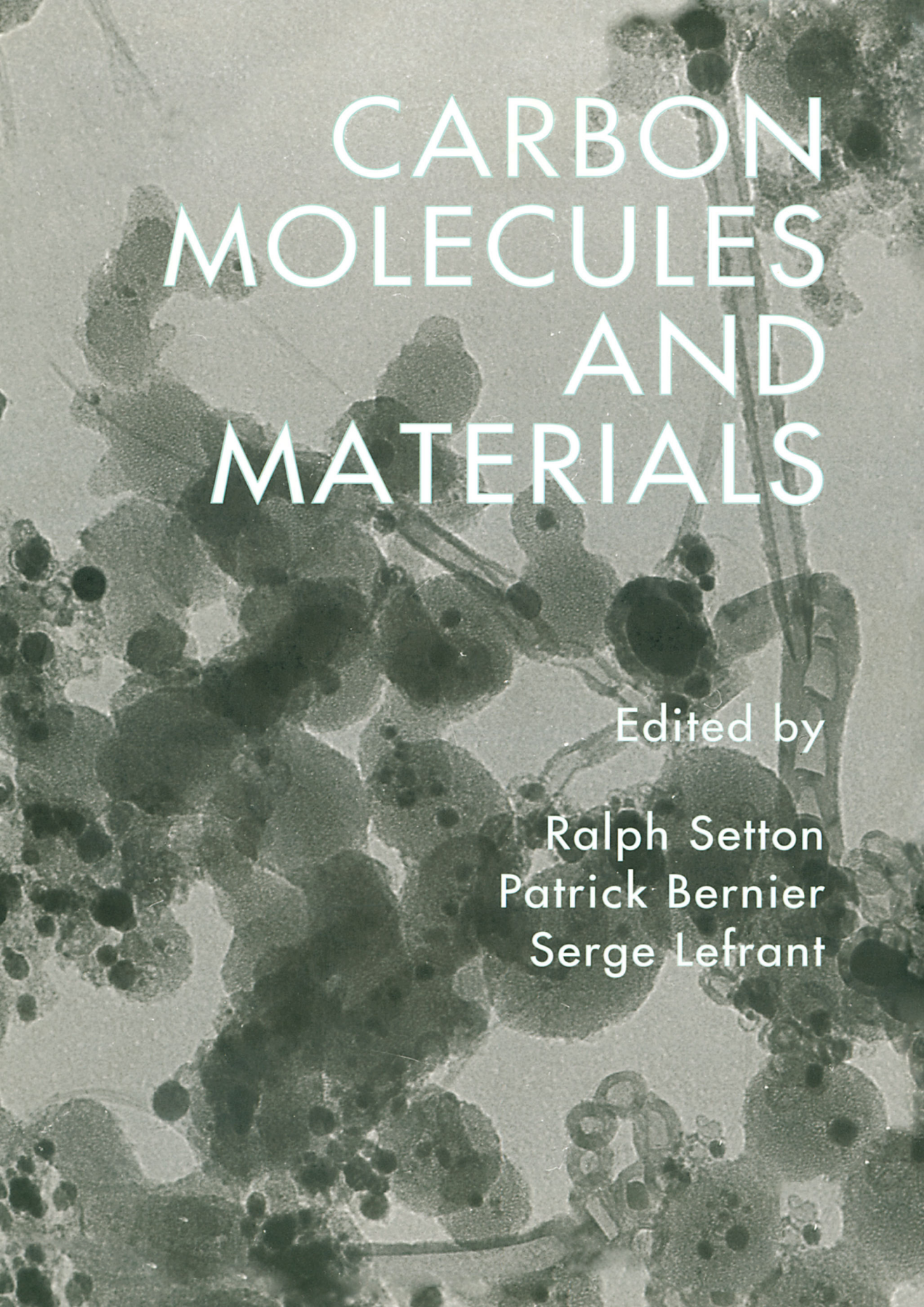


A grayscale electron micrograph showing a complex network of carbon-based structures. There are numerous dark, irregular, and somewhat spherical clusters of varying sizes, some appearing as small dots and others as larger, more textured aggregates. These are interconnected by a web of fine, thread-like or fibrous structures. The background is a lighter, mottled gray, providing contrast for the darker carbon features.

