points but all agree that there is an energy gap between the bonding and anti-bonding σ-bands, but no gap in the π-band spectrum. In addition the energy at which the π-bands are degenerate is located within the σ-band gap. The Brillouin zone of a single layer is a hexagon with the two π-bands degenerate at the corners and a linear energy variation with wave vector near a corner. Computations of the energy bands<sup>367</sup> indicate that interactions up to the ninth neighbour distance still affect the results, throwing interesting light on the range of influence of network defects on the physical and chemical properties.

The band width is calculated to be between 5 and 10 eV and when interlayer interaction is included a perturbation of only about 0.5 eV is introduced. However, the principal effect of the three-dimensional model is a profound change in the properties of the conduction electrons. The Brillouin zone becomes a hexagonal cylinder and there are now four π-bands. Two of the bands overlap slightly so that graphite becomes a metal with free electrons and holes at all temperatures (Fig. 18). A group theoretical study<sup>368</sup> of graphite crystals has led to a model of the energy bands involving only a small number of experimental parameters. Cyclotron resonance<sup>369</sup> and studies of the de Haas–Van Alphen oscillations<sup>370</sup> have yielded information agreeing both with each other and with the theory. The results indicate that

<sup>363</sup> M. G. Holland, L. A. Klein and W. D. Straub, *J. Phys. Chem. Solids*, **27** (1966) 903.

<sup>364</sup> G. Glockler, *J. Chem. Phys.* **22** (1954) 159.

<sup>365</sup> I. L. Spain, A. R. Ubbelohde and D. A. Young, *Proc. 2nd Ind. Carbon and Graphite Conf.*, Soc. Chem. Ind., London (1965).

<sup>366</sup> R. R. Haering and S. Mrozowski, *Progr. in Semiconductors*, **5** (1960) 275.

<sup>367</sup> F. J. Corbato, *Proc. 3rd Carbon Conf.* (1957) 173.

<sup>368</sup> J. C. Slonczewski and P. R. Weiss, *Phys. Rev.* **109** (1958) 272.

<sup>369</sup> J. K. Galt, W. A. Yager and H. W. Dail, *Phys. Rev.* **103** (1956) 1586.

<sup>370</sup> T. C. Berlincourt and M. C. Steele, *Phys. Rev.* **98** (1955) 956.

both electrons and holes are majority carriers in equal numbers of about  $2.3 \times 10^{-5}$  per atom, and that the Fermi surfaces are 11 to 13 times larger parallel to the  $c$ -axis than perpendicular to it. Inoue<sup>371</sup> has recently interpreted these results in terms of the Landau levels in the Slonczewski-Weiss band model.

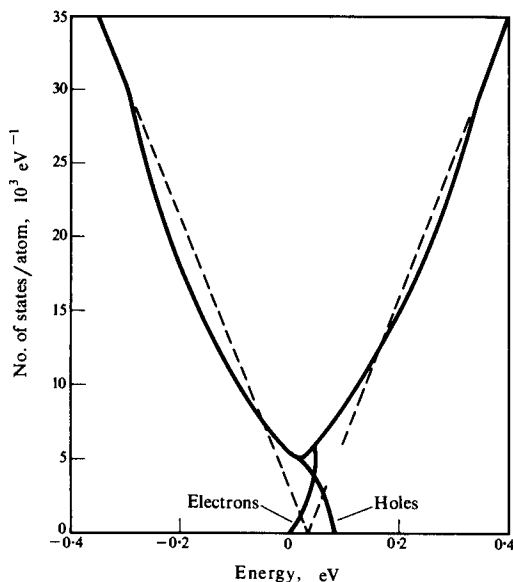


FIG. 18. The density of states in pure graphite. The solid line is calculated on the three-dimensional model and the dotted line is for the two-dimensional one.

The resistivity of polycrystalline graphite is lower than the single crystal because of boundary and defect scattering and porosity. The negative temperature coefficient below ambient and positive above are due to the large defect scattering term dominating carrier mobility at low temperatures and the variation records the change in effective carrier density with temperature. At high temperatures phonon scattering dominates.

Graphite, like the aromatic molecules, exhibits a large anisotropy in its diamagnetic susceptibility. Perpendicular to the principal axis the value is  $-0.5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  independent of temperature, while the difference between the two is about  $-30 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  at liquid helium temperatures, decreasing with increasing temperature<sup>372</sup>. The results may be expressed as<sup>373</sup>

$$\chi/\chi_0 = 1 - \exp(-T_0/T)$$

These results have been adequately explained from the point of view of both the two- and three-dimensional models<sup>374</sup> and indicate a close similarity with aromatic molecules. The principal difference between graphite and aromatic compounds is that in the former the susceptibility is contributed by states very near the band degeneracy, while in the latter it comes more or less uniformly from all the  $\pi$ -electrons.

<sup>371</sup> M. Inoue, *J. Phys. Soc. Japan*, **17** (1962) 808.

<sup>372</sup> N. Ganguli and K. S. Krishnan, *Proc. Roy. Soc. A* **177** (1941) 168.

<sup>373</sup> A. Pacault and A. Marchand, *Compt. Rend.* **241** (1955) 489.

<sup>374</sup> J. W. McClure, *Phys. Rev.* **119** (1960) 606.

Electron spin resonance studies on a wide variety of graphites at temperatures ranging from 20° to 3000°K have been performed. The single line obtained is attributed to both holes and electrons alike while line width studies suggests that spin-lattice relaxation occurs via the spin-orbit coupling of impurity atoms<sup>375</sup>.

The optical properties of graphite are summarized in Table 48<sup>376</sup>. The extinction coefficient has a minimum of about 1.0 at 550 nm and a maximum, attributed to a resonance effect, of about 1.93 at 260 nm.

TABLE 48. THE OPTICAL PROPERTIES OF A GRAPHITE SINGLE CRYSTAL AT 546.1 nm

Property	Basal plane	c-axis
Refractive index $\mu$	2.15	1.81
Absorption index $\chi$	0.66	—
Dielectric constant $\epsilon$	2.61	3.28
Reflectance in air $R$	0.280	0.083

#### 4.7. CHEMICAL REACTIONS

A great deal of research<sup>377</sup> has been devoted to the study of the conversion of graphite into volatile products. The following reactions are commercially important and Table 49 records the equilibrium constants for several reactions.

- (i)  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  liberating heat of combustion
- (ii)  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$  yielding gaseous fuel
- (iii)  $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$  being an important source of hydrogen
- (iv)  $\text{C} + n\text{H}_2 \rightarrow \text{CH}_4, \text{C}_2\text{H}_6, \text{etc.}$
- (v)  $\text{C} + n\text{Cl}_2 \rightarrow \text{CCl}_4, \text{etc.}$
- (vi)  $\text{C} + \text{S}_2 \rightarrow \text{CS}_2$

TABLE 49. EQUILIBRIUM CONSTANTS FOR SEVERAL GRAPHITE REACTIONS

Temperature (°C)	$\log_{10} K_p$			
	(1)	(2)	(3)	(4)
	(1) $\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	(2) $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	(3) $\text{CO} \rightleftharpoons \text{C} + \frac{1}{2}\text{O}_2$	(4) $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$
26.84	+15.86	-8.82	-23.93	-20.81
126.84	+10.11	-5.49	-19.13	-13.28
326.84	+4.29	-2.00	-14.34	-5.72
526.84	+1.36	-0.15	-11.93	-1.97
826.84	-1.06	+1.43	-9.94	+1.08
1126.84	-2.44	+2.36	-8.79	+2.80

<sup>375</sup> G. Wagoner, *Phys. Rev.* **118** (1960) 647.

<sup>376</sup> S. Ergun, *Nature*, **213** (1967) 136.

<sup>377</sup> J. D. Blackwood, *Rev. Pure Appl. Chem.* **4** (1954) 251.

<sup>378</sup> E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.* **44** (1952) 1048.

The increasing interest in graphite as a refractory and neutron moderator has prompted many of the studies on oxidation. Particularly interesting is the large discrepancy in behaviour between ordinary and irradiated graphite when subjected to oxygen attack. Phosphates and borates have been used to inhibit oxidation but most common impurities catalyse the reaction. Oxygen attack appears to proceed on the surface of crystallites and protective coatings have been devised to reduce this.

## GRAPHITE COMPOUNDS

Apart from the high-temperature reactions leading to volatile products, graphite will undergo milder reactions at more normal temperatures with elements and compounds leading to a variety of materials. Table 50 summarizes the position with respect to the elements. Leaving aside the carbides (section 2) there are two principal types of compound—ionic and covalent. In the former group graphitic characteristics are well preserved and their formation is reversible. In the latter group the typical graphitic properties are lacking and on heating straightforward carbon decomposition products are obtained, such as carbon dioxide, from graphitic oxide.

TABLE 50. THE REACTION OF GRAPHITE WITH THE ELEMENTS

Covalent lamellar compounds	Ionic lamellar compounds	Covalent carbides	Ionic carbides
O, F, S	Cl, Br, I, Li, Na, K, Rb, Cs, Fr	B, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Hf, Ta, W	Li, Be, Na, Ag, Al, Ca, Sc, Sr, Y, Ba, La, Ra, Ac, Th, Pa, U

### 4.8. COVALENT COMPOUNDS

#### Graphite Oxide (Graphitic Acid)

This is probably the most fully studied graphite compound, being known as early as 1860 due to the treatment of graphite with certain oxidizing agents<sup>379</sup>. The best known, and still most generally used, method of preparation was originally devised by Staudenmaier<sup>380</sup> and consists of adding solid potassium chlorate to a suspension of graphite in a mixture of concentrated nitric and sulphuric acids (1:2 v/v). The product is a pale lemon colour tending to darken on storage, although no correlation has yet been found between colour and composition. A more recent preparation<sup>381</sup> being sodium nitrate, sulphuric acid and potassium permanganate yields a graphite oxide comparable in degree of oxidation and purity to that of Staudenmaier. The compound can also be prepared by the anodic oxidation of graphite<sup>382</sup>.

<sup>379</sup> B. C. Brodie, *Phil. Trans.* **149** (1859) 249.

<sup>380</sup> L. Staudenmaier, *Ber. deut. chem. Ges.* **31** (1898) 1481.

<sup>381</sup> W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* **80** (1958) 1339.

<sup>382</sup> B. K. Brown and O. W. Storey, *Trans. Am. Electrochem. Soc.* **53** (1928) 140.

Graphite oxide is thermally unstable; decomposition commences above 70°C and at 200°C yields, with spectacular deflagration, carbon monoxide, carbon dioxide, water and soot. The very low decomposition temperature may well explain inconsistencies in the reported compositions since drying temperatures of 100° to 300°C were often used.

The composition of graphite oxide is usually characterized by the C:O ratio after taking into account the hydrogen found in combustion. This ratio has a theoretical maximum value of two which is never realized in practice. Well-oxidized preparations commonly have values ranging from 2.3 to 2.9, but samples with ratios of 3.5 to 4 are nevertheless homogeneous phases showing the same characteristic properties as the "better" samples. Many empirical formulae have been proposed ranging from  $C_7O_4H_2$  to  $C_{24}O_{13}H_9$ . Clauss *et al.*<sup>383</sup> have proposed the structure shown in Fig. 19 in both keto and enol forms, with an empirical

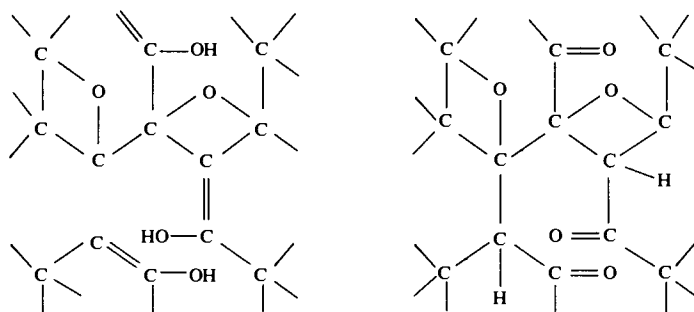


FIG. 19. The keto and enol forms of graphite oxide proposed by Clauss *et al.*<sup>383</sup>.

formula  $C_8O_2(OH)_2$ . These authors found that methylation of graphite oxide with diazomethane produced only partially hydrolysed esters, suggesting the presence of OH groups attached to carbon atoms in an enolic structure possessing exchangeable hydrogen ions. Enol groups could in fact account for the colour changes in graphite oxide without significant change in the structure. The maximum hydroxyl content found by Clauss *et al.* accounts for the hydrogen contained in the compound, but the balance of the oxygen must be linked in a different manner. In addition, the failure of all workers to achieve a C:O ratio of two suggests carbon-carbon double bonding. The structure shown in Fig. 10 is the net result of these findings, with a C:O ratio of 2.67 and a hydroxyl content of 1240 mequiv per 100 g of oxide. The loss of three out of every twenty pairs of hydroxyl groups leads to an empirical formula  $C_8O_2(OH)_{1.7}$  and predicts the experimentally observed C:O ratio of 2.8 and hydroxyl content of 1080 mequiv per 100 g.

The structure in Fig. 19 accounts very nicely for the chemical properties of graphite oxide, but the possibility of tertiary hydroxyl groups and ether-like oxygen bridges cannot be ruled out. However, a structural model based on these groups does possess a more satisfactory basis than other models based on peroxide groups and ionically attached hydroxyl groups<sup>384</sup>. Infrared evidence provides little new information, but does confirm the presence of -OH, C-O and C=O groups (Table 51).

<sup>383</sup> A. Clauss, R. Plass, H.-P. Boehm and U. Hofmann, *Z. anorg. und allgem. Chem.* **291** (1957) 205.

<sup>384</sup> J. H. de Boer and A. B. C. van Doorn, *Proc. k. ned. Akad. Wetenschap.* **57B** (1954) 181.

TABLE 51. THE INFRARED FREQUENCIES OF GRAPHITE OXIDE<sup>385</sup>

Frequency (cm <sup>-1</sup> )	Assignment
3440	C (fixed)-OH stretch
1720	C=O stretch
1620	H <sub>2</sub> O bend
1420	O-H deformation
1360	C-OH deformation
1070	C-OH stretch, C-O-C bridge stretch
980	Epoxide or peroxide

It can be concluded that the formula of graphite oxide remains uncertain in detail, but the existence of a keto/enol equilibrium is well established. The structure of Clauss *et al.* represents the best interpretation to date.

Graphite oxide is observed under a microscope as small flakes with a presumably rhombic or monoclinic structure. The lattice is found to possess a six-fold axis of symmetry along the normal to the flakes similar to graphite itself. X-ray investigation reveals that the interlayer spacing in graphite increases on forming the oxide—a variable distance from 0.6 to 1.1 nm is found, depending on the water content. X-ray powder photographs show a C-C spacing in the 10 $\bar{1}$ 0 and 11 $\bar{2}$ 0 planes of 0.144 nm compared with the value 0.141 nm in graphite. A comparison with buckled layers in alicyclic compounds shows that the projection onto a plane of the normal C-C bonds (0.153 nm) gives an apparent spacing of 0.145 nm. This lends some credence to the lattice picture of graphite oxide proposed by Ruess<sup>386</sup> and shown in Fig. 20.

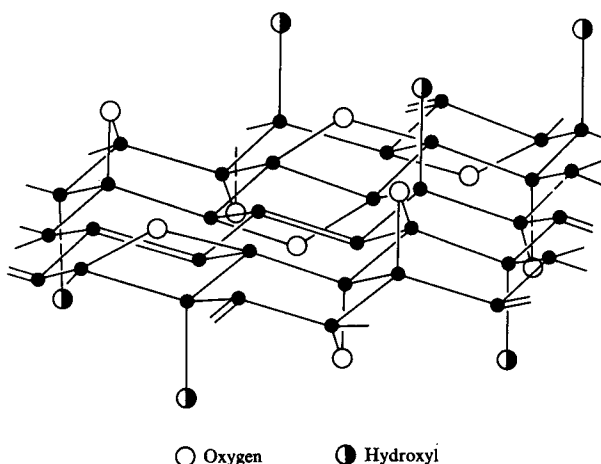


FIG. 20. The lattice structure of graphite oxide.

<sup>385</sup> D. Hadzi and A. Novak, *Trans. Faraday Soc.* **51** (1955) 1614.

<sup>386</sup> G. Ruess, *Monatsch. Chem.* **76** (1946) 381.



Table 52 summarizes the principal physical properties of graphite oxide.

TABLE 52. PHYSICAL PROPERTIES OF GRAPHITE OXIDE

Property	Value
Density <sup>a</sup>	1.918 g cm <sup>-3</sup> (mean)
Specific surface <sup>b</sup>	1.7 to 108.5 m <sup>2</sup> g <sup>-1</sup>
Magnetic susceptibility <sup>c</sup>	$-0.54 \times 10^{-6}$ cm <sup>3</sup> g <sup>-1</sup>
Electrical conductivity <sup>d</sup>	$\sim 10^5$ ohm cm
Heat of combustion <sup>a</sup>	4.7 kcal g <sup>-1</sup>

<sup>a</sup> U. Hofmann, A. Frenzel and E. Csalan, *Liebigs Ann. Chem.* **510** (1934) 1.

<sup>b</sup> H.-P. Boehn and W. Scholz, *Liebigs Ann. Chem.* **691** (1966) 1.

<sup>c</sup> N. Ganguli, *Phil. Mag.* **12** (1936) 355.

<sup>d</sup> U. Hofmann and A. Frenzel, *Ber. deut. chem. Ges.* **63** (1930) 1248.

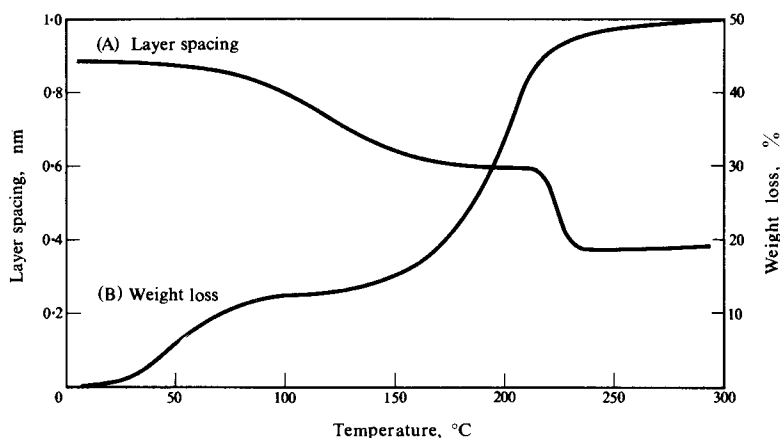


FIG. 21. The behaviour of graphite oxide as a function of temperature. Curve A represents the change in interlayer spacing. Curve B represents the percentage change in weight.

The thermal instability of graphite oxide has already been mentioned; Fig. 21 shows the weight loss and change in interlayer spacing as a function of temperature during slow pyrolysis. The experiment was performed over a period of two days on a sample made by the Staudenmaier method using Ceylon graphite<sup>387</sup>. The curves may be analysed as several separate regions.

(i) Up to 100°C there is a substantial weight loss attributed to the expulsion of adsorbed water. The analytical work of de Boer and Van Doorn<sup>388</sup> also suggests a considerable evolution of oxygen in the region of 70°C.

<sup>387</sup> E. Matuyama, *J. Phys. Chem.* **58** (1954) 215.

<sup>388</sup> J. H. de Boer and A. B. C. van Doorn, *Proc. Ind. Carbon and Graphite Conf.*, Soc. Chem. Ind., London (1957).

(ii) Between 150° and 190°C there is a further weight loss, the end of which is marked by a sharp drop in the interlayer spacing.

(iii) Between 190° and 220°C there is a loss of weight again terminated by a sharp, and in this case, massive contraction in the layers. Corresponding with these two regions, there is an increase in carbon dioxide evolution and, at the higher temperatures, carbon monoxide begins to be formed.

(iv) Above 220°C the decomposition proceeds slowly and is essentially complete at 280°C.

When heated rapidly to 200°C, explosive deflagration occurs with the formation of an unusual variety of soot with a high specific area<sup>389</sup>. Electron micrographs reveal a structure likened to a heap of crumpled paper sheets with dimensions depending on the nature of the oxide. The thickness ranges between 2 and 10 nm while the area can be 100 nm<sup>2</sup>. Structural determinations<sup>390</sup> show the carbons to be linked hexagonally within layer plates making a structure similar to graphite. This is confirmed by the evidence that the anisotropy of the electrical conductivity behaves similarly. The catalytic activity of graphite oxide soot, measured by hydrogen bromide synthesis, is among the highest recorded for activated carbons<sup>391</sup>. Experiments suggest that the catalytic centres are the same as those at which surface oxidation takes place.

TABLE 53. SPECIFIC VOLUME MEASUREMENTS ON GRAPHITE  
OXIDE <sup>388</sup>

Solvent	Specific volume (cm <sup>3</sup> g <sup>-1</sup> )
Methanol	0.383
Pyridine	0.412
Water	0.423
Benzene	0.488
Carbon tetrachloride	0.515

The most striking physical phenomena shown by graphite oxide are found when various polar liquids are intercalated into the lattice. The oxide layer planes are penetrated and eventually dispersed as giant two-dimensional molecules. The swelling behaviour toward water is particularly interesting—light yellow, highly viscous sols can be formed simply by shaking the oxide with water, without recourse to peptizing agents<sup>392</sup>. The sols are typical, structurally viscous, negatively-charged molecular colloids resembling protein sols. They possess a remarkably high viscosity at low concentrations, for example, a 1 % sol will not flow from an inverted vessel. The viscosity is directly related to the size of the dispersed oxide lamellae and is independent of the type of graphite oxide used. This is yet further evidence that colour changes in the oxide are a result of internal structural rearrangement and not changes in composition.

The intercalation of other liquids is demonstrated by specific volume measurements in various solvents presented in Table 53 (the X-ray density yields a value of 0.466 cm<sup>3</sup> g<sup>-1</sup>).

<sup>389</sup> G. L. Ruess, *Kolloid-Z.* **109** (1944) 149.

<sup>390</sup> K. Beyersdorfer, *Optik.* **7** (1950) 192.

<sup>391</sup> G. L. Ruess and W. R. Ruston, *Fuel*, **25** (1946) 156.

<sup>392</sup> H. Thiele, *Kolloid-Z.* **111** (1948) 15.

The data show quite clearly that the specific volume is smallest for polar liquids, implying that these molecules only can be accommodated within the interlamellar spaces. X-ray studies<sup>393</sup> on a series of fifty polar molecules indicate that small linear molecules lie flat between the lamellae, while larger ones tend to be fixed perpendicular to the networks.

In weakly alkaline solutions (0.01 M) the swelling, due to the assimilation of cations, is so large that the interplanar distance can no longer be measured with X-rays. Graphite oxide is capable of absorbing at least 10 mequiv of cation per gram of oxide, with maximum swelling observed for ammonium ions.

Graphite oxide behaves as a mild oxidizing agent, reacting incompletely with reducing agents to yield graphite. In this connection it has been employed as a depolarizing agent in Leclanché cells, and in secondary cells when incorporated into carbon plates<sup>394</sup>. The compound has had limited commercial exploitation, being used to artificially increase the density of carbon blocks for atomic reactors<sup>395</sup> and as a membrane for water vapour measurements<sup>396</sup>.

### Carbon Monofluoride

In common with many other elements, carbon will burn in fluorine, producing a variety of carbon fluorides, the nature of which is in some degree dependent on the character of the carbon used. By a careful selection of the reaction temperature and fluorine pressure<sup>397</sup> it is possible to achieve the conversion without combustion to produce grey solids with molecular formula  $(CF)_n$ . Typical reaction conditions are 420°C and 1 atm of fluorine. The conversion is shown in Fig. 22. At elevated temperatures ( $\sim 600^\circ\text{C}$ ) the reaction proceeds

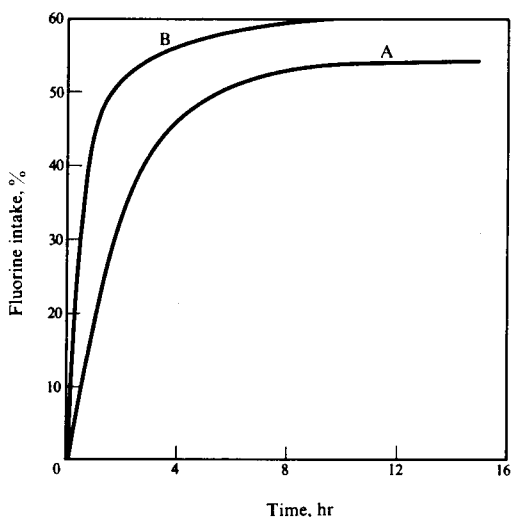


FIG. 22. The uptake of fluorine at 1 atm pressure to form  $(CF)_n$ . Curve A 500°C. Curve B 450°C.

<sup>393</sup> F. Aragon de la Grutz, J. Cano Ruiz and D. M. C. MacEwen, *Nature*, **183** (1959) 740.

<sup>394</sup> H. Jedlicka, *Z. Naturforsch.* **2a** (1947) 534.

<sup>395</sup> Frechette and Yung Tao, *Nucl. Sci. Abs.* **8** (1954) 161.

<sup>396</sup> A. Clauss and U. Hofmann, *Angew. Chem.* **58** (1954) 215.

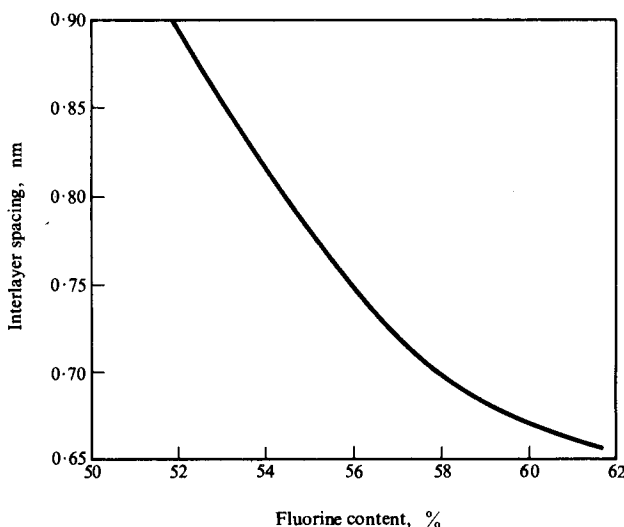
<sup>397</sup> O. Ruff, *Z. Electrochem.* **44** (1938) 333.

explosively yielding a mixture of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{C}_5\text{F}_{12}$ . The reaction is catalysed by hydrogen fluoride<sup>398</sup> and will proceed at  $250^\circ\text{C}$  with a partial pressure of 200 mm HF. The destruction of graphite electrodes in the electrolysis of  $\text{KF}/\text{HF}$  melts is felt to be entirely due to this action. The catalysis is however markedly dependent on the type of carbon used, for example retort carbon is resistant to fluorine at  $250^\circ\text{C}$  irrespective of catalyst concentration, yet it becomes more reactive than flake graphite above  $320^\circ\text{C}$ .

TABLE 54. THE MOLECULAR COMPOSITION OF  $(\text{CF})_n$ <sup>399</sup>

X in $(\text{CF}_x)_n$	Colour
0.676 to 0.715	Black
0.773	Grey, opaque
0.780 to 0.805	Silver-grey, opaque
0.858 to 0.885	Silver-grey, almost transparent
0.983 to 0.988	Silver-white, transparent

The composition of  $(\text{CF})_n$  prepared in the temperature range  $420^\circ$  to  $550^\circ\text{C}$  varies from  $\text{CF}_{0.68}$  to  $\text{CF}_{0.99}$  as shown in Table 54. X-ray examination reveals a graphitic structure with carbon layer planes separated by 0.817 nm and a density of  $2.43 \text{ g cm}^{-3}$ . These figures can only be regarded as an average value, since it is well known that the interlayer spacing is a function of the fluorine content (Fig. 23).

FIG. 23. The interlayer spacing in  $(\text{CF})_n$  as a function of fluorine content.

<sup>398</sup> W. Rüdorff and G. Rüdorff, *Chem. Ber.* **80** (1947) 413.

<sup>399</sup> O. Ruff, O. Bretschneider and F. Ebert, *Z. anorg. und allgem. Chem.* **217** (1934) 1.

Bigelow<sup>400</sup> has suggested that the fluorine atoms lie in parallel planes about each carbon plane, linked by polarized covalent bonds. This has been supported by Palin and Wadsworth<sup>401</sup> who concluded from differences between spacing ratios in the (100) and (110) reflections for graphite and  $(\text{CF})_n$ , that there is an expanded C-C distance and slight distortion from the true hexagonal. The weak (200) and (120) reflections give a calculated mean C-C bond length of 0.149 nm, which must suggest a loss of double bond character. However Rüdorff<sup>402</sup> is able to interpret essentially the same data using conventional C-C distances with covalent carbon-fluorine bonding and tetrahedrally-sited carbon atoms (Fig. 24). This implies the complete loss of aromatic character, which is consistent with the colour and electrically insulating character (the resistivity is greater than 3000 ohm cm). That C-F bonds do exist has been demonstrated by the existence of an unsymmetric C-F stretch at  $1215\text{ cm}^{-1}$  in the infrared spectrum<sup>403</sup>. The structure in Fig. 24 is supported by the available evidence if it is assumed that the separate CF layers are irregularly arranged with respect to each other and only approximately the same distance apart. This would account for the absence of general  $(hkl)$  reflections.

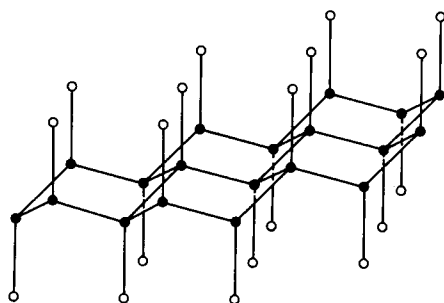


FIG. 24. The lattice structure of  $(\text{CF})_n$  according to Rüdorff<sup>402</sup>.

Carbon monofluoride is thermally stable up to about  $600^\circ\text{C}$ , further slow heating to  $1000^\circ\text{C}$  liberates  $\text{CF}_4$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_5\text{F}_{12}$  and higher fluorides. Rapid heating to  $500^\circ\text{C}$  in an inert atmosphere causes explosive deflagration with the evolution of  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ .  $(\text{CF})_n$  is strikingly unreactive, being unwetted by water and resistant to attack by even concentrated acids and alkalis. Even when heated in an atmosphere of hydrogen reaction does not take place below  $400^\circ\text{C}$ . Above this temperature, deflagration and flaming occurs increasing in vigour with increasing fluorine content. The reaction products include  $\text{CF}_4$  and higher fluorocarbons.

#### Tetracarbon Monofluoride

During the investigation of the catalytic activity of HF in the formation of  $(\text{CF})_n$  it was found that gaseous mixtures of fluorine and hydrogen fluoride will react with finely-divided graphite at room temperature<sup>398</sup>. The reaction rate is favoured by high partial pressures of HF, but reaction essentially ceases above  $80^\circ\text{C}$ . It is suggested that the reaction proceeds

<sup>400</sup> L. A. Bigelow, *Chem. Rev.* **40** (1947) 83.

<sup>401</sup> D. E. Palin and K. D. Wadsworth, *Nature*, **162** (1948) 925.

<sup>402</sup> W. Rüdorff and G. Rüdorff, *Z. anorg. und allgem. Chem.* **253** (1947) 281.

<sup>403</sup> W. Rüdorff and K. Brodersen, *Z. Naturforsch.* **12b** (1957) 595.

by the condensation of HF onto the graphite, initially forming a bifluoride which is readily oxidized to  $C_4F$ . Using powdered graphite the compound has a velvet-black appearance often accompanied by a bluish tinge. The composition varies in the range  $C_4F$  to  $C_{3.6}F$  depending on the conditions of preparation.

The X-ray pattern is quite distinct from that of  $(CF)_n$  with fewer reflections. The in-plane C-C distances are normal, i.e. the same as graphite, but the interlayer spacing varies from 0.550 nm in  $C_{3.57}F$  to 0.534 nm in  $C_{4.03}F^{398}$ . The intensities of the (001) lines indicate that the fluorine atoms are disposed in two layers above and below the plane at approximately 0.14 nm (Fig. 25). The infrared spectrum is practically identical with that of

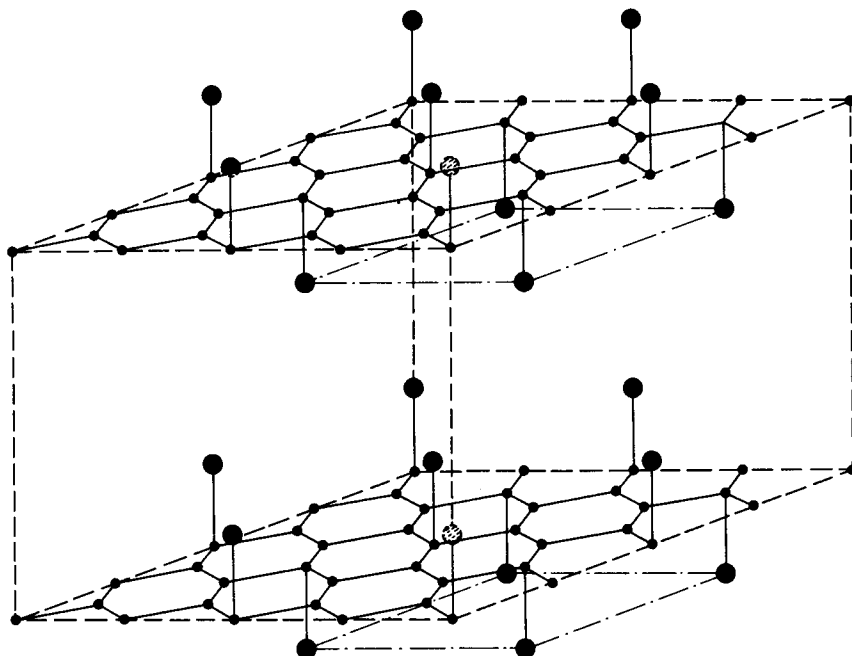


FIG. 25. The lattice structure of  $C_4F^{398}$ .

$(CF)_n$ <sup>404</sup>, confirming the existence of C-F covalent bonding. Densities calculated on this model agree well with the pycnometric value of  $2.077 \text{ g cm}^{-3}$  ( $C_{3.72}F$ ). The structure of  $C_4F$  differs from  $(CF)_n$  in that the interlayer spacing is smaller and the carbon planes are not puckered. Present evidence suggests that in graphite compounds all C-C bond lengths within a plane are the same, differences in bonding being accommodated by ring-puckering. Providing the C:F ratio is high the aromatic character of graphite is retained with planar layers as in  $C_4F$ . When the C:F ratio is close to unity the majority of carbon atoms are involved in  $sp^3$  bonding producing puckered rings. Intermediate ratios between these extremes will produce highly strained versions of either structure and this is confirmed by the absence of any stable compound between  $CF_{0.28}$  and  $CF_{0.68}$ . In complete accordance with its structural similarity to graphite  $C_4F$  has an electrical resistivity between 2 and 4 ohm  $\text{cm}^{398}$  and a diamagnetic susceptibility of  $-0.5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  at  $90^\circ\text{C}^{405}$ .

<sup>404</sup> W. Sprissler, Diss. Univ. Tübingen (1960) 1.

<sup>405</sup> F. R. M. McDonnell, R. C. Pink and A. R. Ubbelohde, *J. Chem. Soc.* (1951) 191.

Tetracarbon monofluoride is very inert although appreciably less stable thermally than  $(CF)_n$ . Slow heating causes the progressive loss of fluorine, even taking place at  $250^\circ C$  under a fluorine-rich atmosphere. Thus one cannot prepare  $(CF)_n$  from  $C_4F$ . Rapid heating causes deflagration with the liberation of  $CF_4$ ,  $C_2F_6$ , etc.

### Graphite Sulphide

When a suspension of graphite oxide in water is continuously shaken at  $50^\circ C$  under an atmosphere containing  $H_2S$  at a pressure of 100 mm, a black solid is produced<sup>406</sup>. The interlayer spacing is 0.358 nm and the substance has an electrical resistivity of 0.16 ohm cm. Above  $400^\circ C$  the whole of the sulphur content is lost.

## 4.9. IONIC COMPOUNDS

Graphite is capable of forming lamellar compounds with a variety of elements and compounds in which the bonding is predominantly ionic. With any one particular reactant, many stages of intercalation can be achieved, the first five of these being particularly well established as shown in Fig. 26<sup>332</sup>. In the first stage compound the intercalated substance occupies every interlayer space and so on until in the fifth stage only one space in every five is filled.

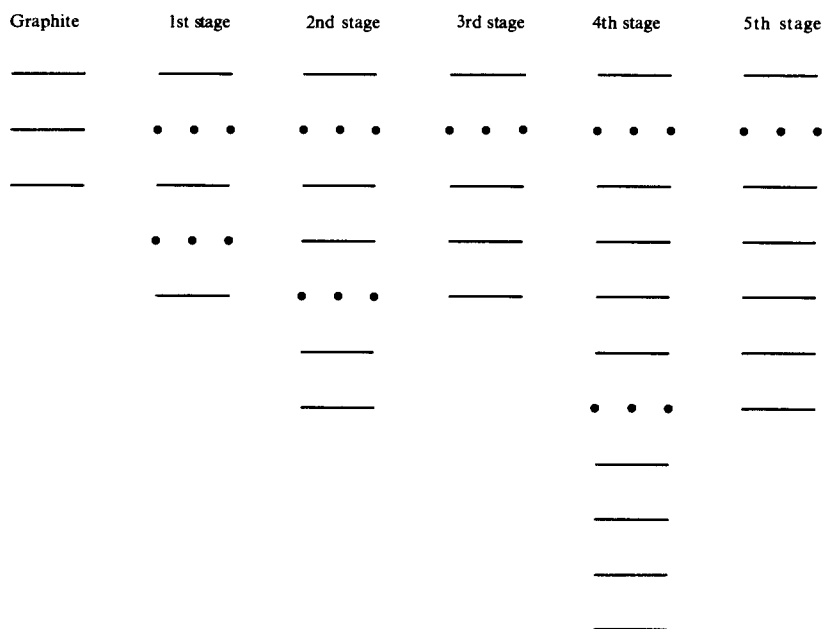


FIG. 26. The first five stages of intercalation into graphite<sup>332</sup>.

### Graphite-Alkali Metal Compounds

As indicated in Table 50 (p. 1262), graphite forms ionic compounds with all the alkali metals, but it is only comparatively recently that lithium and sodium compounds have been

<sup>406</sup> U. Hofmann, A. Frenzel and E. Csalan, *Liebigs Ann. Chem.* **510** (1934) 1.

discovered and consequently they are sparingly documented. The conditions of formation and the product structure with these two metals are very different from the rest of the group. Potassium, rubidium and caesium all form compounds of the type  $C_8M$ ,  $C_{24}M$ ,  $C_{36}M$ ,  $C_{48}M$  and  $C_{60}M$  although defect structure can change these values very slightly.

### Lithium

The reaction between lithium and graphite at 500°C in a high vacuum produces a variety of products depending on the length of heating<sup>407</sup>. The final product is the carbide  $Li_2C_2$ , but at intermediate times the lamellar  $C_4Li$  is produced. This compound is harder than graphite and exists as a homogeneous golden yellow powder when crushed. Further heating at 700°C yields a black product ( $Li:C \leq 0.5$ ) and lithium vapour.

If the reaction is carried out with spectroscopically pure graphite and 99.98% pure lithium vapour, then compounds corresponding to the first three stages of intercalation (Fig. 26) are obtained<sup>408</sup>, together with  $Li_2C_2$ . Table 55 summarizes the results.

TABLE 55. LITHIUM–GRAPHITE INTERCALATION COMPOUNDS

Compound	Stage	Appearance	Structure	Lattice constants (nm)
$C_6Li$	1	brass	hexagonal $D_{6h}^{12}-P6/mmm$	$a = 0.429$ $c = 0.373$
$C_{12}Li$	2	copper	hexagonal	$a = 0.429$ $c = 0.702$
$C_{18}Li$	3	steel	hexagonal	$a = 0.428$ $c = 1.044$

Recently,  $C_{16}Li$  and  $C_{40}Li$  have been prepared from graphite and a naphthalene–lithium complex in tetrahydrofuran solution under an inert atmosphere<sup>409</sup>. The two compounds were prepared using Ceylon graphite and Madagascar graphite respectively. The reaction is said to proceed more quickly using a diphenyl–lithium complex.

### Sodium

Stirring finely-divided graphite in molten sodium at 450°C produces, after about 1 week, a deep violet product with the composition  $C_{64}Na$ <sup>410</sup>. X-rays reveal a pure phase with a sodium ion occupying every eighth interlayer space. The spacing is 0.46 nm.

$C_{32}Na$  and  $C_{120}Na$  have been made using a naphthalene–sodium complex<sup>409</sup>. Once again the lower metal content is obtained with Madagascar graphite.

### Potassium

$C_8K$  was the first graphite–alkali metal compound to be reported<sup>411</sup>. The bronze-coloured compound is formed by the reaction of graphite with potassium at 300°C. At

<sup>407</sup> A. Hérold, *Bull. Soc. Chim. France* (1955) 999.

<sup>408</sup> R. Juze and V. Wehle, *Naturwissenschaften*, **52** (1965) 560.

<sup>409</sup> C. Stein, *Compt. Rend.* **C264** (1967) 16.

<sup>410</sup> R. C. Asher, *J. Inorg. and Nuclear Chem.* **10** (1959) 238.

<sup>411</sup> C. K. Fredenhagen and G. Cadenbach, *Z. anorg. und allgem. Chem.* **158** (1926) 249.



higher temperatures ( $\sim 380^\circ\text{C}$ ) a bluish product  $\text{C}_{24}\text{K}$  is formed, after which further heating drives off the metal.

This work was subsequently repeated<sup>412</sup> using finely-divided graphite and carefully-weighed amounts of potassium and enabled the separation of the first five stages of intercalated compounds— $\text{C}_8\text{K}$ ,  $\text{C}_{24}\text{K}$ ,  $\text{C}_{36}\text{K}$ ,  $\text{C}_{48}\text{K}$  and  $\text{C}_{60}\text{K}$ .

Again, the recent method of production using naphthalene-alkali metal complexes<sup>409</sup> yields a new compound  $\text{C}_{32}\text{K}$ , together with  $\text{C}_{24}\text{K}$ .

The structure of potassium graphites have received intensive study and will be covered thoroughly since the extension to many other ionic lamellar compounds is straightforward. The most striking feature lies in the observation that the carbon layer planes are exactly superimposed and not offset as in graphite<sup>412</sup>. Figure 27 illustrates the arrangement in  $\text{C}_8\text{K}$ .

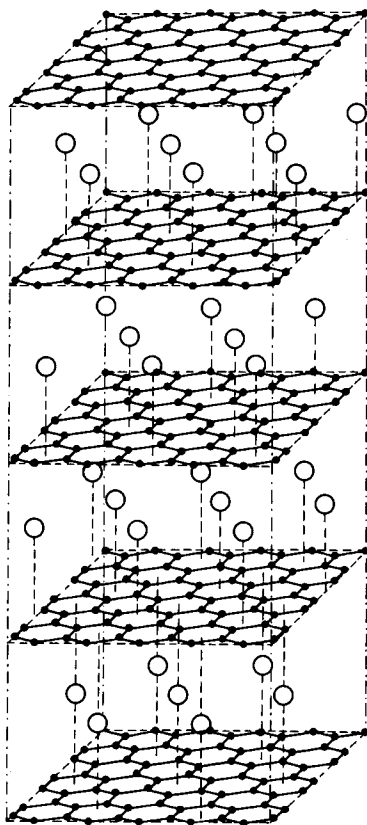


FIG. 27. The crystal lattice of  $\text{C}_8\text{K}$ .

In this compound the potassium atoms form a triangular net with an edge of 0.491 nm, exactly twice the axis of the hexagonal carbon network. On transforming to the second-stage ( $\text{C}_{24}\text{K}$ ) every third metal atom is removed yielding a hexagonal net which still fits the carbon network, with the same K-K distances as in  $\text{C}_8\text{K}$  (Fig. 28). Subsequent alkali-

<sup>412</sup> W. Rüdorff and E. Schultz, *Z. anorg. und allgem. Chem.* **277** (1954) 156.

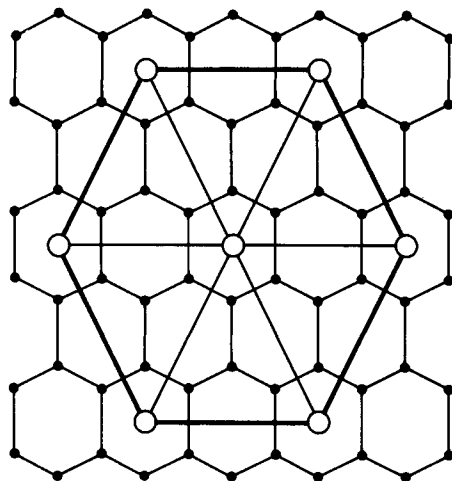


FIG. 28. The triangular location of alkali-metal atoms in potassium graphites. The central atom is only present in  $C_8K$ .

poor stages involve multiples of twelve carbon atoms and will still fit the hexagonal network. The lattice constants are presented in Table 56. This tabulation shows quite clearly that the introduction of the metal layer leads for all stages to the same increase in interlayer spacing. Simultaneous lateral displacement of the carbon planes must also occur to preserve the structure.

TABLE 56. THE LATTICE CONSTANTS OF POTASSIUM GRAPHITES

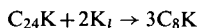
Compound	Lattice constant $c$ (nm)
$C_8K$	0.541 ( $D_5^h-C222$ )
$C_{24}K$	$0.876 = 0.541 + 1 \times 0.335$
$C_{36}K$	$1.212 = 0.541 + 2 \times 0.335$
$C_{48}K$	$1.548 = 0.541 + 3 \times 0.335$
$C_{60}K$	$1.883 = 0.541 + 4 \times 0.335$

Accurate calorimetric determination of the heats of formation of the alkali metal graphites is not easily realized due to the difficulty in obtaining a pure phase. Transitions between the stages are more or less continuous and, as the determination is made by dropping graphite into the molten metal, an attempt must be made to allow for heat loss involved in the "wetting" of the compound by excess metal. Many determinations have been made to estimate the enthalpy of formation of  $C_8K$ , since values for the further stages are then calculated from this initial point. The most recent value<sup>413</sup> (using Ceylon graphite), and probably the most accurate, gives



<sup>413</sup> C. D. Saeher, *Bull. soc. chim. France* (1964) 1287.

Artificial graphite gave a value approximately 10% higher than this. The most recent calorimetric determination of the reaction



gave a value for  $\Delta H$  of  $-3.65 \text{ kcal mole}^{-1}$ <sup>414</sup>, which yields  $\Delta H = -21.40 \text{ kcal mole}^{-1}$  for the heat of formation of  $\text{C}_{24}\text{K}$ . This value depends, of course, on the accuracy of the measurements for  $\text{C}_8\text{K}$  and errors in this quantity have led to literature values for the enthalpy of formation of  $\text{C}_{24}\text{K}$  ranging from  $-12$  to  $-30 \text{ kcal mole}^{-1}$ . Many of these inconsistencies may well be due to determinations being made at different temperatures. Setton<sup>414</sup> has proposed the empirical relation,

$$-\Delta H(\text{C}_8\text{K}) = 9317.86 - 3.75T$$

The electrical conductivity and magnetic susceptibility have been measured in order to determine the effects of the intercalated metal atom on the  $\pi$ -bond structure of graphite (Table 57). The data show that metal intercalation has destroyed the original diamagnetism

TABLE 57. THE ELECTRICAL AND MAGNETIC PROPERTIES OF POTASSIUM GRAPHITES<sup>405, 412</sup>

Compound	Conductance ( $\text{ohm}^{-1} \text{ cm}^{-1}$ )		Susceptibility ( $10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ )		
	90°K	288°K	90°K	195°K	288°K
Graphite	26.5	35.2	-94.81	-81.08	-72.48
$\text{C}_8\text{K}$	1302	980	+16.55	+16.48	+16.42
$\text{C}_{12}\text{K}$	1073	870	—	—	—
$\text{C}_{28}\text{K}$	—	565	—	—	—

of graphite, producing compounds that are obviously semi-metallic. The paramagnetism is of the correct order of magnitude for that of the electron gas in a metal. The temperature coefficient of the electrical conductivity is negative like that for a true metal. These effects are attributed to the transfer of electrons from the intercalated metal atoms to the carbon layer. More recently<sup>415</sup>, additional evidence has been provided by electron spin resonance indicating localized metal-carbon interatomic bonds. Ubbelohde<sup>416</sup> has also shown that metal intercalation reduces the electrical resistance of graphite by a factor of 10 along the  $a$ -axis, but a reduction of 100–200 is produced perpendicular to the carbon planes (Fig. 29). This diagram shows clearly that along the  $c$ -axis the compounds become more metallic with increasing metal atom content. Quasi-metallic bonds would permit conduction paths in the direction of the  $c$ -axis only. This behaviour is reflected to a lesser extent in the susceptibility properties of the potassium graphites (Table 58)<sup>412</sup>.

$\text{C}_8\text{K}$  reacts fairly rapidly with hydrogen at room temperature to yield a deep blue product containing 0.75 hydrogen atoms per metal atom. The formula of the compound is thought to be either  $\text{C}_{32}\text{KH}_3$  or  $\text{C}_{32}\text{K}.3\text{KH}$ <sup>417</sup>. Reaction with  $\text{C}_{24}\text{K}$  is more difficult and only 0.25 atoms of hydrogen per metal atom are incorporated. The reaction is partially

<sup>414</sup> R. Setton, *Bull. soc. chim. France*, (1960) 521.

<sup>415</sup> K. A. Muller and R. Kleiner, *Phys. Letters*, **1** (1962) 98.

<sup>416</sup> A. R. Ubbelohde, L. C. F. Blackman and J. F. Mathews, *Nature*, **183** (1959) 454.

<sup>417</sup> A. Hérolde and D. Saehr, *Compt. Rend.* **250** (1960) 545.

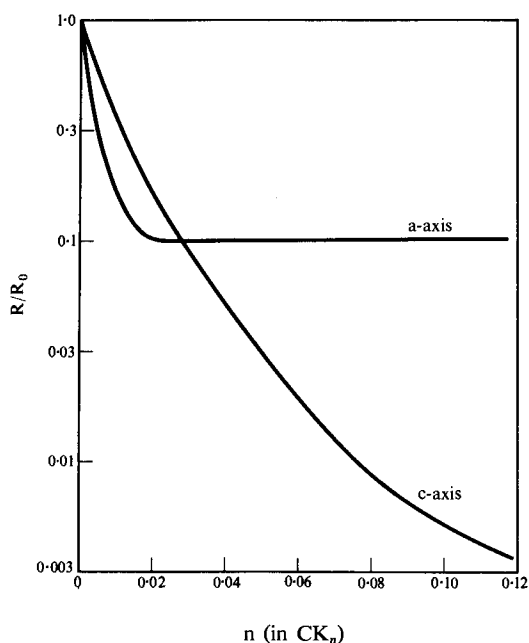


FIG. 29. The relative resistance of potassium graphites as a function of metal content.