CARBON MOLECULES AND MATERIALS

Edited by

Ralph Setton
Patrick Bernier
Serge Lefrant

CARBON MOLECULES AND MATERIALS

This page intentionally left blank

CARBON MOLECULES AND MATERIALS

Edited by

Ralph Setton
CNRS, Orléans, France

Patrick Bernier
Université de Montpellier, France

Serge Lefrant
Institut des Matériaux de Nantes, France

Translated from the French by
Ralph Setton



London and New York

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2002 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Version Date: 20140416

International Standard Book Number-13: 978-1-4822-6313-8 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

CONTENTS

<i>Preface</i>	xiii
<i>Contributors</i>	xv
1 Carbon, a fundamental element for research and its applications	1
<i>Ralph Setton</i>	
1.1 Introduction	1
1.2 Coals and combustible materials	1
1.3 Carbons	2
1.3.1 Cokes and artificial graphites	2
1.3.2 Flexible graphite	4
1.3.3 Carbon blacks	4
1.3.4 Pyrocarbons	5
1.3.5 Glassy carbon	6
1.3.6 Carbon fibres	6
1.3.7 Active carbons	9
1.4 Carbon as an element	16
1.4.1 The thermodynamic phase diagram of carbon	17
1.4.2 Diamond	21
1.4.3 Carbynes	26
1.4.4 Graphite	27
1.5 Lamellar compounds of graphite	31
1.5.1 General features	32
1.5.2 Covalent compounds	34
1.5.3 Ionic graphite lamellar compounds	34
1.6 The fullerenes	38
1.6.1 Brief history of the discovery of fullerenes	38
1.6.2 The C ₆₀ molecule	39
1.6.3 Nanotubes	41
1.6.4 Negative curvature surfaces	42
2 The polymorphism of solid carbons	51
<i>Pierre Delhaès</i>	
2.1 Introduction	51
2.2 General considerations on the crystalline forms	51
2.2.1 Chemical bonds and electronic structures	51
2.2.2 The search for and characterisation of new solid phases	56
2.3 Real and virtual allotropic forms of carbon	59
2.3.1 Structures with a fixed coordination number	59
2.3.2 Tricoordinated structures on curved surfaces	63
2.3.3 "Exotic" structures with a variable coordination number	68
2.4 Non-crystalline carbons and solid solutions	70
2.4.1 Non-crystalline carbons	71
2.4.2 Solid solutions and analogous compounds	74
2.5 Conclusion	79

3	Carbon chemical species in extraterrestrial media	83
	<i>François Robert</i>	
3.1	Definitions and natural states	83
3.2	Paths of synthesis: isotopic composition	85
3.2.1	Equilibrium isotope fractionation: definition and notation	85
3.2.2	The source effect, and isotopic anomalies	86
3.2.3	Mass fractionation	86
3.3	Inorganic species of presolar origin: graphite, diamond, and silicon carbide	87
3.3.1	The origins of the discovery: the rare gases	88
3.3.2	The traces of stellar nucleosynthesis: the isotopic anomalies	90
3.3.3	Presolar carbon grains in the protosolar nebula	93
3.4	The origin of metallic phases in solar system objects: the role of carbon	95
3.5	Organic carbon in meteorites: soluble molecules and macromolecules	99
3.5.1	Historical account	99
3.5.2	Amino acids	99
3.5.3	Aliphatic hydrocarbons	100
3.5.4	Aromatic hydrocarbons	101
3.5.5	Carboxylic acids	102
3.5.6	Nitrogenous compounds	102
3.5.7	Macromolecules	103
3.6	Comets, asteroids and planets	104
3.7	Carbon in the interstellar medium	105
3.7.1	Interstellar organic molecules: detection, distribution, speciation	105
3.7.2	Observations	106
3.7.3	Distribution	106
3.7.4	Speciation	109
3.8	The origin of extraterrestrial carbon in the solar system	110
3.8.1	Organic syntheses in the protosolar nebula	110
3.8.2	Hydrothermalism and metamorphic processes	112
3.8.3	Organic syntheses in the interstellar medium	112
3.9	Remarks and conclusion	120
3.10	Acknowledgements	120
4	Structure, texture, and thermal behaviour of polyaromatic solids	127
	<i>Marc Monthioux</i>	
4.1	Introduction	127
4.2	Global aspect of carbonisation	128
4.2.1	Primary carbonisation	128
4.2.2	Secondary carbonisation	137
4.3	Global aspect of graphitisation	137
4.3.1	Graphitisation as seen by X-ray diffraction	137

4.3.2	Role of the chemical composition	142
4.4.	Transmission electron microscopy applied to the study of polyaromatic carbons	142
4.4.1	Basic principles	142
4.4.2	Electron diffraction	144
4.4.3	Dark field imaging	155
4.5	Local aspects of carbonisation and graphitisation	159
4.5.1	Primary carbonisation	159
4.5.2	Secondary carbonisation and graphitisation	166
4.6	Conclusion	174
5	Sheets, cones, balls and tubes	179
	<i>Thomas Ebbesen</i>	
5.1	Introduction	179
5.2	Geometry and graphitic structures	179
5.2.1	Euler's theorem	179
5.2.2	Chirality	181
5.2.3	sp^2/sp^3 rehybridisation	183
5.3	Production and purification of curved carbon species	186
5.3.1	Soot and fullerenes	186
5.3.2	Nanotubes and nanoparticles	190
5.4	Growth mechanism of curved graphitic surfaces	196
5.5	Future potential	198
6	Structure and bonding in solid state fullerene phases	201
	<i>Gavin Vaughan</i>	
6.1	Introduction	201
6.2	The fullerenes: plastic crystals	201
6.2.1	C_{60}	204
6.2.2	C_{70}	210
6.3	Higher fullerenes	216
6.4	Chemical modifications of the fullerenes	216
6.4.1	Structures and transitions of $C_{60}O$ and $C_{61}H_2$	217
6.4.2	Other fulleroids in the solid state	218
6.5	Conclusion	218
7	Carbons: Their electronic structure and magnetic resonances	225
	<i>Jacques Conard</i>	
7.1	Introduction	225
7.2	Classification of carbons by their local structure	225
7.3	Hybridisation of the carbon orbitals and nature of the bonds	226
7.4	Electronic states of the solid and inorganic types of carbon	230
7.5	Simplified band structure models of graphite	234
7.5.1	Graphite and carbons	234
7.5.2	Donor graphite intercalation compounds	234
7.5.3	Acceptor graphite intercalation compounds	237
7.5.4	C_{60} and its metal derivatives	237

7.6	Static magnetic susceptibility	237
7.7	Electron paramagnetic resonance	239
7.8	Nuclear magnetic resonance	240
7.8.1	NMR of alkali metals in their electrically conducting graphite intercalation compounds	240
7.8.2	^{13}C NMR in carbon and carbon molecular compounds	241
7.9	Relationship between the charge transfer and the shifts observed	245
7.10	Conclusions	246
8	Electronic structure of the solid forms of carbon	249
	<i>Eric Sandré and Françoise Cyrot-Lackman</i>	
8.1	Introduction	249
8.2	Methods of calculation of the electronic structure	250
8.2.1	Quantum mechanics and electronic structure	250
8.2.2	The tight binding approximation (TBA) method	252
8.2.3	Slater-Koster formulation for the transfer integrals: dependence on the coordination geometry of the atoms	254
8.2.4	Modelisation of the infinite perfect crystal: the Bloch theorem	257
8.3	Comparison of the electronic structures of graphite and diamond	259
8.3.1	Crystal and electronic structures of the graphite and diamond forms	260
8.3.2	Comparative study of the electronic structures of graphite and diamond: the continuous topological transformation of rhombohedral graphite into cubic diamond	268
8.3.3	The $\beta_{p_z p_z} < 0$ domain: energy features close to the Fermi level in carbon structures	276
8.4	Electronic structure of fullerenes and nanotubes	277
8.4.1	Application of the Tight Binding Approximation (limited to the p_z orbitals) to the fullerenes	277
8.4.2	Electronic structure of the nanotubes	281
8.5	Conclusion	286
9	Vibrational properties of carbon in the solid state	289
	<i>Jeffrey Lannin and Serge Lefrant</i>	
9.1	Introduction	289
9.2	Vibrational probes and order	290
9.3	Vibrational results	292
9.3.1	Diamond	292
9.3.2	Graphite and nanocrystalline graphite	294
9.3.3	Graphite intercalation compounds	299
9.3.4	Fullerenes	300
9.3.5	Alkali-metal fullerene derivatives, M_xC_{60}	306
9.3.6	Amorphous Carbon (a-C)	314
9.3.7	Carbon nanotubes	318