TABLE 58. THE MAGNETIC SUSCEPTIBILITIES OF POTASSIUM AND RUBIDIUM GRAPHITES

Compound	Susceptibility ( $10^{-6} \text{ cm}^3 \text{ mole}^{-1}$ )
Graphite	-110
$\text{C}_8\text{K, Rb}$	+10.0, +5.0
$\text{C}_{24}\text{K, Rb}$	+8.7, +5.1
$\text{C}_{36}\text{K, Rb}$	+8.5, +5.6
$\text{C}_{48}\text{K, Rb}$	+5.7, +6.2
$\text{C}_{60}\text{K, Rb}$	+4.0, +3.7

reversible and is thought to yield a product with composition  $\text{C}_{96}\text{K}_4\text{H}$ . Comprehensive isotherms for the  $\text{C}_8\text{K/H}$  system and for reactions with the halogens are contained in a review by Hérold *et al.*<sup>418</sup>. Typical products produced by reaction with halogens are  $\text{C}_8\text{KCl}$ ,  $\text{C}_{24}\text{KCl}$ ,  $\text{C}_8\text{KBr}$  and  $\text{C}_8\text{KI}$ .

In general potassium graphites are extremely reactive in air and may explode with water. Controlled reaction with water or alcohols produces only the alkali hydroxide and hydrogen, no acetylene or other hydrocarbons are evolved.

Potassium graphite has been used as a polymerization catalyst for ethylene<sup>419</sup>.

<sup>418</sup> A. Hérold, M. Colin, N. Daumas, R. Diebold and D. Saehr, *Chem. Soc. Spec. Pub.* **22** (1967) 309.

<sup>419</sup> H. Podall, W. E. Foster and A. P. Giraitis, *J. Org. Chem.* **23** (1958) 82.

### Rubidium

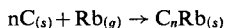
The first five stages of intercalation are achieved in exactly the same way as with the potassium compounds. In addition  $C_{32}Rb$  has been made using a naphthalene-rubidium complex and Madagascar graphite, and a new phase  $C_{10}Rb$  has recently been reported<sup>420</sup>.

The structures follow those of the potassium compounds with appropriate modifications to the lattice constants (Table 59).

TABLE 59. THE LATTICE CONSTANTS OF RUBIDIUM GRAPHITES

Compound	Lattice constant $c$ (nm)
$C_8Rb$	0.565 ( $D_2^h$ -C222)
$C_{24}Rb$	$0.902 = 0.565 + 1 \times 0.335$
$C_{36}Rb$	$1.234 = 0.565 + 2 \times 0.335$
$C_{48}Rb$	$1.575 = 0.565 + 3 \times 0.335$
$C_{60}Rb$	$1.908 = 0.565 + 4 \times 0.335$

Heats and entropies of formation in the gas phase have recently been reported for the whole series<sup>420</sup>. The results for the reaction



are given in Table 60.

TABLE 60. ENTHALPIES AND ENTROPIES OF FORMATION OF RUBIDIUM AND CAESIUM GRAPHITES

Compound	$-\Delta H$ (kcal mole <sup>-1</sup> )	$-\Delta S$ (cal mole <sup>-1</sup> deg <sup>-1</sup> )
$C_8Rb, Cs$	28.8, 34.2	23.3, 24.0
$C_{10}Rb, Cs$	27.5, 32.2	18.5, 19.2
$C_{24}Rb, Cs$	30.6, 34.8	17.6, 18.7
$C_{36}Rb, Cs$	32.2, 35.8	18.0, 18.7
$C_{48}Rb, Cs$	33.1, 36.4	18.1, 18.8
$C_{60}Rb, Cs$	33.6, 36.7	18.1, 18.8

Electron spin resonance has been observed in  $C_{24}Rb$  but not in  $C_8Rb$ . Magnetic susceptibility measurements (Table 58) confirm that rubidium graphites are weakly paramagnetic, but no firm trend with metal content is found in contrast to potassium graphites.

The chemical reactions of rubidium graphites are similar to the potassium analogues with the exception that very little activity is shown towards hydrogen.

### Caesium

Exactly the same caesium-graphite compounds are obtained as with rubidium, including  $C_{10}Cs$ . The structures follow the potassium analogues with a lattice constant of 0.494 nm for  $C_8Cs$ .

<sup>420</sup> F. J. Salzano and S. Aronson, *J. Chem. Phys.* **44** (1966) 4320.

The thermodynamic quantities are shown in Table 60. This collection confirms the general increase in stability in the order  $K \rightarrow Rb \rightarrow Cs$  for a particular metal atom content. Caesium graphites show the same chemical reactions as the potassium and rubidium counterparts, but no activity towards hydrogen has been observed. Iodine compounds such as  $C_8CsI$ ,  $C_8CsI_3$  and  $C_8CsI_4$  have been prepared<sup>418</sup>.

Electron spin resonance has not been observed in any compound and magnetic susceptibility data are not available.

The low optical density of  $C_8Cs$  ( $\lambda_{max} = 0.46 \mu$ ,  $\alpha = 54\%$ ) coupled with the high electrical conductivity along the  $c$ -axis (an order of magnitude greater than graphite) has led to the suggestion that plasma-oscillations of the excess caesium-donated electrons in the conduction band occur<sup>421</sup>.

### Alkali-Ammine Compounds

A useful method of intercalating alkali metal atoms into the graphite lattice consists of reacting the graphite with a solution of the metal in liquid ammonia at  $-50^\circ C$ <sup>422</sup>. This route has particular importance for lithium and sodium where the usual preparation is difficult. The resultant product depends on the metal concentration and graphite particle size and may be blue  $C_{12}M(NH_3)_2$  or black  $C_{28}M(NH_3)_2$ . The lattice constants ( $c$ ) are 0.66 nm and 0.99 nm respectively, regardless of the nature of the metal  $M$ . The structure of these materials appears to be very similar to the alkali-metal graphites with metal atoms and ammonia occupying every interlayer space and every third space respectively. The similarity in magnetic susceptibilities supports this view.

The potassium, rubidium and caesium derivatives are stable under a nitrogen atmosphere while the sodium compound decomposes in a matter of days and the lithium derivative even faster. The decomposition leads to the liberation of hydrogen and the formation of the metal amide. In the same manner, liquid ammonia will only extract the metal atom from the lithium and sodium compounds. The compounds are all sensitive to water in the same way as the alkali metal graphites.

Solutions of the alkali metals in solvents other than ammonia can be made to yield intercalation compounds with graphite<sup>423</sup>. Table 61 summarizes the more important preparations.

TABLE 61. ALKALI AMMINE GRAPHITE COMPOUNDS

Compound	Colour	Lattice spacing (nm)
$C_{12}Li(NH_2CH_3)_2$	deep blue	0.69
$C_{28}Li(en)$	grey-black	0.835
$C_{12}K(NH_2CH_3)$	dark blue	0.69
$C_{12}K(py)$	olive-green	—

<sup>421</sup> G. R. Hennig, *J. Chem. Phys.* **43** (1965) 1201.

<sup>422</sup> W. Rüdorff, E. Schultz and O. Rubisch, *Z. anorg. und allgem. Chem.* **282** (1955) 232.

<sup>423</sup> W. Rüdorff, *Angew. Chem.* **71** (1959) 487.

### Alkaline Earth Ammine Compounds

Solutions of the alkaline earth metals in liquid ammonia will react with graphite to give metal ammine intercalation<sup>423</sup>. The compounds have received little study and are consequently poorly documented. Table 62 contains the information available at present.

TABLE 62. ALKALINE EARTH AMMINE GRAPHITE COMPOUNDS

Compound	Colour	Lattice spacing (nm)
$C_{12}Ca(NH_3)_2$	deep blue	0.662
$C_{28}Ca(NH_3)_4$	blue-black	0.995
$C_{12}Sr(NH_3)_2$	red-violet	0.636
$C_{28}Sr(NH_3)_4$	blue-black	0.987
$C_{12}Ba(NH_3)_2$	red-violet	0.636
$C_{28}Ba(NH_3)_4$	blue-black	0.979

### Ammonium Compounds

When solutions of ammonium nitrate in liquid ammonia are electrolysed using graphite electrodes it is found that the resistance of the cathode decreases steadily to about 20% of its initial value<sup>424</sup>. It is assumed that ammonium ions are intercalated into the lattice in just the same manner as metal atoms, yielding compounds of general formula  $C_mNH_4^+ \cdot nNH_3$ .

The electrolysis of solutions of alkylammonium, alkyl phosphonium and alkyl arsonium salts in liquid ammonia will also yield intercalated compounds<sup>423</sup>. The tetraethyl ammonium compound is prepared, for example, by allowing the blue solution obtained by electrolysis of the azide in liquid ammonia to react with finely powdered graphite. The following compounds have been prepared:



### Halogen Compounds

Much of the chemistry of the halogens suggests a steady gradation in their properties. This is not reflected in their behaviour towards graphite. Fluorine and bromine react readily, although the former yields covalent compounds. Chlorine reacts slowly under favourable conditions and there is some doubt whether iodine reacts at all (see section 4.10). Hérolde has suggested<sup>407</sup> that the electron affinity of the halogen is the dominant factor accounting for the passivity towards iodine while the small size of the chlorine ion limits its ability to associate with a large number of carbon atoms. This latter effect localizes the chlorine atom with respect to a few carbon atoms, preventing the stabilization of C-Cl bonding by resonance—a mechanism held to be responsible for the stability of the bromine compounds. The low ionic radius of fluorine favours the formation of  $(CF)_n$  and  $C_4F$  rather than  $C_8F$ .

<sup>424</sup> M. L. Dzurus and G. R. Hennig, *J. Chem. Phys.* **27** (1957) 275.

### Chlorine

Graphite chloride, like many lamellar graphite compounds, was discovered after studying the electrical conductivity of graphite under liquid chlorine at  $-33^{\circ}\text{C}$ <sup>425</sup>. After three days the conductivity fell to 10% of its original value, attributed to the chlorine intercalated. Juza and Seidel<sup>426</sup> have studied the formation of graphite chloride, using the change in magnetic susceptibility, as a function of graphite particle size and temperature (Figs. 30 and 31). The graphs show quite clearly that a smaller particle size promotes the

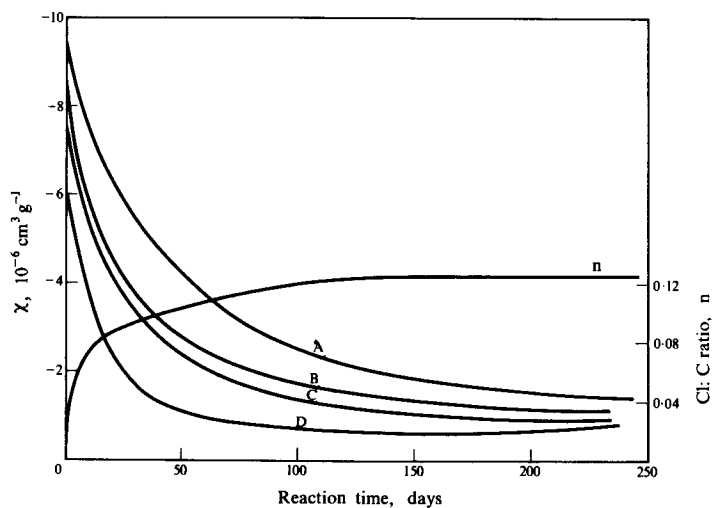


FIG. 30. The reaction of Ceylon graphite with liquid chlorine at  $-78^{\circ}\text{C}$ . Curve A: graphite particle size 0.5 to 1 mm. Curve B: 0.25 to 0.5 mm. Curve C: 0.1 to 0.25 mm. Curve D: 0.03 mm.

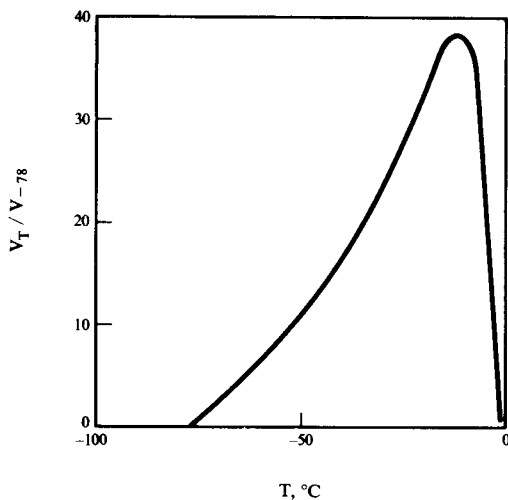


FIG. 31. The reaction of Ceylon graphite (0.5–1 mm particles) with chlorine as a function of temperature.

<sup>425</sup> G. R. Hennig, *J. Chem. Phys.* **20** (1952) 1443.

<sup>426</sup> R. Juza and H. Seidel, *Z. anorg. und allgem. Chem.* **317** (1962) 73.



formation and that a maximum rate occurs at  $-12^{\circ}\text{C}$ . At  $0^{\circ}\text{C}$  and above no reaction can be observed. Figure 23 also indicates that a limiting C:Cl ratio is found in all cases, corresponding to the formation of a compound  $\text{C}_8\text{Cl}$ . Degradation studies on  $\text{C}_8\text{Cl}$  have also pointed to the existence of a distinct stage corresponding to an approximate composition  $\text{C}_9\text{Cl}$ , but no supporting evidence has been found. Impurities intentionally introduced into the graphite exercise a marked effect on chlorine inclusion. A large increase in the amount of chlorine absorbed is found with bromine or bisulphate impurities (in the form of residue compounds), and compounds such as  $\text{C}_{19}\text{Cl}$  and  $\text{C}_{81}\text{Cl}$  have been postulated.

Pycnometric data at  $-78^{\circ}\text{C}$  show that the volume of the graphite is increased by 42% by reaction due to the inclusion of chlorine atoms between the planes. X-ray measurements indicate the presence of chlorine atoms in every second interlayer space, with lattice constants  $a = 0.245\text{ nm}$  and  $c = 1.009\text{ nm}$ .

### Bromine

When graphite is left in contact with either liquid bromine or the vapour, it occludes from 0.82 to 0.84 g of bromine per gram of carbon corresponding to the formation of  $\text{C}_8\text{Br}$ . The exact amount is critically dependent on the type of graphite used and the particle size and the maximum absorption occurs after 12 to 1000 hr<sup>427</sup>. Isobaric studies<sup>407</sup> confirm the existence of  $\text{C}_8\text{Br}$  and, with artificial graphites  $\text{C}_{10}\text{Br}$  was also indicated. More recent measurements with artificial graphites have provided evidence for the existence of  $\text{C}_9\text{Br}$  and  $\text{C}_{10}\text{Br}$ <sup>428</sup>.

The lamellar character of blue  $\text{C}_8\text{Br}$  has been confirmed by X-ray diffraction<sup>429</sup>. The external shape of graphite single crystals is unaltered by the reaction but the lamellar spacing increases to 0.705 nm, corresponding to bromine inclusion into every second space. Magnetic susceptibility measurements (Table 63) show a rapid increase in diamagnetism with

TABLE 63. THE MAGNETIC SUSCEPTIBILITY OF GRAPHITE BROMIDES

	Bromine content (g per g of carbon)			
	0	0.051	0.67	0.71
$\chi$ ( $10^{-6}\text{ cm}^3\text{ mole}^{-1}$ )	-5.29	-4.14	-3.1	-0.31

increase in bromine content<sup>430</sup>. This can only be explained on current theories<sup>431</sup> if some bromine ionization takes place. Further investigation of this proposal using resistance measurements<sup>432</sup> suggested a 17% ionization leading to a probable formula  $\text{C}_n\text{Br} \cdot 3\text{Br}_2$ . The recent work of Ubbelohde *et al.*<sup>433</sup> on the specific resistance of graphite bromide

<sup>427</sup> W. T. Eeles and J. A. Turnbull, *Proc. Roy. Soc.* **A283** (1965) 179.

<sup>428</sup> T. Mukaibo and Y. Takahashi, *Kogyo Kagaku Zasshi*, **65** (1962) 754.

<sup>429</sup> W. Rüdorff, *Z. anorg. und allgem. Chem.* **245** (1940) 383.

<sup>430</sup> M. Goldsmith, *J. Chem. Phys.* **18** (1950) 523.

<sup>431</sup> R. Smoluchowski, *Rev. Mod. Phys.* **25** (1953) 178.

<sup>432</sup> G. R. Hennig and J. D. McClelland, *J. Chem. Phys.* **23** (1955) 1431.

<sup>433</sup> L. F. C. Blackman, J. F. Mathews and A. R. Ubbelohde, *Proc. Roy. Soc.* **A256** (1960) 15.

(Fig. 32) shows a striking resemblance to the behaviour of  $C_8K$  as a comparison with Fig. 29 will show. This "metallic" behaviour suggests that specific ionic bonds are not formed between carbon and bromine, but rather that a resonance condition is achieved between the carbon planes and intercalated bromine atoms.

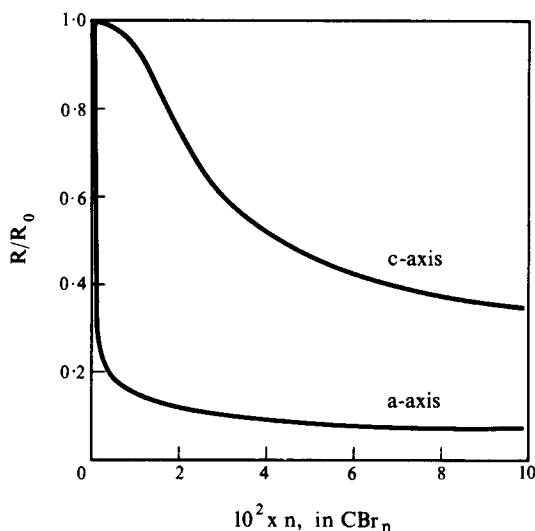


FIG. 32. The relative resistance of graphite bromide as a function of bromine content.

The synthesis of hydrogen bromide from its elements occurs at  $500^\circ\text{C}$  without a catalyst, but a measurable rate can be detected at  $120^\circ\text{C}$  with a carbon catalyst. It was first thought that graphite bromide plays an intermediate role in the reaction, but an examination of the experimental conditions renders this unlikely. The high catalytic activity of graphite oxide soot with respect to the same reaction points towards the chemisorption of bromine onto the basal planes rather than intercalation.

### Graphite Iodide Chloride

Graphite can absorb iodine monochloride from either the vapour or a solution in carbon tetrachloride at room temperature, producing a volume increase of the order of 300%. The product varies in composition from  $C_{5.1}ICl$  to  $C_{5.4}ICl$ <sup>434</sup>. Compounds containing 4, 8, 12, 16 and 24 carbon atoms ( $C_nI_xCl_{1-x}$ ) have also been reported<sup>435</sup>. X-ray diffraction indicates an interlayer spacing of 0.705 nm with intercalation in every second space.

The intercalation of  $ICl_3$  has also been reported.

### Graphite Iodide Bromide

Bromine iodide is readily absorbed in graphite leading to compounds with uncertain stoichiometry.  $C_nI_xBr_{1-x}$ , where  $n = 8, 9, 10$  and 12 are thought to be formed<sup>436</sup>.

<sup>434</sup> G. A. Saunders, A. R. Ubbelohde and D. A. Young, *Proc. Roy. Soc.* **A271** (1963) 499.

<sup>435</sup> B. Bach and A. Hérol, *Compt. Rend.* **257** (1963) 1706.

<sup>436</sup> G. Colin and A. Hérol, *Compt. Rend.* **245** (1957) 2294.

## 4.10. RESIDUE COMPOUNDS

Many of the lamellar graphite compounds can be decomposed with the recovery of the intercalated material. Most of this material is recovered unchanged but a small amount tends to remain in the graphite and can be removed only by drastic treatment.

Heating graphite chloride leads to three postulated residue compounds, depending on the temperature and other reaction conditions. At  $-58^{\circ}\text{C}$ ,  $\text{C}_{29}\text{Cl}$  is produced which on warming at  $220^{\circ}\text{C}$  for 12 hr yields  $\text{C}_{81}\text{Cl}$ . Heating in the presence of liquid chlorine on the other hand gives  $\text{C}_{19}\text{Cl}$ <sup>426</sup>. Both the latter compounds are diamagnetic with susceptibilities of  $-6.69$  and  $-2.07 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  respectively.

Residue compounds formed from graphite bromide have been studied comprehensively. The amount of "impurity" retained after heating depends critically on the source of the original graphite as shown in Figs. 33 and 34<sup>425</sup>. An enormous variety of compositions have been reported, ranging from  $\text{C}_{14}\text{Br}$  to  $\text{C}_{115}\text{Br}$  due to different graphites and heating temperatures ( $200^{\circ}$  to  $3000^{\circ}\text{C}$ )<sup>426, 427, 434</sup>.

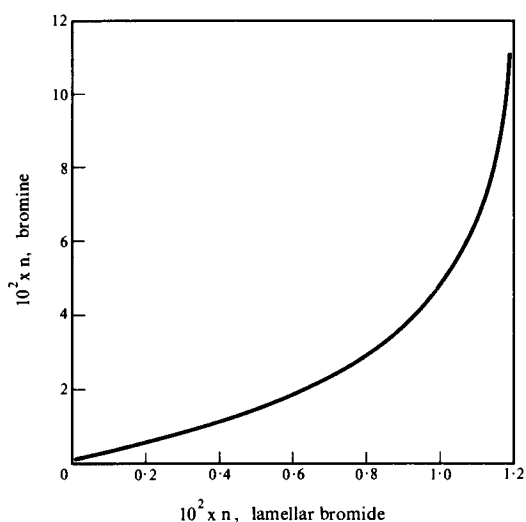


FIG. 33. The composition of graphite bromide residue compounds as a function of the composition of the lamellar starting material.

Bromine residue compounds are very stable to heat with only slow decomposition at  $700^{\circ}\text{C}$  *in vacuo*, yielding bromine and bromine compounds. Again, the stability depends on the type of graphite used in the preparation. Residual bromine lowers the susceptibility; a value of  $-5.70 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  has been reported for  $\text{C}_{115}\text{Br}$ .

The residue compounds are thought to arise from bromine entrapment at lattice defect sites since X-ray diffraction measurements indicate an interlayer spacing identical to that of graphite<sup>434</sup>. The trapping can occur at crystallite boundaries and at hole and claw defects in the layer planes. This is supported by Fig. 34 which shows that larger particles of graphite retain more impurity than small ones.

Residue compounds are chemically interesting in that they possess greater reactivity than pure graphite. For example, they are capable of taking up ten times more chlorine than

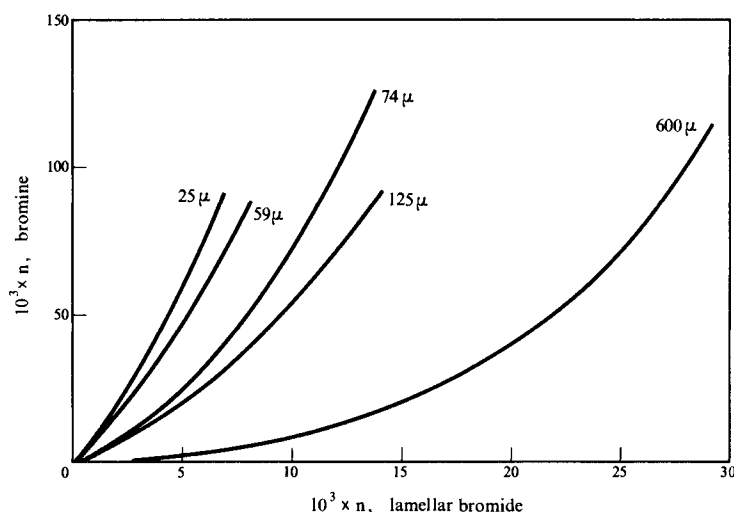


FIG. 34. The composition of graphite bromide residue compounds as a function of the lamellar starting material.

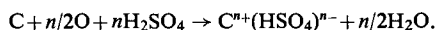
graphite and thirty times more  $\text{AlCl}_3$ . Graphite will not react with iodine (see section 4.9) but there is strong evidence that the bromine residue compound will absorb some material<sup>425</sup>. An iodine residue compound has in fact, been reported recently<sup>437</sup>.

Residue compounds from graphite bisulphate have also been extensively studied<sup>425</sup>. The preparation is straightforward, the compounds being generated by concentrated sulphuric acid treatment of graphite anodes used in electrolysis. Compounds with composition  $\text{C}_{24}^+\text{HSO}_4^-$ ,  $\text{C}_{48}^+\text{HSO}_4^-$  and  $\text{C}_{96}^+\text{HSO}_4^-$  have been observed.

A graphite nitrate residue compound has been reported recently<sup>438</sup>.