10	Optical properties of the allotropic forms of carbon	325
	<i>Pierre-Alain Chollet and François Kajzar</i>	
10.1	Introduction	325
10.2	Macroscopic and microscopic polarisations	326
10.3	Linear optical properties	328
10.3.1	Linear absorption and transmission	328
10.3.2	Determination of the refractive indices from the Kramers–Kronig relationships	332
10.3.3	Dispersion of the refractive indices	338
10.4	Photo-induced optical properties	338
10.4.1	Luminescence and phosphorescence	338
10.4.2	Raman spectra	340
10.5	Non-linear optical properties	343
10.5.1	Advantages of carbon allotropes and compounds in non-linear optics	343
10.5.2	Second-order non-linear optical properties	343
10.5.3	Third-order non-linear optical properties	345
10.6	Conclusion	358
11	Crystallochemistry of intercalation in the crystalline forms of carbon	365
	<i>François Béguin</i>	
11.1	Introduction	365
11.2	Comparison of the amphoteric characteristics of graphite and C ₆₀	366
11.2.1	Electron acceptor characteristics of graphite and C ₆₀	369
11.2.2	Electron donor characteristics of graphite and C ₆₀	370
11.3	Crystallochemistry of intercalation into graphite	371
11.3.1	Preparation of intercalation compounds by spontaneous intercalation	371
11.3.2	General structural characteristics of the graphite intercalation compounds	375
11.4	Crystallochemistry of intercalation in the fullerite C ₆₀	389
11.4.1	Intercalation of alkali metals	389
11.4.2	Spontaneous intercalation of alkali metals	392
11.4.3	Electrochemically assisted intercalation	395
11.4.4	Structure of the phases with the alkali metals	395
11.4.5	Attempted syntheses of acceptor intercalation derivatives of fullerenes	400
11.5	Conclusion	404
12	The superconductivity of carbon derivatives	409
	<i>Michel Cyrot</i>	
12.1	Introduction	409
12.2	Intercalation compounds of graphite	409
12.3	Doped fullerenes	409
12.4	Superconductivity	412
12.5	Vibration modes	413