### Graphite Salts

In the presence of concentrated acids, graphite may be oxidized by strong oxidizing agents or anodic oxidation, to give graphite salts. In these compounds the acid anions are incorporated into the lattice together with molecules of the acid. Reversible transformation between salts is possible by treatment with the appropriate acid. As with metal graphite compounds, several stages of intercalation can be achieved, the first stage usually coloured blue and the remainder black. The regular distribution of the anionic layers and the discontinuous transition from one stage to another, together with facile anion exchange all point to the ionic character of the compounds. The name "salt" is justified by their metallic behaviour,



### Graphite Nitrate

As already stated, the graphite salts are capable of reversible transformation between species. It follows that the simplest preparation involves washing the bisulphate salt six

<sup>437</sup> F. J. Salzano, *N.S.A.* **18** (1964) No. 22001.

<sup>438</sup> M. Inagaki, *Carbon*, **5** (1967) 317.

or seven times with fuming nitric acid<sup>439</sup>. Alternatively the blue first-stage compound can be obtained by the treatment of graphite with  $\text{N}_2\text{O}_5$  in fuming nitric acid. A second stage is achieved using elevated temperatures ( $\sim 120^\circ\text{C}$ ) and an oxidizing agent ( $\text{CrO}_3$ ). Third, fourth and fifth stages can also be made<sup>440</sup>.

In accordance with their nomenclature, the increase in lattice constant through the 1st to 5th stages follows that of the metal graphite compounds (Table 64).

TABLE 64. THE LATTICE STRUCTURE OF GRAPHITE NITRATES

Compound	Lattice constant $c$ (nm)	Structure <sup>441</sup>
1st stage	0.784	hexagonal $P6/mmm$
2nd stage ( $\text{C}_{48}^+\text{NO}_3^- \cdot 3\text{HNO}_3$ )	$1.114 = 0.779 + 1 \times 0.335$	rhombohedral $R\bar{3}m$
3rd stage	$1.449 = 0.779 + 2 \times 0.335$	rhombic $Cmc2_1$
4th stage	$1.784 = 0.779 + 3 \times 0.335$	orthorhombic $R\bar{3}m$
5th stage	$2.119 = 0.779 + 4 \times 0.335$	—

X-ray diffraction, thermal expansion and specific resistance measurements on the first three stages show evidence of a structural re-ordering of the molecules and ions in the spaces at  $-20^\circ\text{C}$ . The data are illustrated in Fig. 35 and Table 65. The transition between the two forms is rapidly achieved by cycling the temperature about the  $\lambda$ -transformation point. Below  $-20^\circ\text{C}$  the acid molecules and nitrate ions exist in a two-dimensional crystalline form. On warming, the structure "melts" to give material exhibiting many characteristics of the glassy state. The reason for the transformation is not clear, but it has been suggested that graphite nitrate behaves like a Hume-Rothery metal and the re-ordering is the result of new Brillouin zones allowing minimization of the electron energy.

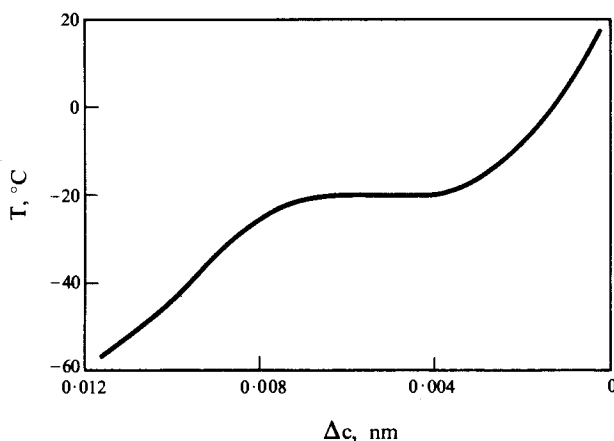


FIG. 35. Temperature dependence of the change in lattice dimension of graphite nitrate as a function of temperature.

<sup>439</sup> U. Hofmann and W. Rüdorff, *Trans. Faraday Soc.* **34** (1938) 1017.

<sup>440</sup> M. J. Bottomley, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. A* **279** (1964) 291.

<sup>441</sup> D. E. Nixon, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. A* **291** (1966) 324.

TABLE 65. THE ELECTRICAL AND THERMAL PROPERTIES OF GRAPHITE NITRATES<sup>442</sup>

Compound	Expansion coefficient ( $\times 10^{-6} \text{ deg}^{-1}$ )		Specific resistance ( $\mu\text{ohm cm}$ )	
	+25° to -15°C	-25° to -50°C	+20° to 0°C	-50°C
1st stage	83.5	94	2.84 to 3.87	1.68 to 2.51
2nd stage	62	72	3.96 to 4.91	2.57 to 3.12
3rd stage	55	66	—	—

### Graphite Hydrogen Fluoride

Hydrogen fluoride intercalation compounds up to the fourth stage have been prepared by the anodic oxidation of graphite in dry liquid HF<sup>443</sup>. X-ray investigation reveals the typical increase in lattice constant, with increasing intercalation (Table 66).

### Graphite Perchlorate

Five stages of intercalation are produced by the reaction between graphite and perchloric acid, and a sixth stage has been reported. The first stage crystallizes in the  $\alpha$ -modification exhibited by bisulphate compounds, and all stages show the familiar pattern of lattice expansion described in Table 66.

The thermal expansion coefficients for the first and second stages ( $98$  and  $55 \times 10^{-6} \text{ deg}^{-1}$  respectively) are constant in the region  $+25^\circ$  to  $-50^\circ\text{C}$ , and the specific resistance relative to graphite is  $R/R_0 = 0.035$ .

### Graphite Bisulphate

This is perhaps the most thoroughly studied of the graphite salts. A comprehensive literature covering the preparation is available and the usual five stages plus an eleventh stage of intercalation are well established<sup>444</sup>. The simplest preparation involves the treatment of graphite with a mixture of concentrated sulphuric and nitric acids.

The blue first-stage compound exists in two crystallographic modifications— $\alpha$  and  $\beta$ . In the  $\alpha$ -form the carbon planes have identical properties in the  $a$ - and  $b$ -directions, while the  $\beta$ -form has a typical graphitic structure. The  $\alpha$ - and  $\beta$ -forms are both produced in preparations using  $\text{CrO}_3$  oxidation while only the latter form is produced using nitric acid oxidation. Heating the bisulphate at  $200^\circ\text{C}$  *in vacuo* leads to a second stage sulphate compound<sup>445</sup>.

The structures of the compound again exhibit the usual regularity (Table 66) with the intercalated groups occupying the positions shown in Fig. 36. The thermal expansion coefficients for the first three stages have been measured. For the first two stages the values are constant between  $+25^\circ$  and  $-50^\circ\text{C}$  ( $62$  and  $42 \times 10^{-6} \text{ deg}^{-1}$  respectively) but the third stage exhibits a discontinuity at  $-3^\circ\text{C}$ <sup>440</sup>. No further information is available on the reason for this anomaly.

<sup>442</sup> A. R. Ubbelohde, *Nature*, **210** (1966) 404.

<sup>443</sup> W. Rüdorff, *Z. anorg. und allgem. Chem.* **254** (1947) 319.

<sup>444</sup> H. L. Riley, *Fuel*, **24** (1945) 8.

<sup>445</sup> M. Inagaki, *Carbon*, **4** (1966) 137.

TABLE 66. LATTICE CONSTANTS OF SOME GRAPHITE SALTS

Stage	Lattice constant $n$ (cm)		
	Graphite hydrogen fluoride	Graphite perchlorate	Graphite bisulphate ( $\alpha$ )
1	0.808 ( $C_{24}^+HF_2^- \cdot 2H_2F_2$ ) 1.129 = 0.794 + 1 $\times$ 0.335 1.468 = 0.794 + 2 $\times$ 0.335 1.803 = 0.794 + 3 $\times$ 0.335 — —	0.794 1.112 = 0.777 + 1 $\times$ 0.335 1.430 = 0.777 + 2 $\times$ 0.335 1.765 = 0.777 + 3 $\times$ 0.335 2.100 = 0.777 + 4 $\times$ 0.335 —	0.798 ( $C_{24}^+HSO_4^- \cdot 2H_2SO_4$ ) 1.133 = 0.798 + 1 $\times$ 0.337 1.472 = 0.798 + 2 $\times$ 0.337 1.809 = 0.798 + 3 $\times$ 0.337 2.146 = 0.798 + 4 $\times$ 0.337 4.168 = 0.798 + 10 $\times$ 0.337
2			
3			
4			
5			
11			

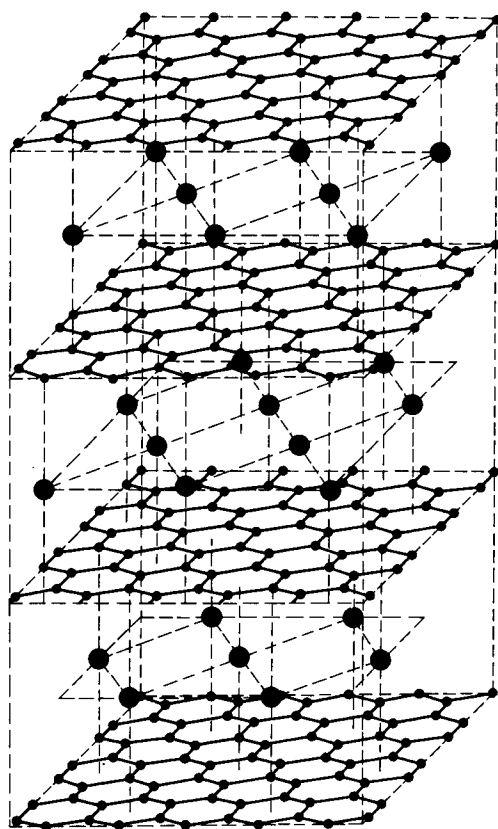


FIG. 36. The lattice structure of graphite bisulphate.

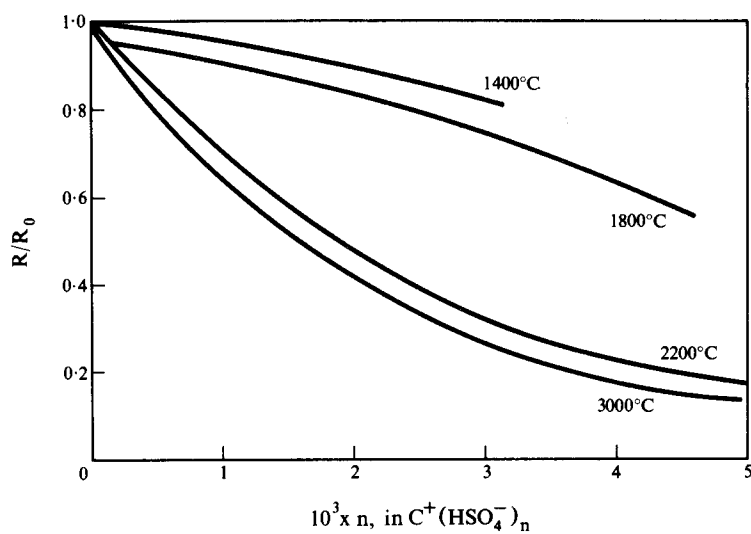


FIG. 37. The relative resistance of graphite bisulphate as a function of anion content.



Graphite bisulphate has received considerable attention in connection with its electronic constitution. The increase in conductivity when graphite is converted to the bisulphate has been used to follow changes in the properties of carbons caused by heat treatment<sup>446</sup>. The measurements show that the oxidation properties of graphites depend on the crystallite size. Electrical resistance measurements (Fig. 37) and Hall coefficient studies are consistent with the view that electrons in graphite fill one conduction band except for a small number that are excited into a nearly empty band. Oxidation depletes the lower band, creating more unpaired electrons and thus increasing the number of current carriers, despite small losses in the upper band<sup>447</sup>. Since temperature has only a small effect on the number of positive

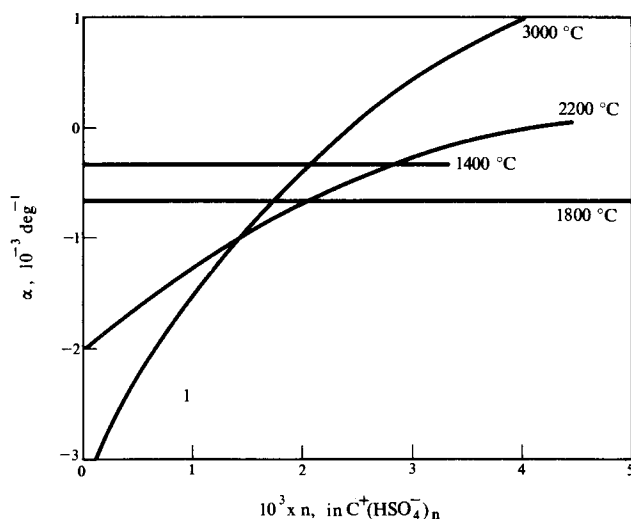


FIG. 38. The temperature coefficient of the electrical conductivity of graphite bisulphate as a function of anion content.

carriers, the temperature coefficient becomes small and eventually changes sign, because disturbance of the lattice increases the resistance beyond the point where it can be compensated by thermal excitation of electrons into the empty band (Fig. 38). The conductivity has recently been shown to be anisotropic<sup>448</sup> (Fig. 39). This effect is not yet completely understood but is believed to have its origin in the two-dimensional theory of the  $\pi$ -bond in graphite (see section 4.6).

Graphite salts are instantly decomposed by water and by polar organic liquids, thus rendering their isolation very difficult. Attempts to remove acid by washing lead to decomposition.

### Miscellaneous Salts

The anodic oxidation of highly orientated pyrolytic graphite in dry fluorosulphonic acid yields the first stage fluorosulphate. The analogous chlorosulphate  $C_{24}SO_3Cl \cdot nHSO_3Cl$

<sup>446</sup> E. A. Kmetko, *Phys. Rev.* **91** (1953) 243.

<sup>447</sup> G. R. Hennig, *J. Chem. Phys.* **19** (1951) 922.

<sup>448</sup> A. R. Ubbelohde, *Proc. 5th Carbon Conf.* (1961) Part 1.

has been detected by X-ray work. Second and third stage compounds have also been postulated<sup>449</sup>.

Selenic acid will readily form a first stage compound and several preparations have been given<sup>439</sup>. The compound has an interlayer spacing of 0.825 nm.

A first stage material has not been found with phosphoric acid, but a brown second stage product (lattice constant = 1.138 nm) is proposed, resulting from treatment with 100%  $\text{H}_3\text{PO}_4$  and  $\text{CrO}_3$  oxidizer at 100°C. The structure is assumed to contain  $\text{H}_2\text{PO}_4^-$  ions by analogy with the bisulphate. A second stage diphosphoric acid compound, with a lattice constant of 1.154 nm, has also been prepared. This is presumed to contain  $\text{H}_2\text{P}_2\text{O}_7^{2-}$  ions<sup>450</sup>.

Arsenic acid will not react with graphite to give a well-defined compound, although recent work shows that the graphite anodes used in the electrolysis of arsenic acid do show some swelling<sup>449</sup>.

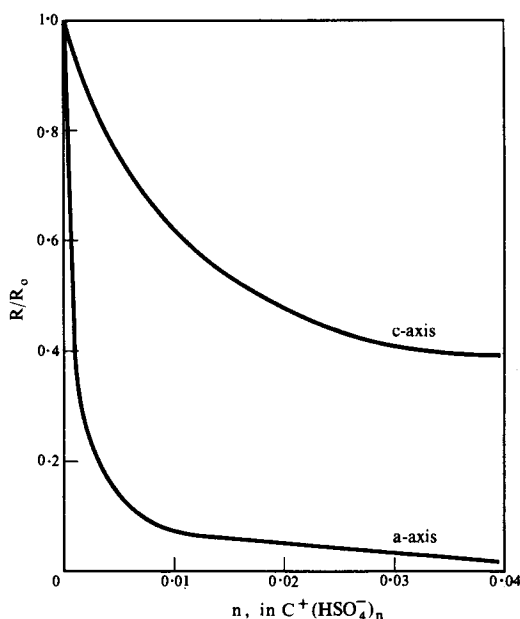


FIG. 39. The relative resistance of graphite bisulphate.

The anodic oxidation of graphite in dry trifluoroacetic acid produces first and second stage intercalation. A third stage compound can also be made. The relative resistance of the first stage material  $R/R_0$  is 0.2 along the  $a$ -axis<sup>433</sup> and the lattice constants are, 1st stage 0.818 nm, 2nd stage 1.152 nm and 3rd stage 1.485 nm.

Boron fluoride diacetate can be made to undergo three stages of intercalation by suitable choice of reaction conditions<sup>451</sup> and the anodic oxidation of well-ordered pyrolytic graphite is said to yield a fourth stage<sup>449</sup>. The lattice constants are 0.808, 1.130 and 1.460 nm respectively.

<sup>449</sup> M. J. Bottomley, G. S. Parry, A. R. Ubbelohde and D. A. Young, *J. Chem. Soc.* (1963) 5674.

<sup>450</sup> W. Rüdorff and U. Hoffman, *Z. anorg. und allgem. Chem.* **238** (1938) 1.

<sup>451</sup> W. Rüdorff and W.-F. Siecke, *Chem. Ber.* **91** (1958) 1348.

Summarizing the oxidation of graphite by acids, it is possible to say that the degree of intercalation depends both on the concentration and strength of the acid. For instance, in 83% sulphuric acid only the second stage compound is formed, in 63% solution oxidation proceeds to the third stage and below 50% the uptake is so large that it cannot be detected by X-ray examination. Furthermore, with  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SeO}_4$  the first stage is obtained easily but  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$  only give a low degree of oxidation, and organic acids will not react at all. A particularly striking example of the influence of acid strength is shown by the gradually increasing oxidation that takes place in the series  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_2\text{ClCOOH}$ ,  $\text{CHCl}_2\text{COOH}$  and  $\text{CCl}_3\text{COOH}$ . In even stronger acids such as  $\text{CF}_3\text{COOH}$  and  $\text{BF}_3(\text{CH}_3\text{COOH})_2$  the graphite electrodes are eventually destroyed.

#### 4.11. MOLECULAR COMPOUNDS

These materials differ from other graphite compounds in that the intercalated molecules are, at least at the moment of penetration, molecular and not atomic or ionic. The preparations are reversible (except for the occasional formation of residue compounds) and the ionic character of the compounds shows in their increased conductivity compared with graphite. In common with other ionic compounds they undergo successive stages of intercalation, the first stage exhibiting the typical blue colour.

The majority of molecular compounds are formed with metal halides, although metal oxides and sulphides are also believed to form molecular compounds. Tables 67 and 68 summarize the molecules known to undergo this type of reaction<sup>452, 453</sup>.

TABLE 67. METAL HALIDES WHICH FORM MOLECULAR COMPOUNDS WITH GRAPHITE

$\text{BeCl}_2$	$\text{BCl}_3$	$\text{AlCl}_3$	$\text{AlBr}_3$	$\text{CrCl}_3$	$\text{CrO}_2\text{Cl}_2$
$\text{CrO}_2\text{F}_2$	$\text{FeCl}_3$	$\text{CoCl}_3$	$\text{CoCl}_2$	$\text{CuCl}_2$	$\text{CuBr}_2$
$\text{GaCl}_3$	$\text{RbCl}_3$	$\text{YCl}_3$	$\text{ZrCl}_3$	$\text{MoCl}_5$	$\text{RuCl}_3$
$\text{RhCl}_3$	$\text{PdCl}_4$	$\text{CdCl}_2$	$\text{InCl}_4$	$\text{SbCl}_5$	$\text{SmCl}_3$
$\text{EuCl}_3$	$\text{GdCl}_3$	$\text{TbCl}_3$	$\text{DyCl}_3$	$\text{YbCl}_3$	$\text{HfCl}_4$
$\text{TaCl}_5$	$\text{WCl}_6$	$\text{ReCl}_4$	$\text{PtCl}_4$	$\text{AuCl}_3$	$\text{HgCl}_2$
$\text{TiCl}_3$	$\text{UCl}_5$	$\text{UCl}_6$	$\text{UO}_2\text{Cl}_2$		
$\text{Br}_2/\text{AlCl}_3$		$\text{I}_2/\text{AlCl}_3$		$\text{ICl}_3/\text{CdCl}_2$	
$\text{WCl}_6/\text{AlCl}_3$		$\text{FeCl}_3/\text{AlCl}_3$			

Iron(III) chloride graphite was the first of these compounds to be synthesized and consequently it has received the most attention. The first stage compound can be prepared by simply heating a mixture of the reactants at 250°C. Further heating at 400°C yields the second and third stages<sup>454</sup>. Heating the third stage at 50°C in a  $\text{FeCl}_3$ -rich nitromethane solution generates the second stage<sup>455</sup>.

The composition of the first stage varies from 56 to 70%  $\text{FeCl}_3$  with a formula  $\text{C}_{6-7}\text{FeCl}_3$ . X-ray diffraction<sup>456</sup> has shown that up to 17% of the carbon exists as free graphite. Detailed analysis indicates that the chlorine atoms attempt to occupy preferred positions in the

<sup>452</sup> R. C. Croft, *Austral. J. Chem.* **9** (1956) 184.

<sup>453</sup> W. Rüdorff, E. Stumpp, W. Sprissler and W.-F. Siecke, *Angew. Chem.* **75** (1963) 130.

<sup>454</sup> R. C. Croft, *J. Appl. Chem.* **2** (1952) 557.

<sup>455</sup> D. Grindorow and R. Setton, *Compt. Rend.* **257** (1963) 687.

<sup>456</sup> J. M. Cowley and J. A. Ibers, *Acta Cryst.* **9** (1956) 421.

TABLE 68. METAL OXIDES AND SULPHIDES FORMING MOLECULAR COMPOUNDS WITH GRAPHITE

Starting material	Product
$V_2S_3$	3.7% $V_2S_{3.5}$
$CrO_3$ (At 200°C, solid)	55% $CrO_3$
(At 100°C, in solution)	38% $CrO_3$
$Cr_2S_3 + S$	4.0% $Cr_2S_{3.5}$
$Fe + S$	12.2% $FeS_2$
$Cu + S$	16.2% $CuS_{1.3}$
$MoO_3$	10.75% $MoO_3$
$Sb_2O_4$	1.36% $Sb_2O_4$
$Sb_2S_5$	9.40% $Sb_2S_{4.8}$
$PdS + S$	8.8% $PdS_{2.2}$
$WS_2$	14.1% $WS_{2.4}$
$Tl_2S + S$	27% $TlS_2$

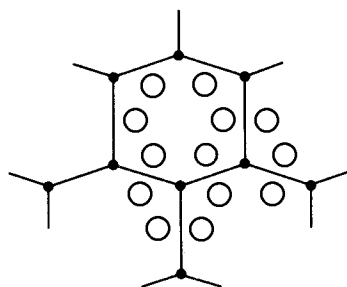


FIG. 40. The preferred positions of chlorine atoms relative to the graphite lattice in iron(III) chloride graphite.

lattice as shown in Fig. 40. Excessive distortion in fact prevents more than half of these atoms occupying the preferred positions which are thus distributed, more or less at random, among the chloride planes. The same data reveal that the variable composition of the first stage is due to variations in the excess carbon content at room temperature, although a single phase exists at higher temperatures. This excess carbon is not due to unreacted material since the original graphite structure is destroyed. The lattice constant varies between 0.937 and 0.945 nm.

The second stage compound has a composition corresponding to  $C_{12}FeCl_3$ <sup>457</sup> with a lattice constant of 1.280 nm. Optical investigations have revealed the presence of material with a composition of  $C_{70}^{+}Cl^{-} \cdot FeCl_2 \cdot 5FeCl_3$ <sup>421</sup>.

The third stage has a  $FeCl_3$  concentration between 30 and 37% with a lattice constant of 1.621 nm, indicating three hexagonal carbon layers between each layer of iron(III) chloride.

Iron(III) chloride molecular compounds lose part of the intercalated material on reaction with water, dilute acids and organic solvents. The first stage compound retains 56%  $FeCl_3$  ( $C:FeCl_3 = 10:1$ ) while the third stage retains only 31% ( $C:FeCl_3 = 30:1$ ). Oxidizing and reducing agents produce some measurable reaction since there is visible swelling.

<sup>457</sup> J. G. Hooley and M. Bartlett, *Carbon*, **5** (1967) 417.

Heating the compounds above 410°C, or treatment with distilled water, 6 M HCl or acetone yields a residue compound<sup>458</sup>.

Table 69 indicates the more important properties of the remaining molecular compounds which have been studied.