12.6	Electronic structure	414
12.7	Critical temperature	417
12.7.1	The strong coupling theories	417
12.7.2	Pressure effects	419
12.7.3	Isotope effect	420
12.8	Electronic properties in the normal state	421
12.9	Type II superconductors	424
12.10	The energy gap parameter	426
12.11	Conclusion	427
13	Diamond and related materials	431
	<i>G�rard Demazeau</i>	
13.1	The ways to synthetic diamonds	431
13.1.1	Processes involving high pressures and high temperatures (HP-HT)	431
13.1.2	Processes involving low pressures and high temperatures (LP-HT)	433
13.2	Cubic boron nitride: an isostructural and isoelectronic homologue of diamond	435
13.2.1	Structural analogies between boron nitride and carbon	435
13.2.2	The controversial thermodynamic stability domain of c-BN	436
13.3	Elaboration techniques for diamond and cubic boron nitride	438
13.3.1	The manufacture of microcrystallites	439
13.3.2	The preparation of dense ceramics	439
13.3.3	The preparation of single crystals	440
13.3.4	The formation of thin layers	441
13.4	Diamond and cubic boron nitride: materials with exceptional properties	442
13.4.1	Applications in mechanics	442
13.4.2	Applications involving the thermal conductivity	445
13.4.3	Optical applications	445
13.4.4	Applications based on the electrical and electronic properties	446
13.5	The challenges: perspectives of research and development	446
13.5.1	Bulk diamond and c-BN	447
13.5.2	Diamond and c-BN as thin layers	448
13.5.3	Elaboration of other forms characterised by exceptional physico-chemical properties	449
13.6	Conclusions	450
14	Applications of carbons	457
	<i>Serge Flandrois</i>	
14.1	Introduction	457
14.2	Applications of the different forms of carbon	458
14.2.1	Applications exploiting structural properties	458
14.2.2	Applications involving chemical properties	459

14.2.3 Applications involving mechanical properties	459
14.2.4 Applications involving thermal and thermomechanical properties	460
14.2.5 Applications involving electrical properties	461
14.2.6 Biological applications	462
14.2.7 Active Carbons	462
14.3 Conclusion	464
Glossary	469
Index	475

This page intentionally left blank

PREFACE

John E. Fischer

One of the fundamental ideas of Materials Science is that the chemical properties of atoms are periodically dependent on the atomic number, as revealed by the Periodic Table of the elements developed by Mendeleev. One expects, from this table, that all the elements in a given column will have roughly the same properties. This simple rule is however only relatively true for the elements in any one column and for all their properties: thus, some of the so-called “noble gases” in the right-most column are not chemically inert, and lithium and cesium, which are both in the left-most column (that of the alkali metals), have fairly different chemical properties. There are many other examples of the fact that certain properties may be common to all the elements of a column but that each element retains a marked specificity.

The tetravalent elements of column IV in the Periodic Table (carbon, silicon, germanium, tin and lead) are the ones showing the largest departures from the rule above. Furthermore, whereas these five elements are, whenever found in a solid medium, most often in tetrahedral bonding with their neighbouring atoms, (sp^3 bonding), only carbon can also adopt, depending on the compounds in which it is found, a plane hexagonal (sp^2) or a linear (sp) configuration, or even a configuration intermediate between any two of the above forms. *What is it, then, which endows carbon with this specific property?* A simplified explanation could be as follows:

The electrons in the innermost shell of the carbon atom constitute an electronic “core” sufficiently compact to allow the outer valence electrons to organise themselves – i.e. to “hybridise” – so as to form linear and one-dimensional (1D), or plane and two-dimensional (2D), or tetrahedral and three-dimensional (3D) structures with the electrons of neighbouring atoms. For all the other atoms of column IV, the effective size of the core is larger, and the orbitals of the valence electrons are further away from the nucleus. In that case, their aptness to form chemical bonds by combinations of s and p atomic orbitals is restricted, and, as a result, only tetracoordinated bonds are favoured. This important difference between carbon and its congeners is found not merely in the solid state but at the molecular level as well. Thus, only carbon yields systems with sp^2 bonds, as in graphite, or sp^3 bonds, as in diamond, or even with bonds intermediate between these two types of hybridisations, as in the fullerenes. Even in the case of non-crystalline solids, the versatility of carbon plays an important part: in the so-called “amorphous carbons”, a whole gamut of bonds can be found owing to the fact that the formation of sp^2 or sp^3 bonds depends on the conditions prevailing locally during the synthesis.

Carbon, which is the most abundant element in the Universe after hydrogen and helium, is of considerable importance on Earth both industrially and economically, mostly thanks to this versatility and to the ease with which it can form bonds with other elements and with itself. The discovery of benzene during the XIXth century and the elucidation of its structure were events of fundamental importance, leading to the development of organic chemistry and thus profoundly modifying our everyday life (fuels, plastics, drugs and chemicals, ...). The discovery of new molecules and of

new materials in which carbon is the principal element is still going on. These discoveries may be of prime importance for our future, with an as yet unknown impact.