TABLE 69. THE PREPARATION AND COMPOSITION OF SOME MOLECULAR COMPOUNDS OF GRAPHITE

Molecule	Stage	Preparation	Average composition	Lattice constants c (nm)	
CdCl <sub>2</sub> <sup>a</sup>	1	CdCl <sub>2</sub> + Cl <sub>2</sub> at 500°C	69.6% CdCl <sub>2</sub>	0.951	
	2		37% CdCl <sub>2</sub>	—	
HgCl <sub>2</sub> <sup>a</sup>	1	HgCl <sub>2</sub> + Cl <sub>2</sub> at 250°C	C <sub>n</sub> <sup>+</sup> (HgCl <sub>3</sub> ) <sup>-</sup> .5HgCl <sub>2</sub>	0.978	
	3		C <sub>20</sub> HgCl <sub>2</sub>	1.648	
AlCl <sub>3</sub> <sup>b</sup>	1	AlCl <sub>3</sub> + Cl <sub>2</sub> at 280°C	C <sub>22.5</sub> Cl <sup>-</sup> .3AlCl <sub>3</sub> <sup>c</sup>	0.952	
	2		370°C	37% AlCl <sub>3</sub>	1.280
	4		450°C	22% AlCl <sub>3</sub>	1.965
Br <sub>2</sub> /AlCl <sub>3</sub> <sup>d</sup>	1	X <sub>2</sub> at 180°C, then	C <sub>n</sub> <sup>+</sup> Br <sup>-</sup> .3AlCl <sub>3</sub>	—	
I <sub>2</sub> /AlCl <sub>3</sub> <sup>d</sup>	1	X <sub>2</sub> + AlCl <sub>3</sub> at 205°C	C <sub>n</sub> <sup>+</sup> I <sup>-</sup> .3AlCl <sub>3</sub>	—	
GaCl <sub>3</sub> <sup>e</sup>	1	GaCl <sub>3</sub> + Cl <sub>2</sub> at 150°C	C <sub>n</sub> <sup>+</sup> Cl <sup>-</sup> .3GaCl <sub>3</sub> <sup>f</sup>	0.954	
	2		250°C	45% GaCl <sub>3</sub>	1.280
	4		400°C	27% GaCl <sub>3</sub>	1.956
	InCl <sub>3</sub> <sup>g</sup>		2	InCl <sub>3</sub> at 450°C	C <sub>n</sub> <sup>+</sup> Cl <sup>-</sup> .6InCl <sub>3</sub> <sup>g</sup>
3		490°C	45% InCl <sub>3</sub>		1.620
4		> 490°C	32% InCl <sub>3</sub>		1.965
InCl <sub>3</sub> /CdCl <sub>2</sub> <sup>a</sup>		1	InCl <sub>3</sub> + 2nd stage		22.6% CdCl <sub>2</sub>
		CdCl <sub>2</sub> compound	42.4% InCl <sub>3</sub>	—	
CrO <sub>2</sub> F <sub>2</sub> <sup>e</sup>	—	CrO <sub>2</sub> F <sub>2</sub> at 20°C	C <sub>15</sub> CrO <sub>2</sub> F <sub>2</sub>	—	
CrO <sub>2</sub> Cl <sub>2</sub>	—	CrO <sub>2</sub> Cl <sub>2</sub> at 100°C	C <sub>12</sub> CrO <sub>2</sub> Cl <sub>2</sub> <sup>h</sup>	—	
	—	CrO <sub>2</sub> Cl <sub>2</sub> at 100°C	C <sub>17</sub> CrO <sub>2</sub> Cl <sub>2</sub> <sup>e</sup>	—	
	—	CrO <sub>2</sub> Cl <sub>2</sub> at 100°C	C <sub>40</sub> CrO <sub>2</sub> Cl <sub>2</sub> <sup>i</sup>	—	
	—	CrO <sub>2</sub> Cl <sub>2</sub> at 100°C	C <sub>130</sub> CrO <sub>2</sub> Cl <sub>2</sub> <sup>h</sup>	—	
	5	WCl <sub>6</sub> + Cl <sub>2</sub> at 300°C	C <sub>70</sub> WCl <sub>6</sub> <sup>a</sup>	—	
WCl <sub>6</sub>	—	WCl <sub>6</sub> at 320°C	C <sub>94</sub> WCl <sub>6</sub> <sup>e</sup>	—	
	UCl <sub>5</sub>	—	UCl <sub>5</sub> at 350°C	C <sub>25</sub> UCl <sub>4</sub> <sup>e</sup>	—
2		UCl <sub>5</sub> + Cl <sub>2</sub> at 420°C	C <sub>37</sub> UCl <sub>5</sub> <sup>a</sup>	1.303	
CoCl <sub>2</sub> <sup>e, j</sup>	—	CoCl <sub>2</sub> + Cl <sub>2</sub> at 20°C	C <sub>4</sub> CoCl <sub>3</sub>	—	
	—		350°C	C <sub>21</sub> CoCl <sub>2</sub>	—
	—		300–400°C	C <sub>26</sub> CoCl <sub>2</sub>	—
	—		300–400°C	C <sub>27</sub> CoCl <sub>2</sub>	—
	—		300–400°C	C <sub>46</sub> CoCl <sub>2</sub>	—
FeCl <sub>3</sub> /AlCl <sub>3</sub> <sup>k</sup>	1	AlCl <sub>3</sub> + FeCl <sub>3</sub> graphite at 300°C	1FeCl <sub>3</sub> :2AlCl <sub>3</sub>	0.962	
CuCl <sub>2</sub> <sup>a</sup>	1	CuCl <sub>2</sub> at 400°C	C <sub>5</sub> CuCl <sub>2</sub>	0.940	
	—	CuCl <sub>2</sub> at 600°C	C <sub>13</sub> CuCl <sub>2</sub> <sup>g</sup>	—	

<sup>a</sup> W. Rüdorff, *Angew. Chem.* **71** (1959) 487.

<sup>b</sup> R. C. Croft, *J. Appl. Chem.* **2** (1952) 557.

<sup>c</sup> L. F. C. Blackman, J. F. Mathews and A. R. Ubbelohde, *Proc. Roy. Soc.* **A256** (1960) 15.

<sup>d</sup> M. L. Dzurus and G. R. Hennig, *J. Am. Chem. Soc.* **79** (1957) 1051.

<sup>e</sup> R. C. Croft, *Austral. J. Chem.* **9** (1956) 184.

<sup>f</sup> W. Rüdorff and A. Landel, *Z. anorg. und allgem. Chem.* **293** (1958) 327.

<sup>g</sup> R. C. Croft, *Nature*, **172** (1953) 725.

<sup>h</sup> W. Rüdorff, V. Sils and R. Zeller, *Z. anorg. und allgem. Chem.* **283** (1956) 299.

<sup>i</sup> J. G. Hookey, *Can. J. Chem.* **40** (1962) 745.

<sup>j</sup> J. J. Pitts and L. L. Lyon, *Proc. 5th Carbon Conf.* (1961).

<sup>k</sup> R. Zeller, *Z. anorg. und allgem. Chem.* **279** (1955) 182.

<sup>458</sup> C. Martin-LeFèvre, *Compt. Rend.* **C264** (1967) 195.

It has been suggested that the intercalation of metal halides can be correlated with the position of the metal in the Periodic Table<sup>330</sup>. With the exception of the Group III elements the cations of successfully-intercalated chlorides have incomplete penultimate electron shells capable of accommodating electrons from the graphite conduction band. Two conditions are necessary for intercalation according to this supposition: electronic interaction between the cation and graphite, and a sufficient electron affinity of the cation to promote this interchange. The latter requirement explains why, with few exceptions, only higher chlorides or transition metal chlorides are intercalated. In the Group III halides it is suggested that interaction occurs via the donation of electron pairs from the  $2p\pi$  graphite orbitals into the (vacant) metal orbitals.

# 14. AN INTRODUCTION TO THE ORGANIC CHEMISTRY OF THE METALLIC ELEMENTS

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## 1. INTRODUCTION

The object of this chapter is to provide a basis for a qualitative, comparative description of the organic chemistry of the metals and of their common inorganic chemistry.

The bonding in most organometallic compounds is best described by the covalent model and to maintain a consistent approach, inorganic derivatives, which are normally discussed in terms of the ionic oxidation-state model, are described in covalent terms also.

The basis of our approach is as follows.

(a) The orbitals of atoms are divided into *core*, *valence* and *supra-valence* orbitals, according to their energy. Core orbitals are filled and strongly bound to the nucleus. It is thought that they maintain very similar energy and location in different chemical environments<sup>1</sup>. Valence orbitals, which may be filled or empty, are largely responsible for covalent bond formation. The supra-valence orbitals are empty and usually make little or no contribution to bonding.

(b) In formation of covalent bonds each atom normally satisfies the *stability rules* which arise from the maximum use of valence orbitals and valence electrons. For example, atoms with *ns* and three *np* valence orbitals (Li to Ne) have four valence orbitals and tend to obey an octet (8e) rule (the *N* and  $(8-N)$  valence rules); atoms with *ns*, three *np* and five  $(n-1)d$  valence orbitals tend to obey the 18-electron (18e) rule (e.g. the  $(n-1)d$ -block transition metals); atoms with *ns*, *np*, and  $(n-2)f$  valence orbitals can attain a 22e shell, possibly as in  $(C_8H_8)_2U$  (see Fig. 2) and, if the  $(n-1)d$  orbitals are also included, then a 32e rule is expected.

(c) We have adopted a *formal* classification of ligands in terms of the *number of electrons that they may be said to contribute to the formation of the metal-ligand bond*. The choice for the number of electrons per ligand has been based on induction from the known chemistry of the ligand, see section 3.1.

(d) The number of electrons associated with an atom in a molecule is found by summation of the number of valence electrons on the neutral atom, the number of electrons from the ligands and the charge, e.g. carbon in methane obeys the  $4+4\times 1=8e$  rule.

(e) Ligands are also further classified according to their donor and acceptor properties.

<sup>1</sup> In fact, very little is known about the variation of energies of core electrons, and it seems unlikely that useful information will become available until the new physical method of electron emission spectroscopy is improved and exploited.

Again, these are also estimated by induction from known chemistry since they cannot be measured independently by any consistent procedure.

The counting of electrons in molecules shows that the stability rules are sometimes

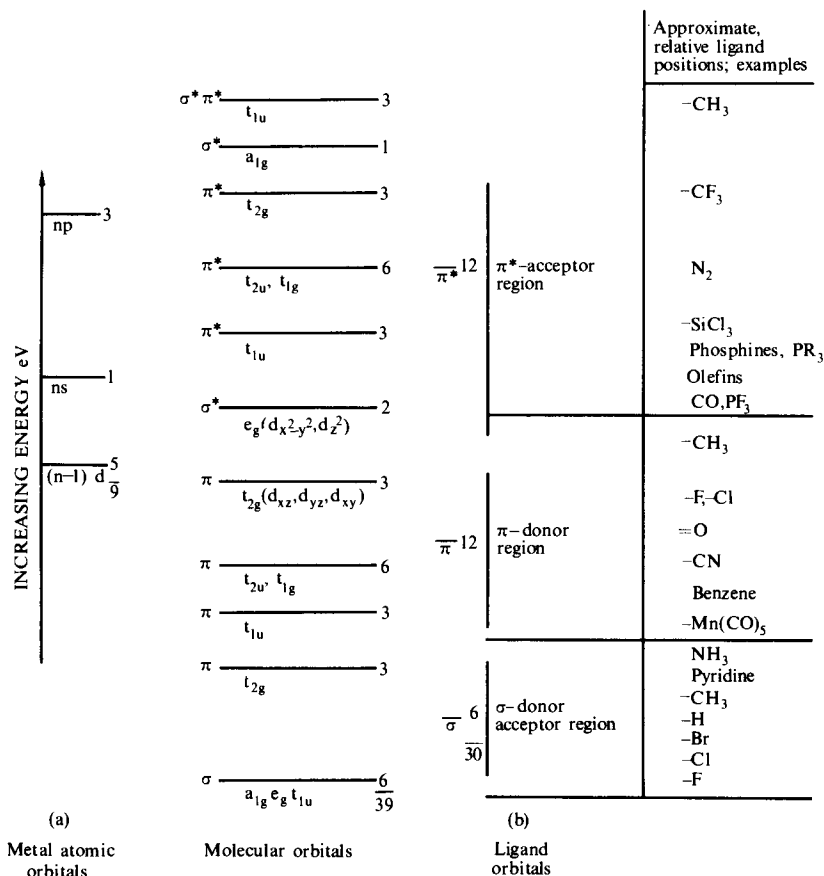


FIG. 1. (a) Molecular orbital diagram for octahedral  $\text{MX}_6$ , where each ligand X has one  $\sigma$ , two  $\pi$ -filled and two  $\pi^*$ -empty orbitals. (b) The regions of  $\sigma$ -donor-acceptor,  $\pi$ -donor or  $\pi^*$ -acceptor energies which are shown are *very* approximate. Also the *relative* order of ligands shown opposite these regions is estimated and not known certainly.

not obeyed, e.g. sulphur in  $\text{SF}_6$  has a  $6+6 \times 1 = 12\text{e}$  system, and boron in  $\text{BMe}_3$  has a 6e system.

This chapter discusses these exceptions in terms of the trends in atomic properties of the central atoms and the nature of the ligand central atom bonding. In this way comparative assessment of organic and inorganic ligands may be made.

## 2. ATOMS IN MOLECULES

In the introduction a molecule ( $\text{MX}_n$ ), or molecular ion, is considered as being composed of ligands X and the central atom M. Unlike the core electrons, however, the



valence electrons of M are considerably modified compared with those in the free atom and, therefore, are properly described in terms of molecular orbitals (MO). The atomic orbitals of an atom M and the molecular orbitals of a molecule containing that atom may approximately be related in terms of the linear combination of atomic orbitals (LCAO) method. Outside such an approach there is no meaning in a statement such as "the *d*-orbitals on the central atom . . .".

From the LCAO approach, in diagrams, molecular orbitals of molecules are often shown as arising from the orbitals of the constituent atoms or groups, as in Fig. 1a.

In a series of related compounds  $\text{MX}_n$ , where M varies, for example down a subgroup,

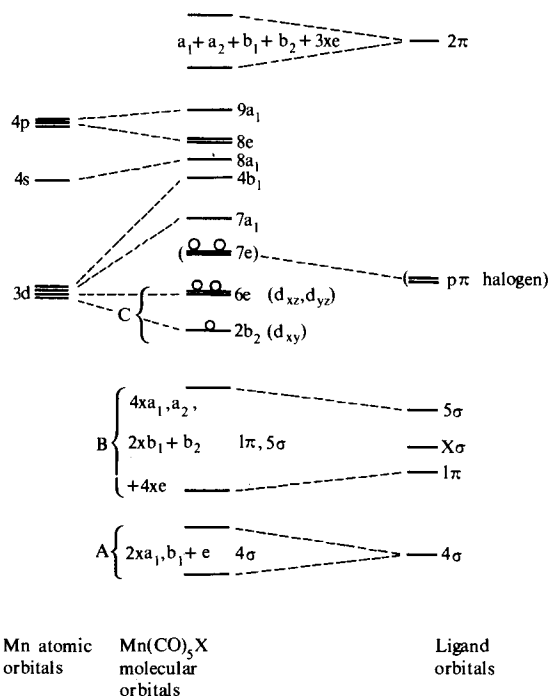


FIG. 2. General MO diagram of the complexes  $\text{Mn(CO)}_5\text{X}$  showing—A: 4σ region (electrons largely localized on CO). B: 5σ, 1π region (also largely CO electrons). C: electrons largely 3d a.o. in character.

the molecular orbital diagrams of the  $\text{MX}_n$  series often show strong similarities but also contain fairly regular changes. These may be interpreted in terms of the changing properties of the atoms from which the molecules are formed. For example, the decreasing thermal stability of the group IV hydrides is associated with the observed decrease in M–H bond strength, which is thought to arise mainly from reduction in overlap between the *ns* and *np* orbitals on M and the 1s orbital of hydrogen on going down the group.

Despite its limitations, the concept of atoms and hence of atomic orbitals in molecules is useful since it enables one to visualize and talk in terms of the "effect of ligands on the central atom". The photoelectron spectra of the complexes  $\text{Mn(CO)}_5\text{X}$  provides evidence for the acceptability of this approach.

The photon electron ionization data are given, together with assignments, in Table 1

and the MO diagram derived from these data in Fig. 2. The main feature of interest is that there are ionizations associated with the  $6e$  and  $2b_2$  symmetry orbitals which may be described as "essentially manganese  $d$ -orbitals". As the ligand  $X$  is varied the average

TABLE 1. IONIZATION POTENTIAL DATA FOR THE COMPLEXES  $Mn(CO)_5X^a$ 

$X =$	Cl	Br	I	$CF_3$	H	$CH_3$	$Mn(CO)_5^c$	Assignment <sup>b</sup>
	8.80	8.76	8.35					7e, lone pair
			8.65					on halogen
	10.43	10.04	9.57	9.20	10.60	8.46	8.02	6e, $d_{xz}$ , $d_{yz}$
	11.00	10.80	10.37	10.30	10.60	8.46	8.43	2b <sub>2</sub> , $d_{zy}$
							8.97	
	14.0 - 17.0	13.8 - 17.4	13.7 - 17.6	13.5 - 17.6	13.5 - 16.9	12.0 - 16.0	12.0 - 16.4	5σ, 1π
	18.7	18.6	18.6	18.5	17.97	18.0	17.7	4σ

<sup>a</sup> Data given in electron volts<sup>1</sup>.

<sup>b</sup> See Fig. 2.

<sup>c</sup> Assignments not applicable (see ref. 1a).

energy of the "manganese  $d$ -orbitals" changes from  $-10.62$  eV,  $X=Cl$ , to  $-8.67$  eV,  $X=CH_3$ , an increase of 1.95 eV. This decrease of binding energy (decrease of ionization potential) may be interpreted as an increase of charge density (electron richness) on the metal atom. Thus with decreasing electronegativity of the ligands  $X$  and a corresponding decrease of partial positive charge on the manganese it is observed that the " $d$ -orbitals" increase in energy. On this basis it is predicted that the electronegativities of the ligands  $X$  decrease in the order  $Cl > Br > I > CF_3 > H > CH_3 > Mn(CO)_5$ , in agreement with values obtained by other methods.

It seems reasonable, therefore, to regard certain molecular orbitals in compounds as being essentially either central atom orbitals or ligand orbitals. Although there are limitations in this approach it can be useful as a basis for a qualitative, comparative description of covalent compounds.

### 3. THE CLASSIFICATION OF LIGANDS

#### 3.1. ELECTRON NUMBERS

The classification is given in Table 2 and discussed below. As stated earlier, it is formally considered that ligands arise from atoms, or *neutral* groups, and form covalent bonds to the central atom. The ligands are classified according to the number of valence electrons which formally they contribute to the bonding. Subsequently electrons may be removed or added to the system forming ions.

In most cases there is no difficulty or ambiguity in deciding upon the *total* number of electrons contributed by ligands (Table 2). A problem which occasionally arises is illustrated by the ligands ethylene and tetrafluoroethylene. Ethylene is to be regarded as a 2e ligand in  $[Mn(CO)_5C_2H_4]^+$  since this cation is very similar to the cation  $[Mn(CO)_6]^+$ . In contrast, in the compound  $(Ph_3P)_2PtC_2F_4$ , tetrafluoroethylene is best regarded as a

<sup>1a</sup> S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard and D. W. Turner, *Disc. Faraday Soc.* **47** (1969) 122.

TABLE 2. A CLASSIFICATION OF SOME COMMON LIGANDS

Ligand and classification by number of electrons	ne	Nature of ligand—central atom bonding				Tendency to form stable ions	Size	Stability properties and other comments
		$\sigma$		$\pi$				
		Donor	Acceptor	Donor	Acceptor			
BH <sub>3</sub>	0	—	s	w	w	None	m	Reactive, only few examples presently known, a Lewis acid
BF <sub>3</sub>	0	—	vs	w	w	None	m	Fairly inert, Lewis acid, BCl <sub>3</sub> , BBr <sub>3</sub> are similar
F	1	vw	vs	w	—	F <sup>-</sup> v. favourable	s	Very electronegative, a characteristic chemistry
Cl	1	vw	s	wm	vw	Cl <sup>-</sup> v. favourable	sm	Electronegative, v. common
Br	1	vw	ms	wm	vw	Br <sup>-</sup> v. favourable	m	Electronegative, common
I	1	w	m	wm	w	I <sup>-</sup> favourable	m	
CF <sub>3</sub>	1	vw	ms	vw	wm	CF <sub>3</sub> <sup>-</sup> unstable	m	Inert, representative of fluoroalkyls
C <sub>6</sub> F <sub>5</sub>	1	w	ms	w	w	C <sub>6</sub> F <sub>5</sub> <sup>-</sup> v. slight	l	Fairly inert, representative of fluoroaryls
H	1	m	m	—	—	H <sup>+</sup> variable	s	Stereochemically labile, common, wide range of polarizability of M-H bond
CH <sub>3</sub>	1	ms	w	—	vw?	H <sup>-</sup> weak	m	Inert as ligand, radical v. reactive and decomposes
C <sub>2</sub> H <sub>5</sub>	1	ms	w	—	vw?	CH <sub>3</sub> <sup>-</sup> v. reactive	m	Tendency to eliminate H <sup>-</sup> from $\beta$ -carbon in transition metal complexes
CH <sub>2</sub> CH=CH <sub>2</sub>	1	ms	w	—	vw?	C <sub>3</sub> H <sub>5</sub> <sup>-</sup> v. weak	m	Undergoes 1,3-shifts, forms $\pi$ -C <sub>3</sub> H <sub>5</sub> with transition metals, uncommon
C <sub>6</sub> H <sub>5</sub>	1	m	w	vw	w	C <sub>6</sub> H <sub>5</sub> <sup>-</sup> v. weak	ml	Radical reactive, tendency to lose ortho-hydrogens. In transition metal complexes
COMe	1	m	w	vw	wm	COMe <sup>+</sup> weak	m	Radical reactive
CN	1	m	w	wm	m	CN favourable	sm	M-CN undergo nucleophilic attack, CN radical quite stable
NNN	1	mw	w	wm	m	NNN <sup>-</sup> favourable	sm	Fairly inert, explosive
SCN	1	mw	vw	wm	wm	SCN <sup>-</sup> favourable	sm	Fairly inert
OH	1	ms	w	m	—	OH <sup>-</sup> medium	m	Very reactive, facile loss of H, strong tendency to bridge

TABLE 2—continued

Ligand and classification by number of electrons	ne	Nature of ligand—central atom bonding				Tendency to form stable ions	Size	Stability properties and other comments
		$\sigma$		$\pi$				
		Donor	Acceptor	Donor	Acceptor			
OMe	1	ms	w	m	—	OMe <sup>-</sup> medium	m	Fairly inert, O—Me bond not readily broken, bridges
SMe NMe <sub>2</sub> (sp <sup>3</sup> )	1	m	w	w	—	SMe <sup>-</sup> medium	m	Fairly inert, bridges
	1	ms	m	—	—	NMe <sub>2</sub> <sup>-</sup> weak	m	Fairly inert, bridges, the planar ligand is a strong $\pi$ -acceptor
	1	m	w	w	m	PMe <sub>2</sub> <sup>-</sup> weak	m	Fairly inert, bridges
PMe <sub>2</sub>	1	wm	wm	vw	m		ml	Quite reactive
SiCl <sub>3</sub>	1	wm	wm	—	m		ml	Quite reactive
GeCl <sub>3</sub>	1	wm	wm	—	m		ml	Quite reactive
SnCl <sub>3</sub>	1	m	wm	w	w	SnCl <sub>3</sub> <sup>-</sup>	m	Fairly inert
HgCl	1	m	w	s	w	HgCl <sup>-</sup> ?	l	Fairly inert, a $\pi$ -base
Mn(CO) <sub>5</sub>	1	wm	ms	ms	w	Mn(CO) <sub>5</sub> <sup>-</sup> medium	m	Readily protonated
O	2 × 1	wm	ms	—	—	O <sub>2</sub> <sup>-</sup> medium	l	Reactive
BH <sub>4</sub>	1	wm	wm	—	—	BH <sub>4</sub> <sup>-</sup> medium	bidentate	Inert
C <sub>2</sub> F <sub>4</sub>	2 × 1	vw	ms	vw	wm	None	m	Moderately reactive, v. common
NH <sub>3</sub>	2	s	vw	—	—	NH <sub>3</sub> <sup>-</sup> v. weak	l	Fairly inert
NMe <sub>3</sub>	2	s	vw	—	—	None	m	Rather reactive
PH <sub>3</sub>	2	wm	w	vw	wm	None	m	Fairly inert
PF <sub>3</sub>	2	w	w	w	s	None	l	Inert
PMc <sub>3</sub>	2	m	vw	vw	m	None	vl	Inert
P(cyclohexyl) <sub>3</sub>	2	wm	vw	vw	m	None	l	Mostly inert, tendency to lose ortho-hydrogens
PPh <sub>3</sub>	2	w	vw	w	ms	None	l	Hydrogens v. labile
H <sub>2</sub> O	2	m	w	—	—	None	m	Inert
R <sub>2</sub> O	2	m	w	vw	—	None	ml	Fairly inert
R <sub>2</sub> S	2	m	vw	w	vw	None	ml	Fairly inert, free ligand stable
C <sub>2</sub> H <sub>4</sub>	2	wm	vw	w	ms	None	bidentate	Inert, free ligand table
N <sub>2</sub>	2	w	vw	vw	wm	None	sm	Inert
CO	2	w	vw	vw	ms	None	sm	Inert

TABLE 2—continued

Ligand and classification by number of electrons	ne	Nature of ligand—central atom bonding				Tendency to form stable ions	Size	Stability properties and other comments
		$\sigma$		$\pi$				
		Donor	Acceptor	Donor	Acceptor			
Pyridine	2	ms	w	w	w	v. small	m	Inert
RNC	2	wm	w	w	ms	None	m	Inert
RCN	2	m	w	w	wm	None	m	Inert
NO	1+2	vw	vw	m	ms	NO <sup>+</sup> readily NO <sup>-</sup> v. weak	ms	Inert, unique since monodentate
$\pi$ -C <sub>3</sub> H <sub>5</sub>	3	wm	w	m	m	C <sub>3</sub> H <sub>5</sub> <sup>-</sup> medium		Pseudo-bidentate, tendency to partial displacement, reactive in free state
$\pi$ -Cyclohexenyl	3	vw	w	m	m	v. weak		Pseudo-bidentate but large
Acetylacetonyl	3	ms	w	w	m	Anion medium		Bidentate, conjugated
Dimethylglyoximyl	3	ms	w	w	m	Anion medium		Bidentate, conjugated
Cyclobutadiene	4	wm	w	m	ms	v. weak		Pseudo-bidentate, compact, unstable in free state
Butadiene	4	wm	w	m	ms			Pseudo-bidentate, stable in free state
<i>o</i> -Phenanthroline	4	m	w	vw	wm	Anion weak—medium		Bidentate, rigid, geometrical requirement
$\alpha$ , $\delta$ -Bipyridyl	4	m	ww	vw	wm	Anion weak—medium		Bidentate, semi-rigid
$\pi$ -C <sub>5</sub> H <sub>5</sub>	5	m	w	m	m	Anion medium		Pseudo-tridentate, compact, radical reactive
Benzene	6	wm	w	wm	m	Anion v. weak		Pseudo-tridentate, moderately compact, stable in free state
$\pi$ -Cycloheptatrienyl	7	mw	m	wm	m	Cation weak—medium		Pseudo-tridentate, unstable in free state
Cyclo-octa-tetraene	8	m	w	w	m	C <sub>8</sub> H <sub>6</sub> <sup>2-</sup> medium		Pseudo-tetradentate, compact, stable in free state, flexible

$2 \times 1e$  ligand. This latter compound has a planar  $P_2PtC_2$  system and is comparable to *cis*-( $Ph_3P$ ) $_2Pt(CF_3)_2$ .

Some ligands, especially hydrocarbon ligands, can bond to a central atom in more than one way. For example, cyclo-octa-tetraene may act as a  $4e$ ,  $6e$ ,  $8e$ ,  $2 \times 4e$ , or  $4 \times 2e$  ligand (Fig. 3). We shall use the nomenclature exemplified in the legend to Fig. 3 to distinguish between such possibilities.

Ligands such as chlorine may occur either as terminal  $1e$  ligands or as bridging  $3e$  ligands. The symbol  $\mu$  is used to indicate the occurrence of bridging ligands, e.g.  $\mu\text{-Cl}$ .

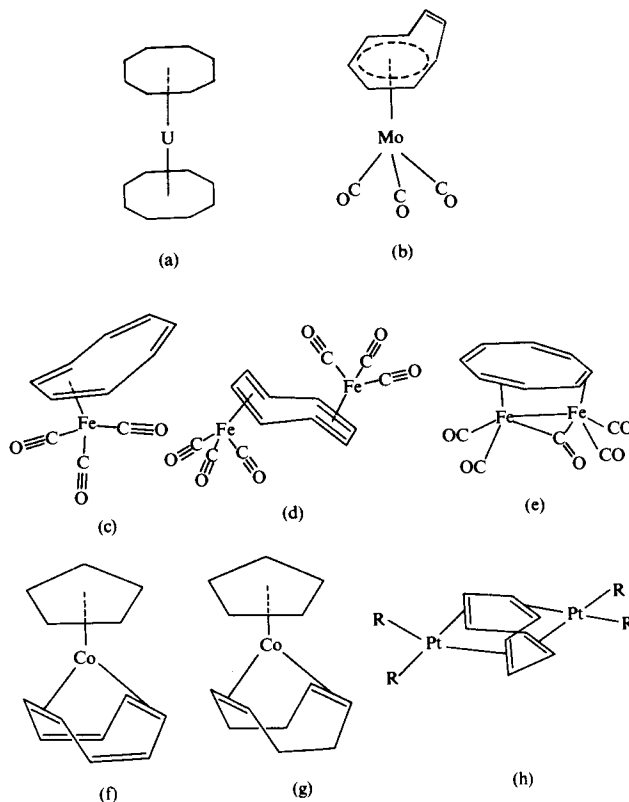


FIG. 3. Structures of some cyclo-octa-tetraene and related complexes. (a) Cyclo-octa-tetraene acting as an  $8e$  ligand. (b) As a  $6e$  ligand. (c) As a  $4e$  ligand. (d) As a  $2 \times 4e$  ligand. (e) As an  $8e$  ligand to binuclear system. (f) As a  $2 \times 2e$  ligand, compare the cyclo-octa-1,5-diene complex (g). (h) As a  $4 \times 2e$  ligand.

It should be noted that there is no simple relationship between the number of electrons associated with a ligand and the coordination number of the ligand. For example, the halides  $BX_3$  are monodentate, zero-electron ligands; H, O and N atoms are monodentate but  $1e$ ,  $2e$  and  $3e$  ligands respectively; and  $BH_4$  may be a bidentate but  $1e$  ligand.

### 3.2. CHELATE LIGANDS

It is convenient to divide chelate ligands into two classes. Firstly, there are those ligands which may be regarded as multiples of monodentate ligands, the effect of which

on central atom orbitals is comparable with an equivalent number of analogous monodentate ligands. Examples are cyclo-octa-1,5-diene, a  $2 \times 2e$  ligand;  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , a  $2 \times 1e$  ligand; and  $\text{MeSCH}_2\text{CH}_2\text{S}-$ , a  $(2+1)e$  ligand.

The interaction of the second class of ligand with the central atom may not be divided up into the sum of parts but is best considered to result from the integration of the ligand as a whole. It is usually true that such ligands are conjugated. Examples of this class are butadiene as a  $4e$  ligand (not a  $2 \times 2e$ ), the acetylacetonato ligand as a  $3e$  ligand [not  $(1+2)e$ ] and the maleonitriledithiolato ligand as a  $2e$  ligand (not  $2 \times 1e$ ). Cyclo-octa-tetraene is a rare example of a ligand that can occur in both classes (Fig. 3).

In Table 2 only the second class of polydentate ligands is considered. In this table, apart from classification by electron numbers, a number of other ligand properties are described. These are:

- (i) Nature of ligand–central atom bonding.
- (ii) Tendency to form stable ions.
- (iii) Size.
- (iv) Stability properties and other comments.

#### (i) Nature of Ligand–Central Atom Bonding

By induction from general chemical trends we have drawn up estimates of the ability of ligands in Table 2 to donate and accept electrons. The ligand bonding has been divided into  $\sigma$ - and  $\pi$ -contributions since with many ligands, e.g.  $\text{M}-\text{CO}$ ,  $\text{M}-\text{C}_2\text{H}_4$ ,  $\text{M}-\text{Cl}$ , the bonding is commonly described in this manner. The values of  $\sigma$ -donor and  $\sigma$ -acceptor strength of a ligand are intended to indicate the possible *range* of the behavior of the ligand with different central atoms. For example, fluorine is described as ranging from a very weak  $\sigma$ -donor (in  $\text{F}_2$ ) to a very strong  $\sigma$ -acceptor (in  $\text{CH}_3\text{F}$ ), the methyl group as varying from a moderately strong  $\sigma$ -donor to a medium-weak  $\sigma$ -acceptor (in  $\text{CH}_3\text{H}$ ), and hydrogen as varying from a moderately strong  $\sigma$ -donor to a moderately strong  $\sigma$ -acceptor. This indicates, for example, that hydrogen is a very flexible ligand and can adapt itself to a wider range of central metal atom properties than the methyl or the fluorine ligand. It would not be expected, however, to reach the extreme position achieved by fluorine in, for example,  $\text{PtF}_6$ .

The description of  $\pi$ -acceptor and  $\pi$ -donor ability is not intended to indicate a range of properties but rather to indicate  $\pi$ -bonding effects which may occur simultaneously.

#### (ii) Tendency to Form Stable Ions

In this column the important overall tendency of the ligand to gain or lose electrons is emphasized, and in this sense the information given in the preceding column is partly duplicated. Attention is also drawn to the possibilities that the metal–ligand bonds may be very polar, or indeed largely ionic, as it is thought to be in  $\text{Mg}^{2+}(\text{C}_5\text{H}_5)_2^{2-}$ , for example, or, that ionic or highly polar bonds are likely to be found under very extreme circumstances, e.g. the sodium–benzene system.

#### (iii) Size

Steric factors sometimes provide the dominant reason for the stability or instability of a compound.

In Table 2 the size of a ligand is described in terms of a rather coarse scale varying

from very small through medium to very large. Some of the polydentate ligands are also classified by the description "compact". This is intended to indicate that the solid angle of the coordination sphere occupied by the ligand about the metal is small compared with that occupied by monodentate ligands which donate an equivalent number of electrons. For example, in order to achieve the 18e rule titanium requires fourteen electrons to be donated by ligands. Steric reasons certainly preclude the formation of 18e compounds using four 1e ligands and five 2e ligands, and with seven 2e ligands also it is likely that steric problems arise. The  $\pi\text{-C}_5\text{H}_5$  ligand is a compact ligand, however, so that an 18e compound can be achieved, e.g. in  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ .

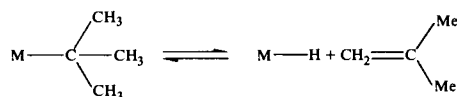
#### (iv) Stability Properties and Other Comments

Another important property of a ligand is its stability in any form in which it is likely to occur in the uncomplexed state. For example, halogen complexes are likely to dissociate by heterolytic fission giving halide ions and a metal complex cation. The halide ion is, of course, stable to further decomposition, and when it encounters the parent ion can re-form the original complex.

In contrast, dissociation of the methyl radical must lead either to an ion ( $\text{CH}_3^+$  or  $\text{CH}_3^-$ ) or to the radical. All these species will attack the solvent, dimerize, or otherwise decompose before recombination with the metal centre is possible. Ligands like the methyl group are classified as "unstable in the free state".

It is largely for the above reasons that methyl derivatives are most commonly found in closed shell and *other kinetically inert* environments such as occur with the 8e, 18e, and square-planar 16e metal complexes and octahedral  $d^3$  chromium compounds. There is no reason to believe that strength of transition-metal carbon  $\sigma$ -bonds are more variable than the strengths of metal-chlorine bonds.

Ligands which are reactive in the coordinate state are mentioned separately, e.g. *t*-butyl complexes tend to decompose giving the corresponding metal-hydride.



Other information given in this column includes the pseudo-coordination number of those ligands which are not obviously *n*-dentate; whether a ligand is unusual in some respect; whether a ligand is representative of a large class or is rare.

## 4. GENERAL TRENDS IN THE CHEMISTRY OF THE MAIN GROUP ELEMENTS<sup>2</sup>

### 4.1. ATOMIC PROPERTIES

The elements of the main groups of the Periodic Table contain *ns* and *np* orbitals in their *valence* shells (where  $n=2-7$ ). Across any one Period there is a general increase in ionization potential, so that whereas the compounds of the alkali metals, especially with electronegative ligands such as the halogens, are largely ionic in character, those of the non-metallic and metalloid elements of Groups VI and VII are essentially covalent.

<sup>2</sup> G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 1, Methuen, London, 3rd edn. (1967).



In the compounds of main group elements there is a strong tendency for full use to be made of all the available *ns* and *np* valence orbitals. This leads in many cases to an octet of electrons around the central atom being favoured (8e rule). This situation may be compared with the 18e rule found in transition metal chemistry. Exceptions to the octet rule will be discussed in terms of central atom and ligand properties, and some possible reasons for these deviations suggested.

## 4.2. IONIC COMPOUNDS

The most electropositive elements, especially the alkali metals and the alkaline earths (apart in general from Be, see Chapter 9), show a strong tendency to form cations (formally zero electron ions) on account of their rather low ionization potentials. This tendency increases as one descends a Group as the ionization potential decreases, although one must bear in mind the concomitant decrease of lattice energy and solvation energy as the size of the metal ion increases. With strongly electronegative ligands such as the halogens, oxide, hydroxide, etc., which also tend to form negative ions (Table 2), the compounds of these metals may be regarded as essentially ionic in character. Complexes with  $\sigma$ -donor ligands such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc., also involve interactions primarily of an ion-dipole nature. In  $\text{Na}^+(\text{H}_2\text{O})_6$ , for example, the ligands are labile, and the coordination sphere is continually varying. The coordination number is thus determined essentially by size rather than by the number of available orbitals on the metal.

With less electronegative ligands such as H, or organic groups such as methyl, phenyl, 2,2'-bipy,  $\text{PhCH}_2$ , or  $\text{C}_5\text{H}_5$ , compounds of predominantly ionic character are less readily formed. They do occur when a negative charge on the anion can be stabilized. For unsaturated organic systems this may often be achieved by delocalization of the charge over several carbon atoms. A particularly good example is the  $\text{C}_5\text{H}_5$  group, for which the ion  $\text{C}_5\text{H}_5^-$  possesses aromatic character. Thus the cyclopentadienides of the alkali metals and of the alkaline earths Mg, Ca, Sr and Ba are considered to have a high degree of ionic character. Structural considerations for determining ionic bonding are insufficient; magnesium bis-cyclopentadienide has a symmetrical sandwich structure which is consistent with an ionic formulation, but which is similar to that of ferrocene which is predominantly covalent.

Other examples of delocalization of negative charge over an organic group occur in sodium acetylacetonate, the bipyridyl, and *o*-phenanthroline complexes of alkali metals and alkaline earths, e.g.  $\text{Be} \cdot \text{bipy}_2$ , and in the compounds formed by alkali metals with aromatic hydrocarbons in ether solvents such as THF. In the last an electron is donated from the metal atom into an antibonding orbital of the hydrocarbon. The deeply coloured solutions which result are paramagnetic and contain solvated alkali metal ions and hydrocarbon anions, e.g.  $\text{Na}^+(\text{S})_n$ ,  $\text{C}_{10}\text{H}_8^-$ . These solutions are strongly reducing, behaving like alkali metal—ammonia, or alkali metal—ether solutions. The ligand in all these cases is a poor or medium acceptor of electrons, and such compounds are therefore formed only where the metal atom loses electrons particularly easily.

Where the ionization potential sum of the valence electrons is higher (as with Be, B) or where the ligands form ions less readily, covalence becomes an important feature of the bonding. In neutral covalent compounds of the elements of Groups I, II and III, there are insufficient electrons on the central atom to achieve an octet of electrons with

le ligands. In monomeric complexes of such ligands only, therefore, the electron environment of the central atom must be restricted to 2, 4 and 6 respectively. Such compounds, however, often show a strong tendency to achieve an octet configuration by acting as Lewis acids, i.e. by accepting electron pairs from 2e donor ligands as in  $\text{H}_3\text{N}\cdot\text{BF}_3$  or  $\text{BH}_4^-$ . Similarly, bridging ligands such as  $-\text{NR}_2$ ,  $-\text{OR}$ , or halogen, which possess lone pairs of electrons, often donate these lone pairs as in  $(\text{Me}_2\text{N}\cdot\text{BCl}_2)_n$  and  $(\text{BeCl}_2)_n$ . In the latter compound the binding chloro ligand is acting as a 3e ligand to two beryllium atoms.

Another factor which influences the type of bonding and also the stability of complexes is the charge : radius ratio of the metal ion. Where this is high (as in  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ) and the anion is fairly polarizable, distortion of the electron cloud of the anion can occur. In other words there is covalency in the bonding or, where there is a suitable route for anion

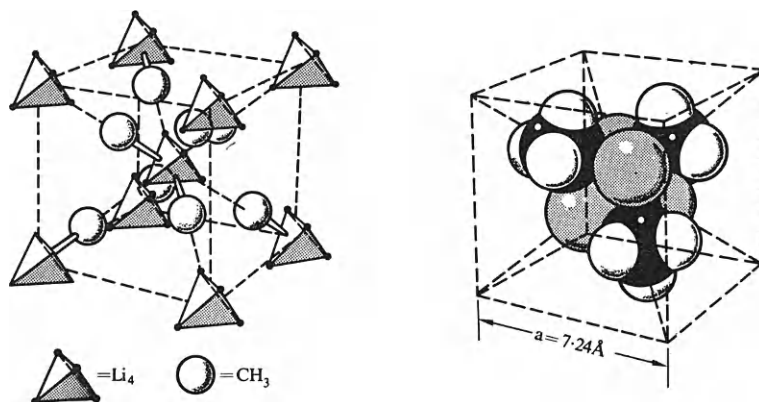


FIG. 4. Unit cell of methyllithium. The  $(\text{CH}_3\text{Li})_4$  tetramer. (After E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.* **2** (1964) 197.) Reprinted by courtesy of Elsevier Publishing Company, Amsterdam.

decomposition, destruction of the complex. An example of the latter is the instability of  $\text{BeCO}_3$  or of  $\text{Li}_2\text{O}_2$ , owing to the considerable gain in lattice energy, to form  $\text{BeO}$  or  $\text{Li}_2\text{O}$  respectively. The high kinetic stability of organic groups, however, enables them to persist in situations where other groups, such as  $\text{SiH}_3$ , might decompose.

#### 4.3. BRIDGE BONDING

The structures of many of the hydrides, alkyls and aryls of the elements of Groups IA to IIIA illustrate another way in which full use of the available valence orbitals is achieved, although the metal atom does not attain an octet configuration.

Many of these compounds form oligomers or polymers in which the ligand bridges two or more metal atoms. In such compounds the bonding is best described in terms of multicentre molecular orbitals rather than by the ionic model. Thus methyllithium<sup>3</sup> (Fig. 4) and methylsodium exist as tetrameric units in the solid state. (Methylpotassium, however, crystallizes with the nickel arsenide structure, thus showing more ionic character, in agreement with the lower ionization potential and larger size of the  $\text{K}^+$  ion compared with  $\text{Na}^+$ .) The high melting point and insolubility of methyllithium in organic solvents

<sup>3</sup> E. Weiss and E. A. C. Lucken, *J. Organometallic Chem.* **2** (1964) 197.

which are normally characteristic of an ionic lattice are explained by interactions between neighbouring tetramer units.

Bridging alkyl groups are generally present in the alkyls of Be, Mg and Al. The structures of  $(\text{Me}_2\text{Be})_n$ <sup>4</sup> and  $(\text{Me}_3\text{Al})_2$ <sup>5</sup> are illustrated in Figs. 5 and 6.

Steric effects are important *inter alia* in determining the degree of polymerization in such compounds. Thus  $\text{Me}_2\text{Be}$  exists as long chain polymer at ordinary temperatures, whereas the association of monomeric  $\text{Bu}_2\text{Be}$  is prevented by the bulky tert-butyl groups. In agreement with the greater size of the magnesium atom compared with the beryllium

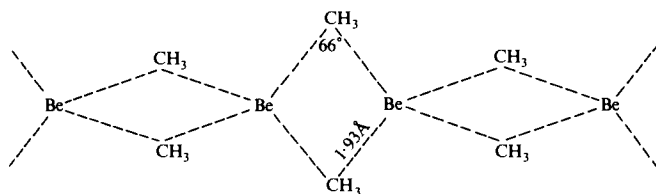


FIG. 5. Structure of dimethylberyllium.

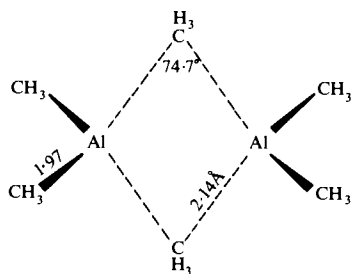


FIG. 6. The trimethylaluminium dimer.

atom, the degree of polymerization of organomagnesium compounds is the greater. The interaction between the methylene groups of one bridge and the methyl groups of the adjacent bridge in diethylberyllium prevents polymerization. Similarly, whereas the small hydrogen atoms are able to act as bridging groups between two boron atoms in diborane, alkyl and aryl groups are too large, and their boron derivatives are all monomeric.

In understanding the occurrence of structural types in the organic compounds of the elements of Groups II and III one should remember that the dissociation energies of dimers to monomers (or polymers to oligomers or monomers) are rather small (for trimethylaluminium only about 10 kcal/bridge bond). This tends to explain the otherwise apparently random variations observed on going from one element to another or from one organic group to another. Phenyl groups are slightly better bridging groups than methyl for aluminium.<sup>6</sup> Trimethylgallium is monomeric although trivinylgallium is dimeric at room

<sup>4</sup> A. I. Snow and R. E. Rundle, *Acta Cryst.* **4** (1951) 348.

<sup>5</sup> P. H. Lewis and R. E. Rundle, *J. Chem. Phys.* **21** (1953) 986.

<sup>6</sup> E. A. Jeffrey, T. Mole and J. K. Saunders, *Chem. Commun.* (1967) 696.

temperature. In the crystal, trimethylindium<sup>7</sup> and trimethylthallium<sup>8</sup> form weakly bonded tetrameric units in which, however, the planar arrangement of the  $C_3M$  skeleton is preserved. The last two compounds are monomeric, however, in the vapour and in benzene solution. The activation energy for exchange of methyl groups through a bridged intermediate or transition state in trimethylthallium is only about 6 kcal/mole.

The lower tendency of organic groups to bridge between the Group IIIB metal atoms compared with aluminium is (as with Mg and Zn, Cd and Hg) presumably associated with two factors. Firstly, the  $s/p$  gap in Ga, In, and especially Tl, is increased, and there will thus be less tendency to make use of all the  $p$ -orbitals. Secondly, as the size of the metal atom increases, bridging by organic groups will become less favourable; the size factor is probably most suitable for Mg and Al.

The alkyls and aryls of Groups I, II and III are strong Lewis acids. Bridging through organic groups can often be broken by Lewis bases such as amines or ethers. In this way full use of the metal valence orbitals is maintained, while an octet environment is

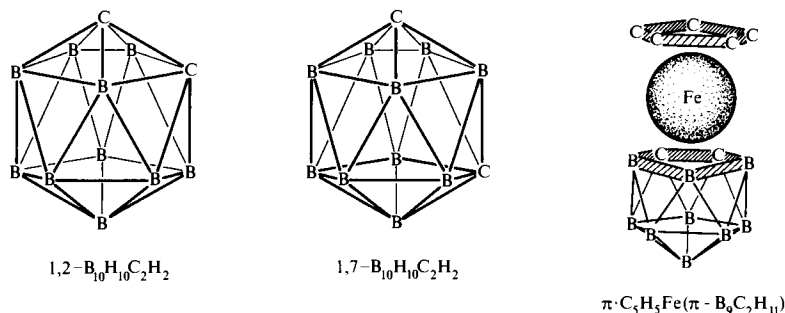


FIG. 7. Structures of 1,2- and 1,7-dicarbavododecaborane and of a related metal complex (hydrogen atoms omitted).

attained in the adduct. The products in such reactions reflect the preferences of the central atom for different types of ligand. These elements behave as class a acceptors, preferring donor atoms of the first row elements (i.e. N, O, F). Sulphur and phosphorus donors generally form much weaker complexes, and are displaced by oxygen or nitrogen donors. (Cf. ready hydrolysis of phosphides and sulphides of these elements especially of Be, Mg and Al.) These stability relationships depend, in part, on  $\sigma$ -donor power (a-class) rather than  $\pi$ -properties as well (b-class).

#### 4.4. CLUSTER COMPOUNDS

The strong tendency of these elements to make use of all their available valence orbitals in essentially covalent derivatives also leads to the formation of cluster compounds such as the polynuclear boron hydrides (cf. lithium methyl). The bonding in such compounds is also best described in terms of multicentre molecular orbitals, some of which involve all and some part of the framework. Other atoms than boron, which possess similar bonding characteristics, but which are unable through sufficiency of electrons (e.g. C) or the inability to form three-dimensional networks (e.g. Be with only two valency electrons) can often be incorporated into boron hydride structures. The most important class of such compounds

<sup>7</sup> E. L. Amma and R. E. Rundle, *J. Am. Chem. Soc.* **80** (1958) 4141.

<sup>8</sup> G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A* (1970) 28.

is the carboranes<sup>9</sup>. Particular features of these compounds are the often highly symmetrical structures of the cages, and their resistances to oxidation, hydrolysis and thermal decomposition. This kinetic stability allows the skeleton to be preserved throughout a wide range of chemical reactions, in a similar way to hydrocarbon groups. Most known carboranes belong to a series of general formula  $B_nC_2H_{n+2}$  ( $n=3-10$ ). The structures of some examples are illustrated in Fig. 7.

In addition to the cage compounds present in the boron hydrides and carboranes, boron forms other cluster compounds. Elemental boron contains  $B_{12}$  icosahedra, and similar clusters of boron atoms are found in metal borides (e.g.  $B_6$  in calcium boride). In a somewhat similar way, chains of carbon atoms are present in  $Cr_3C_2$ , and chains and sheets of silicon atoms in various metal silicides. Such compounds can be understood as being intermediate between metals (band model) and either covalent (bond) or ionic compounds. Certain boron halides, e.g.  $B_4Cl_4$  and  $B_8Cl_8$ , which contain clusters of boron atoms are also known, and may be compared to cluster compounds formed by the elements early in the three *d*-block transition series, i.e. those elements with less than a half-filled valence shell; examples are  $Mo_6Cl_8^{4+}$ ,  $[(Me_6C_6)_3Ti_3Cl_6]^+Cl^-$ .

#### 4.5. EXPANSION OF OCTET

The elements of Groups IV–VII form a wide range of derivatives in which the central atom possesses an 8e environment (e.g.  $CX_4$ ,  $NX_3$ ,  $OX_2$ ,  $FX$ ). Typical of these are the compounds of carbon, which are extraordinarily kinetically stable and of considerable variety. In addition to forming four covalent 2e bonds with 1e ligands, carbon is able to form strong formal double and triple bonds either to itself or to other elements (e.g. N, O, S) of the First and in some cases Second Short Periods.