Carbon, the chameleon element of the periodic classification, has probably not ceased to surprise us. New molecular forms are potentially available, and new synthetic procedures may soon emerge, all of which allow us to envisage quite serenely the future of carbon-based materials.

CONTRIBUTORS

François Béguin

CNRS, CRMD
1 B, rue de la Férollerie
F-45071 Orléans Cedex 2
France
Tel: 0238255375; Fax: 0238633796
e-mail: beguin@cnrs-orleans.fr

Patrick Bernier

GDPIC, Université de Montpellier II
F-34095 Montpellier Cedex 5
France
Tel: 0467143538; Fax: 0467522504
e-mail: PAT@gdpc.univ-montp2.fr

Pierre-Alain Chollet

LETI/CEA
F-91191 Gif-sur-Yvette Cedex
France
Tel: 0169084749; Fax: 0169087679
e-mail: pierre-alain.chollett@cea.fr

Jacques Conard

CNRS, CRMD
1 B, rue de la Férollerie
F-45071 Orléans Cedex 2
France
Tel: 0238255356; Fax: 0238633796
e-mail: conard@cnrs-orleans.fr

Michel Cyrot

LMLN
BP 166
F-38042 Grenoble Cedex 9
France
Tel: 0476881091; Fax: 0476881191
e-mail: cyrot@labs.polycnrs-gre.fr

Françoise Cyrot-Lackman

CNRS, LEPES
25 Avenue des Martyrs 166X
F-38042 Grenoble Cedex
France
Tel: 0476881082; Fax: 0476887988
e-mail: eric@lepes.polycnrs-gre.fr

Pierre Delhaès

CNRS, CRPP
Avenue Albert Schweitzer
F-33600 Pessac
France
Tel: 0556845656; Fax: 0556845600
e-mail: delhaes@crpp.u-bordeaux.fr

Gérard Demazeau

ICMCB
Avenue Albert Schweitzer
F-33608 Pessac
France
Tel: 0556848358; Fax: 0556842710
e-mail: demazeau@chimsol.icncb.u-bordeaux.fr

Thomas W. Ebbesen

ISIS
4 rue Blaise Pascal
F-67070 Strasbourg Cedex
France
Tel: 0388358042; Fax: 0388359043

John E. Fischer

LRSM
University of Pennsylvania
Philadelphia PA 19104-6272
USA
Tel: (1)215-8986924;
Fax: (1)215-5732128
e-mail: fischer@sol1.lrsm.upenn.edu

Serge Flandrois

CNRS, CRPP
115, Avenue Albert Schweitzer
F-33600 Pessac
France
Tel: 0556845632; Fax: 0556845600
e-mail: flandrois@cnrs.u-bordeaux.fr

François Kajzar

DEIN/LERA,
F-91191 Gif-sur-Yvette Cedex
France
Tel: 0169086810; Fax: 0169087819
e-mail: kajzar@cea.fr

Jeffrey Lannin*

Penn State University
University Park, PA-16802
USA

Serge Lefrant

LPC/IMJR
F-44072 Nantes Cedex 03
France
Tel: 0240373990; Fax: 0240373990
e-mail: lefrant@cnrs-imn.fr

Marc Monthieux

CEMES/CNRS
B.P. 4347
F-31055 Toulouse Cedex 4
France
Tel: 0562257800; Fax: 0562257999

François Robert

LM/MHN
F-75005 Paris
France
Tel: 0140793538; Fax: 0140793524
e-mail: robert@cimrs1.mnhn.fr

Eric Sandré

CNRS, LPS
Bat. 510, Université de Paris Sud
F-91405 Orsay Cedex,
France
Tel: 0169154831; Fax :0169158004
e-mail: sandre@lps.u-psud.fr

Ralph Setton

CNRS, CRMD,
1 B, rue de la Férollerie
F-45071 Orléans Cedex 2
France
Tel: 0238255369; Fax: 0238633796
e-mail: setton@cnrs-orleans.fr

Gavin Vaughan

ESRF
F-38403 Grenoble Cedex
France
Tel: 0476882341; Fax: 0476882707
e-mail: vaughan@esrf.fr

*deceased.