As one descends Groups IVB–VIIB one notices several trends, the effect of which is to differentiate the chemistry of the first-row elements from those of the later rows. Although the 8e environment of the central atom is still a very common one, the possibility arises of the formation of formally 10e, 12e, or even 14e compounds. This occurs especially where strongly electron attracting ligands such as F and O are present. Such compounds are exemplified by the series  $PF_5$ ,  $SF_4$ ,  $ClF_3$ ,  $XeF_2$  (10e compounds),  $SiF_6^-$ ,  $PF_6^-$ ,  $SF_6$ ,  $IF_5$ ,  $XeF_4$  (12e) and  $TeCl_6^-$ ,  $IF_7$ ,  $XeF_6$  (14e). This tendency to expand the octet, especially in anions such as  $SnCl_6^-$  and  $SnBr_6^-$ , extends to less electronegative ligands such as the heavier halogens for elements later in the Groups and 1e carbon and 1e nitrogen ligands. Maximum covalence in many elements is found not only with oxygen and fluorine ligands but with ligands such as hydrogen, methyl, phenyl, dimethylamino, methoxy; examples are  $Ph_5P$ ,  $Me_3AsCl_2$ ,  $W(NMe_2)_6$  and  $(R_3P)_2WH_6$ . This observation suggests that hydrogen and 1e ligands of first-row elements may form especially strong bonds compared with heavier congeners. A mixture of  $\sigma$ -donor and  $\sigma$ -acceptor ligands as in  $Me_3SnCl \cdot py$ ,  $Me_3PCl_2$  (and even organic groups only as in  $Ph_5P$  and  $Me_5Sb$ ) can also have a similar effect.

It appears that the ability of ligands to form the highest valency of a central atom occurs in the order



The high kinetic stability associated with an 8e spherically symmetrical environment which is observed in saturated hydrocarbons has its counterpart in the inertness of the tetraalkyls and tetraaryls of Si, Ge, Sn and Pb to hydrolysis and to oxidation. Where

<sup>9</sup> E. L. Muetterties and W. H. Knoch, *Polyhedral Boranes*, Edward Arnold and Marcel Dekker, London and New York (1968).

electron attracting groups, e.g. Cl, OMe, are present, hydrolytic stability is reduced; this is often associated with the lowering in energy of empty orbitals ( $3d$ ,  $4s$  in silicon) and the greater polarity of the M-X bonds (contrast the ease of hydrolysis of  $\text{CCl}_4$  and  $\text{SiCl}_4$  although the former reaction is thermodynamically the more favoured). Fragments such as  $\text{Me}_3\text{Sn}$  and  $\text{Ph}_3\text{Si}$ , however, exhibit considerable stability and persist unchanged in many reactions, so that reactions at the metal centre may be studied in compounds such as  $\text{Me}_3\text{Sn}\cdot\text{NMe}_2$ .

The expansion of the octet when a B-group element is coordinated by electron withdrawing ligands may well be due to an increase in participation in the valence band of  $nd$  orbitals although to what extent it is difficult to assess precisely<sup>10</sup>. The energy of the  $nd$  orbitals will be lowered with increasing positive charge on the central atom. This effect would be expected to be most significant in B-elements following the transition series where the  $nd$  orbitals,  $n=4$ , 5, or 6, are better able to penetrate towards the nucleus than the  $3d$ , and hence come under the influence of an enhanced positive charge. This could explain the greater variety of compounds showing octet expansion in the B-elements in this region of the Periodic Table, as compared with the elements Si to Cl, which, in general, show such expansion only with strongly  $\sigma$ -bonding ligands such as Ph, O, F and Cl. Table 3 shows electron numbers in some typical compounds of tin.

#### 4.6. OCCURRENCE OF FORMAL DOUBLE AND SINGLE BONDS

Other evidence for the participation of  $nd$  orbitals in the bonding comes from structural and bond energy considerations. Unlike carbon, the later elements of Group IVB show a very weak tendency to form formal double or triple bonds to themselves or to other elements (e.g. the first Short Period elements C, N or O). Examples of this are the non-existence of silicon analogues of benzene and the structures of silica (giant covalent lattice) and carbon dioxide (monomeric gas).  $np\pi-2p\pi$  overlap is thought to be weak except where  $n=2$ . Silicon, and to a lesser extent germanium and tin, form very strong bonds to fluorine, oxygen and nitrogen which are formally single (as in  $\text{SiF}_4$ , silicates and silicones). These ligands are not only  $\sigma$ -acceptors but also act as  $\pi$ -donors into empty  $d$ -orbitals on silicon. The wider bond angles in  $(\text{H}_3\text{Si})_3\text{N}$  ( $\text{SiNSi}=120^\circ$ ) and  $(\text{H}_3\text{Si})_2\text{O}$  ( $\text{SiOSi}=144^\circ$ ) compared with their carbon analogues have also been cited as evidence for  $p\pi-d\pi$  overlap in the former compounds.

The expansion of the octet for B-element derivatives in which electron attracting ligands are present may be contrasted with the low electron numbers for transition metal compounds containing such ligands. In the former case the high lying  $nd$  orbitals are brought down in energy into the valence band, making them available for bonding. In the latter, however, the presence of an increased positive charge on the metal atom may well have the effect of removing some of the valence orbitals [ $ns$ ,  $np$  or  $(n-1)d$ ] into the core.

<sup>10</sup> The bonding in compounds of these elements in which octet expansion has apparently occurred and which we have explained in terms of the participation of  $nd$  orbitals of the central atom can also be described in terms of molecular orbitals derived solely from  $ns$  and  $np$  atomic orbitals. We have adopted the approach we have because, in the light of available evidence, we believe that  $nd$  orbital participation may be significant, and its assumption leads to a consistent description of the chemistry of such compounds, and a basis for comparison with transition metal chemistry.

## 4.7. INERT PAIR EFFECT—OCCURRENCE OF GROUP-2 VALENCE

One consequence of the increase in nuclear charge across the transition series when the  $(n-1)d$  orbitals are being filled, is that the  $ns/np$  gap in post-transition elements is greater than in the elements immediately preceding the transition series on account of the greater stabilization of  $ns$  electrons compared with  $np$  on increase of nuclear charge. This effect is especially pronounced in the last row of the Periodic Table (i.e. Hg, Tl, Pb, etc.) there being an increase of +32 in nuclear charge between it and the elements of the previous row (Cd, In, etc.). To this increase in the  $s/p$  gap is often attributed the "inert pair effect", which causes the N-2 valence state to be preferred over the N valence state in certain compounds.

TABLE 3. ELECTRON NUMBERS IN TIN COMPOUNDS

	Compound	No. of electrons from metal and charge	No. of electrons from ligands	Total
Increasing partial positive charge on metal; also increasing tendency to complex with neutral 2e ligands ↓	$R_3Sn \begin{pmatrix} R \\   \\ -Sn- \\   \\ R \end{pmatrix}_n SnR_3$	4	$4 \times 1$	8
	$H_4Sn$	4	$4 \times 1$	8
	$Me_4Sn$	4	$4 \times 1$	8
	$Ph_4Sn$	4	$4 \times 1$	8
	$Sn(SR)_4$	4	$4 \times 1$	8
	$Sn(NMe_2)_4$	4	$4 \times 1$	8
	$SnCl_2$ , i.e. $Cl \searrow \begin{pmatrix} Cl \\   \\ -Sn- \\   \\ Cl \end{pmatrix}_n \nearrow Cl$	4	$1+3$	8
	$SnCl_2 \cdot py$	4	$2 \times 1 + 2$	8
	$SnCl_3^-$	5	$3 \times 1$	8
	$Me_3SnCl$	4	$4 \times 1$	8
	$(Me_3SnF)_n$ bridging F atoms	4	$3 \times 1 + 3$	10
	$SnO$ (see Fig. 8)	4	$2 \times 1 + 2 \times 2$	10
	$Me_3SnCl \cdot py$	4	$4 \times 1 + 2$	10
	$Me_2SnCl_2 \cdot 2py$	4	$4 \times 1 + 2 \times 2$	12
	$(Me_2SnF_2)_n$ bridging F	4	$2 \times 1 + 2 \times 3$	12

In N-2 valence compounds it is considered that the  $ns^2$  pair of electrons do not contribute significantly to the bonding on account of their special stability. Sometimes, as in the  $Tl^+$  and  $Sn^{2+}$  ions, these electrons are not removed on ionization, and in certain cases they are not stereochemically active, i.e. the pair of electrons is spherically symmetrical about the metal atom. However, as is shown by the structures of  $SnO$  or  $PbO$ , they may be directed to some extent away from the metal atom in a definite direction, which indicates that they can possess some  $p$  orbital character.

Consideration of the table of ligands and also Table 3 shows that N-2 valence compounds (e.g.  $Sn^{II}$ ) arise when the ligands have a good ability to form stable ions, e.g. the halogens, oxide, sulphide, cyclopentadienyl. Most of these ligands form Group valence compounds as well with tin, e.g.  $SnCl_4$ ,  $SnO_2$ , but other ligands which do not form ions so readily and which have some  $\sigma$ - (e.g. H, alkyl, aryl) or  $\pi$ - (e.g.  $NMe_2$ ) donor properties form no compounds of the N-2 valence state, but only of the Group valence state. Apart from  $SnF_4$  (the fluoride ligand readily forms a stable ion and is also a very strong  $\sigma$ -acceptor) and  $SnO_2$  (the oxide ion is also fairly readily formed, and with it some  $\pi$ -back donation

to the metal is possible, reducing the charge separation between Sn and O), the Group valence compounds of tin, e.g.  $\text{SnCl}_4$ ,  $\text{SnH}_4$ ,  $\text{Me}_4\text{Sn}$ ,  $\text{Sn}(\text{NMe}_2)_4$  and  $\text{Sn}(\text{SR})_4$ , are essentially covalent in character in accordance with the Pauling electro-neutrality principle.

The so-called "dialkyl" and "diaryl" tin derivatives have been shown to contain tin-tin bonds, and to have cyclic [e.g.  $(\text{Ph}_2\text{Sn})_6$ ] or polymeric structures in which each tin atom is 4-coordinate and has a typical 8e configuration. The cyclopentadienide  $(\text{C}_5\text{H}_5)_2\text{Sn}$  is possibly an exception and may well contain divalent tin.

In Table 3 a number of common tin compounds are listed together with the formal

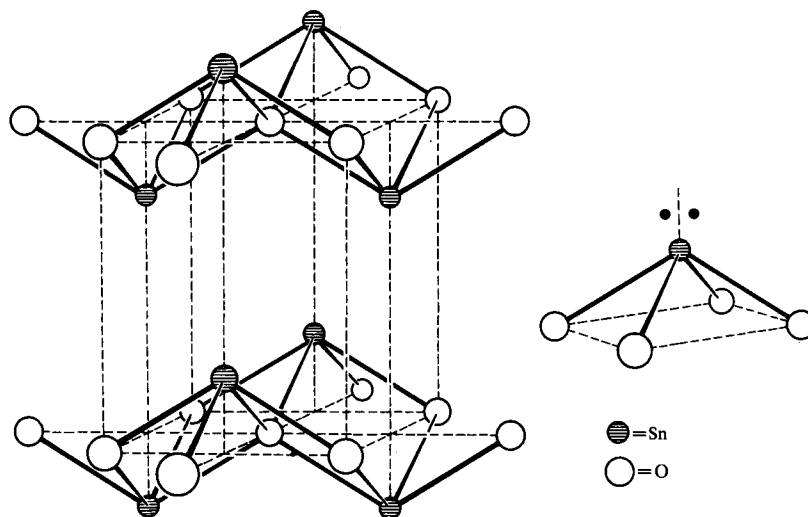


FIG. 8. The structure of tetragonal  $\text{SnO}$ . (After Wells, *Structural Inorganic Chemistry*, O.U.P.) (See Phillips and Williams, ref. 14, Vol. 2, p. 492.) (Reprinted by Courtesy of the Clarendon Press, Oxford.)

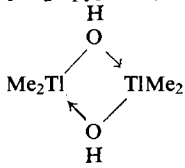
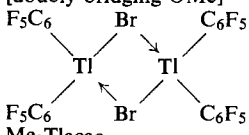
electron configuration of the tin atom in each case. It will be seen that in many of these, including some which are classified normally as derivatives of  $\text{Sn}(\text{II})$ , e.g.  $\text{SnCl}_3^-$ , the tin atom has the common 8e environment. The same seems to apply to  $\text{SnCl}_2$  itself, for which the structure consists of chain polymers  $(\text{SnCl}_2)_n$  involving 3-coordinate tin.  $\text{SnCl}_2$  is soluble in donor solvents such as ethers and forms complexes  $\text{SnCl}_2 \cdot \text{L}$  and  $\text{SnCl}_2 \cdot \text{L}_2$  (where  $\text{L} = \text{H}_2\text{O}$ , py, thiourea) in which the tin atom attains an 8e or a 10e environment respectively. In  $\text{SnO}$  (or  $\text{PbO}$ ), if a bond model is assumed in counting the electrons, the tin atom would have a 10e environment (Fig. 8).

Table 4 shows the electron count about the metal atom in some thallium compounds. As noted above, ligands such as  $\text{Cl}$ ,  $\text{C}_5\text{H}_5$  form compounds with considerable ionic character, derived from the  $\text{Tl}^+$  ion. When the ligand has strong bridging tendencies, e.g.  $\text{OMe}$ , oligomeric or polymeric structures result in which the metal atom formally has an 8e environment, e.g.  $(\text{TlOMe})_4$ . No monoalkyls or monoaryls of thallium are known. Attempts to prepare them lead to disproportionation to  $\text{R}_3\text{Tl}$  and thallium metal. The property of the  $\text{R}_2\text{Tl}^+$  group to attain an octet of electrons is very much stronger than for the isoelectronic  $\text{R}_2\text{Hg}$  on account of the positive charge on the former, and this is exemplified by  $\text{Me}_2\text{Tl}(\text{acac})$  and  $\text{R}_2\text{Tl}(\text{o-phen})^+\text{ClO}_4^-$ .



To summarize, with most ligands the Group valence state is the normal one for Groups II, III and IV, and leads to electron counts of 4, 6 and 8 respectively in monomeric com-

TABLE 4. ELECTRON NUMBERS IN THALLIUM COMPOUNDS

	Compound	No. of electrons from metal and charge	No. of electrons from ligands	Total
Increasing partial positive charge on metal: increasing tendency to complex with neutral 2e ligands	$\text{Me}_3\text{Tl}$	3	$3 \times 1$	6
	$\text{Ph}_3\text{Tl}$	3	$3 \times 1$	6
	$(\text{C}_5\text{H}_5^-)\text{Tl}^+$	2 (3)	0 (5)	2 (8 covalent)
	$\text{Tl}^+\text{Cl}^-$	2 (3)	0 (1)	2 (4 covalent)
	$[\text{Me}_2\text{Tlpy}]^+\text{ClO}_4^-$	2	$2 \times 1 + 2$	6
		3	$2 \times 1 + 3$	8
	$(\text{MeTlOMe})_4$ [doubly bridging OMe]	3	$1 + 2 \times 2$	8
		3	$2 \times 1 + 3$	8
	$\text{F}_5\text{C}_6$ $\text{Me}_2\text{Tl}(\text{acac})$	3	$2 \times 1 + 3$	8
	$[\text{Me}_2\text{Tlbipy}]^+\text{ClO}_4^-$	2	$2 \times 1 + 4$	8
	$\text{TlCl}_6^{3-}$	6	$6 \times 1$	12

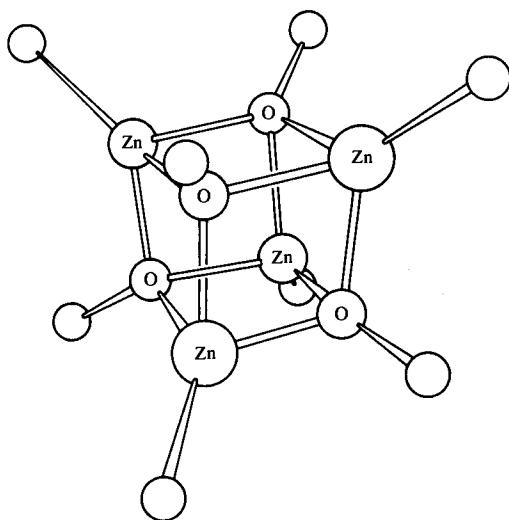


FIG. 9. Crystal structure of methylzinc methoxide tetramer. (After H. M. M. Shearer and C. B. Spencer, ref. 11.)

plexes with 1e ligands. As noted for the pre-transition elements, 4e and 6e compounds tend to accept electrons from Lewis bases (e.g. py) or bridging groups (e.g. halogens, OMe)

to attain an octet configuration. Where the  $s/p$  gap is largest (as in Hg) the Lewis acidity is relatively low (e.g.  $\text{Me}_2\text{Hg}$  has little or no tendency to complex with Lewis bases, and  $\text{MeHgCl}$  is monomeric, whereas  $\text{R}_2\text{Zn}$  forms complexes such as  $\text{R}_2\text{Zn}\cdot\text{bipy}$ ) and  $\text{RZnCl}$  and  $\text{MeZnOMe}^{11}$  are associated with a tetrameric cubane structure in the crystalline state (Fig. 9). Expansion of the octet becomes increasingly favoured as one goes across any period, especially where electron attracting ligands are present.

#### 4.8. a- AND b- CHARACTER: POLARIZABILITIES

As one descends any group of the Periodic Table, the polarizabilities of the atoms increase, and this increase is especially significant for the elements late in the transition series and for those immediately following. These elements are classified as class b acceptors, that is they prefer to bond to ligand atoms of the second and third rows of the Periodic Table (e.g. P, As, S, Se) rather than to those of the first row (N, O, F). In addition to the polarizability effect, the relative sizes of the overlapping orbitals are clearly also significant, being more compatible with good overlap when they are comparable than when very different in size. For  $d$ -block transition elements (and possibly for elements such as Hg and Tl in which the  $(n-1)d$  electrons have hardly entered the core)  $\pi$ -donor-acceptor interaction between filled metal and empty ligand orbitals is also important. Thus Hg, Tl, Sn, Pb, etc., form strong complexes with ligands such as  $\text{S}^{=}$ ,  $\text{SR}^-$ , which are generally stable to hydrolysis by water, in contrast to the alkoxides which are very readily hydrolysed. These elements also form rather stable complexes with transition elements which contain metal-metal bonds, e.g.  $\text{R}_3\text{SnMn}(\text{CO})_5$  and  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ . It is also possible that groups such as  $\text{Cl}_3\text{Sn}$  can act as weak  $\pi$ -acceptors through the  $d$ -orbitals on the metal atom. These transition metal ligand groups resemble sulphur and phosphorus donors in that they possess polarizable metal centres.

#### 4.9. INTERACTION OF MAIN GROUP ELEMENTS WITH $\pi$ -ACCEPTOR LIGANDS

In general the main group elements and their derivatives show little or no tendency to enter into  $\pi$ -bonding with unsaturated ligands such as  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{C}_2\text{H}_4$  which form strong complexes with transition elements. Weak complexes such as  $\text{BH}_3\cdot\text{CO}$  and  $\text{BH}_3\cdot\text{PF}_3$  are known, but, again, these probably involve little or no  $\pi$ -component in the bonding. Infrared studies have indicated a weak interaction of an olefinic group and aluminium in *cis*-hex-4-enyl-di-*iso*-butylaluminium, owing to weak  $\pi$ -donation to the metal from the  $\pi$ -bonding orbitals of the olefin<sup>12</sup>. It is possible that such weak interactions are significant in the reactions of olefins with Al-H, Al-R and B-H groups.

It therefore seems that a criterion for effective  $\pi$ -bonding between unsaturated systems and a metal centre is the presence of  $(n-1)d$  [and possibly as for uranium  $(n-2)f$ ] electrons in the valence shell.

<sup>11</sup> H. M. M. Shearer and C. B. Spencer, *Chem. Commun.* (1966) 194.

<sup>12</sup> Go Hata, *Chem. Commun.* (1968) 7.

## 5. GENERAL TRENDS IN THE CHEMISTRY OF THE *d*-BLOCK TRANSITION METALS<sup>13</sup>

### 5.1. ATOMIC PROPERTIES AND SOME CONSEQUENCES

The *d*-block transition metals normally contain the  $(n-1)d$ ,  $ns$  and  $np$  orbitals in their valence shells, where  $n=4, 5$ , or  $6$ . There is an increase in the ionization potential across all three series, as shown in the binding energy diagram (Fig. 10). Figure 10 also shows there is an increasing separation between the  $4s$  and  $4p$  orbitals, which becomes quite large towards the end of the series.

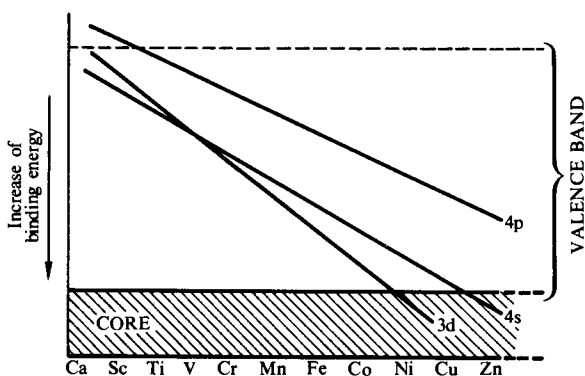


FIG. 10. The change in energy of the  $3d$ ,  $4s$  and  $4p$  orbitals of the first transition series. (After Phillips and Williams<sup>14</sup>). (Reprinted by courtesy of the Clarendon Press, Oxford.)

Another important trend is the decrease in the sum of the ionization potentials of the valence electrons down subgroups. The decrease is not regular and there is a greater change between the first and second series than between the second and third series due to the neutralizing effect of the lanthanide  $4f$  core electrons in the third series.

The chemical consequences of these trends in atomic ionization potentials are more marked in complexes with electronegative ligands such as the halogens than with neutral or donor ligands. This is because the electronegative  $1e$  ligands are tending to pull the valence electrons away from the central atom. For example, the chemistry of the metals with carbon monoxide and other donor-acceptor ligands appears to be controlled largely by electron numbers, e.g. the  $18e$  rule, rather than by variation in orbital energies. Also, relatively slight changes are observed within subgroups so that the first row complexes  $\text{Cr}(\text{CO})_6$ ,  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ ,  $(\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2)_2$  and  $(\text{Ph}_3\text{P})_4\text{Ni}$  all show close analogy with their heavier congeners. Contrast the binary halide derivatives of the transition metals which show two clear trends. Firstly, across a given series there is a decreasing tendency to obey the maximum group valence. Secondly, down a subgroup there is an increased tendency to achieve the maximum valence. For example, the maximum group valence

<sup>13</sup> G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 2, Methuen, London, 3rd edn. (1968).

<sup>14</sup> C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, O.U.P. (1965).

of  $MX_n$  is 4, 5, 6 and 7 for Ti, V, Cr and Mn respectively, but for V, Cr and Mn and  $X=Cl$ , maximum values of  $n=4$ , 3 and 3 only are observed. Similarly, when  $M=Cr$ , Mo, or W, then the maximum value of  $n$  is 3, 6 and 6 respectively.

It is thought that these two trends may largely be associated with the trends in ionization potentials, in so far as an increase in ionization potential implies that the electrons are being more drawn towards the core and thus becoming more unsuitable for bonding to  $\sigma$ -acceptor ligands.

## 5.2. TRENDS IN ELECTRON NUMBERS

Ligands in Table 2 may be divided into those which are largely electron attracting (oxidizing ligands), those which are strongly electron donating (reducing ligands), and those which do not cause more than a small increase or decrease in the electron density associated with the central atom (donor-acceptor ligands). It is found that classification by electron numbers leads to three classes:

- Complexes in which the metal is bound by donor-acceptor ligands or by combinations of donor and acceptor ligands. These show a marked tendency to obey the 18e rule.
- With basic  $\sigma$ -donor ligands, electro-neutrality of the central atom is achieved by loss of electrons from the metal and complexes with these ligands are usually cationic. Electron numbers in these complexes vary widely, normally within the range 14 and 20e.
- With strongly electronegative ligands any neutral molecules formed have relatively low electron numbers and are strongly electron attracting as a result. They may accept electrons forming anions, or add donor ligands.

Examples of these three classes are shown in Table 5. The table also shows the obvious point that electron numbers are greater with the complexes of the later metals within

TABLE 5. SOME EFFECTS OF LIGAND PROPERTIES ON TRENDS IN ELECTRON NUMBERS OF TRANSITION METALS COMPLEXES

Increasing $\sigma$ -acceptor ←				Mixed $\sigma$ - and $\pi$ -donor-acceptor ←		Increasing $\sigma$ -donor →	
9 VCl <sub>4</sub>	10 VOCl <sub>3</sub>	12 VF <sub>6</sub> <sup>-</sup>	13 VO(acac) <sub>2</sub>	17 ( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> VCl <sub>2</sub> [V(dipy) <sub>3</sub> ]	18 [C <sub>6</sub> H <sub>6</sub> V(CO) <sub>4</sub> ] <sup>+</sup> [V(CO) <sub>6</sub> ] <sup>-</sup>	14 [V(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	
12 MoCl <sub>6</sub>	13 MoCl <sub>5</sub> - $\mu$ -Cl	15 [MoCl <sub>6</sub> ] <sup>3-</sup>		17 [( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> MoCl <sub>2</sub> ] <sup>+</sup> [(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> Mo] <sup>+</sup>	18 $\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> Cl Mo(CO) <sub>6</sub> Mo(P-P) <sub>2</sub> (N <sub>2</sub> ) <sub>2</sub> Mo(NH <sub>3</sub> ) <sub>3</sub> (CO) <sub>3</sub>	15 [(NH <sub>3</sub> ) <sub>6</sub> Mo] <sup>3+</sup>	
		15 [CoCl <sub>4</sub> ] <sup>2-</sup>		17 [Co(CN) <sub>4</sub> ] <sup>4-</sup> ?	18 Co(acac) <sub>3</sub> [Co(CN) <sub>6</sub> ] <sup>3-</sup> HCo(CO) <sub>4</sub> Co(Dmg) <sub>2</sub> pyCH <sub>3</sub> ( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co	18 [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> [Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	19

each series than the earlier, just because the former have more valence electrons in their valence shells.

The trends illustrated in Table 5 may be understood by considering ligand and central atom properties together with the electro-neutrality principle. This principle states that in

molecules and complex ions the charge associated with the central atom, or indeed with any other atom in the system, will normally lie within the limits of  $\pm$  one electronic charge.

Exceptions to this principle are most likely to occur in the direction of an unusually high positive charge rather than the reverse, in particular when there are several highly electron-attracting ligands attached to the central atom. However, it is probable that the electro-neutrality principle is valid for complexes which contain a majority of less electron-attracting ligands. With this assumption, the principle may be used to predict whether a molecule or ion is likely to be stable, and an estimate of partial charge on the atom may be made. The explanation of the trends in Table 5, using the electro-neutrality principle, proceeds as follows:

(i) As donor-acceptor ligands, or combinations of donor and acceptor ligands, do not cause any large increase or decrease of partial charge on the central atom, the energies of the central atom orbitals will be about the same as found in the neutral atom. Reference to Fig. 10 shows that for most of the first-row transition metals there are nine valence orbitals, i.e. five  $3d$ , three  $4p$  and one  $4s$ . Therefore the metals in this situation tend to fill their valence shells, giving rise to the 18e rule.

(ii) Ligands which are strongly basic and have little  $\pi$ -acceptor ability, such as ammonia, cause a large build-up of charge on central atoms. It is therefore not surprising that neutral molecules such as  $\text{Mo}(\text{NH}_3)_6$  or  $\text{Fe}(\text{NH}_3)_5$  are unknown, since the partial negative charge on the central atom would be too large. It follows that complexes of these ligands with normal coordination numbers are expected as cations only where central atom electrons have been expelled to reduce electron density. On account of the electron loss such complexes do not obey the 18e rule.

In contrast, since carbon monoxide is a weak  $\sigma$ -donor and a strong  $\pi$ -acceptor, the neutral complexes  $\text{Mo}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  are stable. However, cationic complexes with high charge such as  $[\text{Mo}(\text{CO})_6]^{3+}$  or  $[\text{Fe}(\text{CO})_5]^{3+}$  do not exist because the presence of a relatively high partial charge on the central atom would contract and decrease in energy the central atom  $d$ -orbitals. Thus back donation to the ligands by  $\pi$ -bonding would be reduced and this would lead to weakening of the M-CO bonds, of which the  $\pi$ -bonding is energetically an important component.

(iii) There are several reasons which give rise to low electron numbers in complexes with a large proportion of electronegative 1e ligands. Firstly, there is the trivial observation that with 1e ligands alone there can be too few metal valence electrons, e.g.  $\text{WCl}_7$  is inconceivable. Secondly, for elements late in the transition series ionization potentials are too high for maximum covalency to be achieved, for the reasons given earlier, e.g.  $\text{PtF}_8$  is unlikely to be stable under normal conditions.

With 1e ligands, therefore, the 18e rule can be achieved only when some additional ligands which contribute two or more electrons are present or when electrons are added to form anions, e.g.  $\text{ReH}_9^{2-}$ ,  $\text{IrCl}_6^{3-}$ .

Further reasons for low electron numbers are illustrated by consideration of the known or hypothetical complexes  $\text{MX}_n$ , where  $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$  and  $\text{X}$  is hydrogen or a halogen. In complexes such as  $\text{WCl}_6$  and  $\text{MoCl}_6$  the empty  $t_{2g}$  orbitals (see Fig. 1) have become low in energy owing to the high partial charge on the metal. The halides are highly oxidizing and can readily accept electrons to form complex anions, e.g.  $\text{MoCl}_6$ ,  $[\text{MoCl}_6]^-$ ,  $[\text{MoCl}_6]^{2-}$  and  $[\text{MoCl}_6]^{3-}$ . Complexes of  $\text{MCl}_6$  with donor ligands are likely to be limited both by steric considerations and by the fact that they should be fairly basic yet not readily oxidized. Contrast the complexes  $(\text{R}_3\text{P})_2\text{WH}_6$  and  $(\text{R}_3\text{P})_2\text{ReH}_7$  which are well characterized. In

these hydrides the steric problem is reduced; also hydrogen is not a very electronegative ligand so there will not be a high positive charge on the central atom. Thus the  $MH_n$  systems may complex the donor-acceptor tertiary phosphine ligands which require back-donation from relatively high energy orbitals.

Addition of further electronegative ligands to  $WCl_6$  must be accompanied by electron addition, e.g.  $Cl^-$  addition to give  $WCl_7^-$ . Such additions are limited both sterically and because there appears to be relatively little energy gain in such circumstances. For example, compounds in the series such as  $TaF_5$ ,  $TaF_6^-$ ,  $TaF_7^{2-}$ ,  $TaF_8^{3-}$ , or  $WF_6$ ,  $WF_7^-$ , and  $WF_8^{2-}$  are present in equilibrium with each other when the parent neutral compound is dissolved in hydrofluoric acid. Although the niobium fluoro complexes resemble their tantalum analogues,  $NbCl_5$  adds only one  $Cl^-$  forming  $NbCl_6^-$  and  $NbCl_7^-$  is not known, suggesting that steric problems are quite acute.

### 5.3. THE OCCURRENCE OF COMPLEXES CONTAINING UNSATURATED HYDROCARBON SYSTEMS

One of the most marked features of the transition metals is their ability to form complexes with ligands which contain delocalized  $\pi$ -electron systems, such as benzene, butadiene and ethylene. This ability provides a marked contrast with the main group elements and leads to a very wide range of organometallic complexes.

The occurrence of complexes containing  $\pi$ -bonding organic ligands is directly associated with the presence of  $d$ -orbitals in the valence shell. The important feature of the organic  $\pi$ -bonding ligands is that they are all medium to weak  $\sigma$ -donors and, more significantly, they are all medium to medium-strong  $\pi$ -acceptor ligands; some of them are also weak to weak-medium  $\pi$ -donors. That is to say there are always empty non-bonding or anti-bonding orbitals on the organic ligand which may accept electrons from filled metal  $d$ -orbitals. By the nature of the bonding it follows that ligands in this class are normally fairly neutral ligands and their complexes largely obey the 18e rule.

### 5.4. CATALYTIC PROPERTIES OF TRANSITION METALS DERIVATIVES<sup>15, 16</sup>

Transition metals and their derivatives act as cocatalysts in a very wide variety of chemical systems and environments. This is due to the coincidence of a number of properties:

- (a) The ability of transition metal systems to gain or lose electrons without disruption, and with only relatively small structural changes.
- (b) The lability of ligands in many transition metal complexes. This property may be associated in many instances with the ability of transition metal complexes to expand or decrease their coordination number. Labile complexes often have partially filled valence shells, e.g. some 16e square planar complexes.

In the catalysis of hydrocarbon systems by transition metals other important properties are:

- (i) The ability of the metals to form  $\sigma$ - and  $\pi$ -bonds to organic groups.

<sup>15</sup> For example, C. W. Bird, *Transition Metal Intermediates in Organic Chemistry*, Logos Press, London (1967).

<sup>16</sup> *Advances in Chemistry Series No. 70* (1968), Am. Chem. Soc.

- (ii) The ability of transition metals to form covalent metal-hydrogen bonds.
- (iii) The ability of electron-rich transition metals systems to interact with hydrocarbon groups, which are held near but not strongly bonded to the metal, resulting in enhanced reactivity of the groups ( $\beta$ -effect).
- (iv) The ability of ligands to rearrange their position both about the metal, and with respect to each other, without becoming detached from the coordination sphere.

It is interesting to compare the requirements for catalytic properties with ligand properties in Table 2.

Molecular binary hydrides of the transition metals are unknown or very unstable ( $\text{TiH}_4$ ) presumably because they are unstable with respect to polymeric  $\text{MH}_n$  systems (interstitial hydrides) and hydrogen gas. Discrete metal-hydrides compounds are, however, commonly found when there are also attached to the metal neutral or neutralizing combinations of ligands (see Chapter 48). In fact, the occurrence of metal-hydrides parallels that of the metal-methyl compounds, for similar reasons. It follows that ligands that are favourable for metal- $\sigma$ -carbon bond formation are usually suitable for stabilization of metal-hydrogen bonds as well, as required for catalytic properties.

The ability of transition metal systems to labilize saturated hydrocarbon groups is thought to be due to metal orbitals which are essentially non-bonding and which extend from the metal and interact directly with the hydrocarbon group. Such orbitals are most likely to be found with electron-rich metal systems such as are associated with complexes containing several donor-acceptor ligands, e.g. CO,  $\text{PR}_3$ , and olefinic ligands.

The occurrence of labile ligands is likewise a common feature of electron-rich systems, e.g. compounds such as  $(\text{Ph}_3\text{P})_4\text{Ni}$  in benzene, or  $[(\text{NH}_3)_6\text{Fe}]^{3+}$  in water, readily dissociate ligands.

Finally, the activation of molecular nitrogen by transition metal compounds probably requires, in part, the presence of rather high energy  $d$ -orbitals on the metal. These orbitals are needed for back-donation into the high energy, anti-bonding  $\pi^*$ -orbitals on the nitrogen.

Therefore, neutral nitrogen metal complexes are more likely to occur with tertiary phosphines as ligands than carbon monoxide, since tertiary phosphines are better  $\sigma$ -donors and worse  $\pi$ -acceptors than carbon monoxide so that the former cause greater electron richness, i.e. relatively less lowering of the metal  $d$ -orbitals as a result of  $\pi$ -bonding.

## 5.5. OCCURRENCE OF UNPAIRED ELECTRONS IN ORGANO TRANSITION METAL COMPLEXES

A criterion for the occurrence of unpaired electrons in discrete molecular systems or ions is that vacant orbitals within the valency region are present which may be partially occupied. This situation is realized in transition metal complexes because the metal  $d$ -orbitals are in the valency shell and some are normally fairly close in energy. These orbitals are partially filled when the complex does not obey the 18e rule and reasons for that are discussed above.

Paramagnetism may also occur in delocalized organometallic complex areas where the empty orbitals lie mainly on the organic ligand, e.g. cobaltocene and nickelocene. This situation might be compared with the occurrence of relatively stable delocalized polyaromatic radicals.

It should be noted that, using Table 2, the occupancy of the  $d$ -orbitals in complexes can be found by application of the following relationship:

$$m + l - p = x \text{ for } dI \text{ complex}$$

where  $m$  = number of electrons in  $ns$ ,  $np$  and  $(n-1)d$  orbitals of metal,

$l$  = number of odd-electron ligands (see Table 2),

$p$  = charge on ion (see examples below).

Examples are, for  $\text{CrCl}_3$ ,  $6-3=d^3$ ;  $\text{CrCl}_6^{3-}$ ,  $6-6+3=d^3$ ;  $(\text{NH}_3)_6\text{Co}^{3+}$ ,  $9-0-3=d^6$ ; for  $\text{NiCl}_2(\text{R}_3\text{P})_2$ ,  $10-2=d^8$ ;  $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ ,  $6-4-1=d^1$ ;  $\text{H}_2\text{Fe}(\text{CO})_4$ ,  $8-2=d^6$ ;  $\text{HCo}(\text{CO})_4$ ,  $9-1=d^8$ .

It is in the context of the above expression that it is necessary to classify the oxygen atom as a  $2 \times 1e$  ligand, e.g.  $\text{MnO}_4^- = 7-8+1=d^0$ .

## 5.6. AN EXAMINATION OF THE USAGE OF "OXIDATION STATE" <sup>17</sup>

The definition of the oxidation state of an ion in an essentially ionic environment is unambiguous. The extension of the idea of a *formal* oxidation state to molecules which are largely covalent leads to several difficulties. In order to decide what the formal oxidation state is it is necessary to make an arbitrary decision about what the charges on the ligands in the system would be if it were really ionic. Halogen ligands are reasonably assumed to be uninegative so that the metal in the complex  $\text{MCl}_n$  is in the formal oxidation state of  $n+$ . However, other ligands such as H, NO,  $\text{CH}_3$ ,  $\text{C}_7\text{H}_7$ , bipyridyl, or maleonitriledithiolato present problems; for example, in  $\text{ReH}_9^{2-}$  is the Re in the  $7+$  or  $11-$  state, or, what is the formal oxidation state of Ti in the complex  $\pi\text{-C}_5\text{H}_5\text{TiC}_8\text{H}_8$ ?

More serious are the understandable but incorrect inferences about the partial charge on the central metal that result from an uncritical use of formal oxidation state. Whilst it is clearly true that there will be a greater positive charge associated with the metal in the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$  compared with  $[\text{Co}(\text{NH}_3)_6]^{2+}$ , it is by no means clear how the partial charge on the metal in these complexes will compare with those in  $[\text{CoCl}_6]^{3-}$  or  $[(\pi\text{-C}_5\text{H}_5)_2\text{Co}]^+$ , even though the cobalt is in the same  $3+$  state. Similarly, there is probably a greater partial *positive* charge on iron in  $\text{Fe}(\text{CO})_5$  than in  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ , although the former is in the zero oxidation state whilst the latter is in the  $2+$  state.

The energies of the valence orbitals associated with the central atom are very important in determining reactivity of a molecule or ion, and these bear no relationship, not even a formal one, with oxidation state definitions. Therefore it seems with covalent systems that the formal oxidation state is useful only as a method of classification, and even then confusion may arise.

Since the method of electron counting and classification of ligands described above provides an equally viable, alternative method of classification of complexes, which relates more directly to chemical behaviour, it seems that eventually the use of formal oxidation state classification will be abandoned.

The use of the terms "oxidation" and "reduction" is, of course, still entirely appropriate in the electron number covalent system. Thus the  $18e$  complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  undergoes a one-electron oxidation forming the  $17e$  complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

<sup>17</sup> R. S. Nyholm and M. L. Tobe, *Advances Inorg. Chem. Radiochem.* **5** (1963) 1.



Finally, it is worth while noting that because we live in an oxygen atmosphere and the halides are abundant, a great deal more is known about the derivatives of these ligands than of other ligands. Moreover, these ligands are exceptional as they are atomic and highly electronegative. It follows that the discussion and present view of chemistry has been unduly influenced by the ionic model. Despite the historical importance of these ligands it must be remembered that they are few in number compared to the very large and rapidly increasing number of other ligands. Exceptions to the electro-neutrality principle, the occurrence of ionic lattices, and the break-down of "stability rules" are much rarer with nearly all other ligands.

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J D SMITH *University of Sussex*  
Oxygen  
E A V EBSWORTH *University of Edinburgh*,  
J A CONNOR *University of Manchester*, &  
J J TURNER *Newcastle on Tyne University*  
Sulphur  
M SCHMIDT & W SIEBERT *University of Wurzburg*  
Selenium, Tellurium and Polonium  
K W BAGNALL *University of Manchester*  
Fluorine  
T A O'DONNELL *University of Melbourne*  
Chlorine, Bromine, Iodine and Astatine  
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Copper  
A G MASSEY *University of Technology, Loughborough*  
Silver  
N R THOMPSON *ICI, Runcorn Heath Laboratory, Cheshire*

## INDEPENDENT OPINION

"These books are attractively bound and have clear print. Since the length and cost are not prohibitive, this set of books should be well within the budget of most libraries. Not only will the professional chemist find these books useful, but students and other readers will find them a valuable reference source. (Comprehensive Inorganic Chemistry) should be found in every undergraduate and graduate library, as well as industrial libraries. Many professional chemists may even consider them for personal libraries. Highly recommended."

Choice—A publication of the Association of College and Research Libraries.

## Gold

B F G JOHNSON *University of Cambridge* & R DAVIS *Kingston Polytechnic*  
Group IIB  
B J AYLETT *Westfield College, London*  
Scandium, Yttrium and Lanthanum  
R C VICKERY *Hudson, Florida*  
Titanium  
R J H CLARK *University College, London*  
Zirconium and Hafnium  
D C BRADLEY & P THORNTON *Queen Mary College, London*  
Vanadium  
R J H CLARK, *University College, London*  
The chemistry of Niobium and Tantalum  
D BROWN *Atomic Energy Research Establishment, Harwell*  
Chromium, Molybdenum and Tungsten  
C L ROLLINSON *University of Maryland*  
Manganese  
R D W KEMMITT *University of Leicester*  
Technetium  
R D PEACOCK *University of Leicester*  
Rhenium  
R D PEACOCK *University of Leicester*  
Iron  
D NICHOLLS *University of Liverpool*  
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G W C MILNER & G PHILLIPS  
P G MARDON  
*Atomic Energy Research Establishment, Harwell*  
C KELLER *Kernforschungszentrum, Karlsruhe*  
S H EBERLE *Universität Karlsruhe*  
D BROWN, R M DELL & P E POTTER *AERE, Harwell*  
K W BAGNALL *University of Manchester*  
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# INDEPENDENT OPINION

## Volume 1 1467 pp + index

"This covers the chemistry of hydrogen, the noble gases, and of the elements of Groups IA, IIA, IIIB, carbon and silicon. The first three chapters deal with hydrogen, hydrides, deuterium and tritium and the fourth is an interesting discussion of the proton, protonic acids and the hydrogen bond. Two chapters follow on the inert gases, including interesting and extensive recent knowledge about their compounds set out by N. Bartlett and F. O. Sladky. Four chapters on the alkalis and alkaline earths contain a wealth of detail, although perhaps along traditional lines. N. N. Greenwood has written an excellent account on boron chemistry of book length in itself, and another chapter deals at length with much new information about aluminium, gallium, indium and thallium. Chapters 13 and 15 deal with carbon and silicon. Here it might have been expected that more would have been included on the high pressure chemistry of carbon and silicates, and mineral chemistry. Chapter 14 by M. L. H. Green and P. Powell is a useful introduction to the organic chemistry of the metallic elements, along modern lines of ligand field theory and ideas about metal complexes.

Throughout this volume, with its different authors, it is perhaps inevitable that there is some lack of uniformity in the extent of detail given. There are also a few lapses in symbolism, notation, and uniformity of units. Yet the whole must be regarded as a highly commendable collection of material which will be valuable to chemists of all kinds."

**Professor Sir Harold Thompson FRS**  
Oxford

## Volume 2 1594 pp + index

"Volume 2 is concerned with the chemistry of the elements of Groups IV, V, VI, VII. The general impression on reading the various chapters of this volume is the great effectiveness in reporting a considerable amount of chemistry in a very digestible form. The systematic presentation applied to each chapter allows a rapid assessment of the appropriate chemical information, and the text is well documented with reference to the original literature plus good review articles for a more detailed coverage. Perhaps a minor criticism of this work lies in the indexing; the subject index is relatively sparse for a text of such magnitude and it would have been of considerable utility to have a formulae index to the text.

The area of chemistry covered by this work is obviously very great, but it does appear to have

dealt with it in a very succinct manner for the majority of the text, which extends to approximately 1500 pages. The two major chapters in the book are associated with the chemistry of nitrogen, approximately 240 pages, and the chemistry of the halogens (excepting fluorine), approximately 500 pages. The book thus encompasses in one volume what would normally be a series of books. Both of the above mentioned chapters are admirable and the authors, K. Jones on nitrogen with A. J. Downs and C. J. Adams on the halogens, are to be commended on both the presentation and coverage. The chapter on the halogens illustrates the real strength of the series, in that detailed chemical information is not only presented but discussed in physico-chemical theoretical terms. A scientific compendium of this size often suffers from the "catalogue" approach, but the present text presents the chemistry in critical mode with a realistic assessment of the various physical methods used in property determination. Thus the properties of the halogens are discussed in terms of bond energies, bond lengths, vibrational properties, e.s.r., n.m.r., n.q.r. and Mossbauer spectroscopy, electronic and magnetic properties and dipole moments allowing a detailed appraisal of the use of various modern methods in studying the chemical properties reviewed.

Considering the magnitude of the task undertaken, it is extremely pleasing to note the number of chapters referring to papers in the 1971 period—a truly great commendation on the overall editorship of these volumes. Perhaps a general note in each volume stating the period covered by the references would have been of help. In general this work provides a welcome and unique addition to the inorganic literature."

**Professor J. Lewis FRS**  
Cambridge

## Volume 3 1370 pp + index

"This volume covers the chemistry of the elements of the d-block of the Periodic Table (the transition elements), with the exception of the Lanthanide elements (Vol. 4), the Actinide elements (Vol. 5) and some special aspects which are common to many of the transition elements (Vol. 4). The volume is therefore concerned specifically with the three elements which characterize each of the ten transition groups, and the chapters are mostly grouped in this way. However, the six platinum metals are treated in one chapter which is the best way to fit these similar elements into the overall scheme which is standard for all five volumes. There are altogether 17 chapters, written by 14 authors who are internationally

recognized 1370 pages of text and a useful 17 page index.

The five volumes are quite remarkable, in that they can justifiably claim to be comprehensive, yet at the same time remain interesting and readable; they are probably unique in this respect. Volume 3 serves as an excellent source-book for the essential physical constants of all important compounds (simple and complex) of the transition metals. These are arranged so that significant comparisons are made wherever possible, and there are extensive references. It says much for the ingenuity of the editors, authors, and particularly the printers that the presentation of such an amount of information has been possible, while still maintaining the readability of the text. Throughout the volume chemical properties and reactions are discussed and interpreted rather than listed. The need for skilled correlation of data is particularly important in Volume 3, since it is in the area of the transition elements that a major part of the research work in inorganic chemistry has been published in recent years, and in this area also there has been a major interaction of inorganic with theoretical chemistry.

This volume must surely become the first point of reference for research workers and teachers alike. The transition elements play an important role in Pure and Applied Chemistry, Physics, Materials Science and Biology, and the authors clearly intend their chapters to be of value to this wide audience. Teachers at any level will also appreciate the very high quality of the general presentation, discussion, formulae and diagrams. Apart from reference to the original literature, few scientists will find it necessary to look outside this volume for their material."

**Professor C. C. Addison FRS**  
Nottingham

#### **Volume 4 994 pp + index**

"Volume 4 is concerned with the general chemistry of the lanthanides and some special topics in transition metal chemistry.

Therold Moeller has packed a great amount of the fundamental chemistry of the lanthanides into his 101 pages in an interesting and scholarly manner with tables of essential data. Important recent developments in their organometallic chemistry have come too late to be included, but the chapter provides a useful fairly detailed first reference to their inorganic chemistry.

The subjects of the surveys are topical and obviously bear the mark of the late Sir Ronald Nyholm. They vary considerably in detail of treatment, interest and authority. Generally they emphasize recent work until about 1969-70 but rarely show a sense of history. They vary in length from 60 to 200 pages, mostly around 100 pages. They are authoritative and useful surveys all giving numerous references to recent reviews and

original work. The authors are well known chemists whose style and subject matter are familiar to most inorganic chemists. There are eight surveys as follows:—

Carbonyls, cyanides, isocyanides and nitrosyls by W. Griffith. Compounds of the transition elements involving metal-metal bonds by D. L. Kepert and K. Vrieze. Transition metal hydrogen compounds by J. C. Green and M. L. H. Green. Non-stoichiometric compounds: an introductory essay by D. J. M. Bevan. Tungsten bronzes, vanadium bronzes and related compounds by P. Hagenmuller. Isopolyanions and heteropolyanions by D. L. Kepert. Transition metal chemistry by B. F. G. Johnson. Organo-transition metal compounds and related aspects of homogeneous catalysis by B. L. Shaw and N. I. Tucker.

This volume has its own subject index of sixteen and a half pages, and is well produced with numerous tables of data and references provided at the foot of each page."

**Professor J. Chatt FRS**  
Sussex

#### **Volume 5 635 pp + Master index**

"Volume 5 is devoted to the Actinides (635 pp) and the Master Index (78 pp). The latter serves little purpose since it merely indicates the subsections of CIC, and thus repeats the indexes in each individual volume. Indeed, as the treatment of each element or series of elements follows a standard pattern, the volumes are essentially self-indexing anyway. A one-page table of contents at the beginning of Volume 5 would have been more helpful and is a curious omission. The running headings at the top of each double page are also singularly uninformative, only three being used: 'The Elements' for 102 pages, 'Compounds' for 361 pages and 'Solution Chemistry' for the remaining 171 pages.

The treatment of actinium and the actinides (elements 89-103) is both readable and authoritative. Nine of the contributors are from AERE, Harwell, and the other five (with one exception) are from nuclear chemistry institutes in Sweden and Germany. In reviewing these 5f elements it is salutary to recall that the majority have been synthesized for the first time within the last 30 years—yet the number of compounds known and the amount of information on them has already outstripped the more limited chemistry of their 4f congeners, the lanthanides. The authors have done a magnificent job in assembling, collating, assessing, and systematizing a vast amount of data on the physical and chemical properties of these elements and their numerous compounds. The work, which is extensively referenced, will undoubtedly remain the standard first source of information in this area for many years to come."

**Professor N. N. Greenwood FRIC**  
Leeds