1. CARBON, A FUNDAMENTAL ELEMENT FOR RESEARCH AND ITS APPLICATIONS

Ralph Setton

1.1 INTRODUCTION

During the last few years, our knowledge of the chemistry and physics of carbon have been considerably modified thanks to the results of academic and industrial research on the graphitisation of non-graphitic carbons, on the intercalation compounds of graphite, and to the discovery, the purification and the production in weighable amounts of new forms of elementary carbon, the fullerenes. Apart from the use of coal as a domestic or industrial fuel, many manufactured forms of carbon were already of fundamental importance in industry, e.g. cokes (metallurgy), graphitised carbon (electrodes), ultrapure artificial graphite (nuclear industry), carbon blacks (tyres, printing inks), pyrocarbons (aeronautics, X-ray diffraction, heat-resisting structures), fibres (aeronautics, sports), active carbon (purification processes), synthetic diamonds (electronics, cutting and abrasive tools), natural diamonds (jewellery). It will, of course, be impossible to review in detail all their features, and the present chapter will therefore be restricted to a description of their main specific characteristics.

Carbon in nature is found in all living animal and vegetable species, whose decomposition yields carbon-rich mixtures such as natural gas, oil (petroleum), peat, coal, or metallic carbonates. Elementary carbon is found, in varying proportions, in mineral forms (diamond, graphite, anthracite), and even in a large number of meteorites (cf. Chapter 3).

1.2 COALS AND COMBUSTIBLE MATERIALS

Coals and kerogens are mixtures of (at least partly) combustible materials formed by the metamorphic decay of vegetal organic matter which, besides carbon, contain a number of other elements such as oxygen, hydrogen, sulphur, nitrogen, metals, etc. The composition of the mixtures in the mineral seams depends both on the original nature of the decomposed matter and on the physical conditions prevailing during the successive geological era. When classified according to their increasing carbon content, one thus finds peat, lignite (sub-bituminous coal), bituminous coals, and anthracites.

Nowadays, coal as a fuel is not only obtained merely by its extraction from the seam followed by its purification; since the oil crisis of the 70s, three methods of preparation of a liquid coal other than petroleum have been studied and developed, allowing its transportation over large distances by pipeline or even its direct injection in industrial burners or Diesel engines. A first process was independently elaborated by two research teams (Canadian and French), as a by-product of research on solid rocket propellants. It does not involve any chemical modification of coal since the ultracarbofluid produced is composed of 40–55% purified carbon dispersed in

30–35% water and 6–20% light fuel oil to which a small amount of tensioactive wetting agent has been added (François and Antonini, 1988). With an ash content smaller than $0.24 \cdot 10^{-3}$ kg/MJ — the condition required to allow direct injection of the fuel in burners — the heating power is 24 MJ/kg at a cost per thermal unit smaller than that of light fuel oil.

Both other processes involve chemical modifications of coal: they are its underground and its *ex situ* gasification (Chiche *et al.*, 1981). In the former, two wells separated by 50–200 meters are drilled down to a coal seam which is then fractured by injection of high-pressure water. The coal is next fired by injecting the gasifying agent (oxygen, pure or diluted) down one of the wells, and the gases resulting from the partial combustion in the underground reaction chamber are collected through the other well. Unfortunately, only a fraction of the energy initially present in the coal is available in the final product. This is also the case with *ex situ* gasification, but the yield is now greater and the composition of the final mixture can be varied at will between that of water gas ($\text{CO} + \text{H}_2$) and of natural gas (95% CH_4), or it can even be a mixture of aliphatic and/or aromatic hydrocarbons with or without heteroatoms (N, O, S).

1.3 CARBONS

1.3.1 Cokes and artificial graphites

The denomination coke was first given to the residues of the industrial preparation of lighting gas (street lighting was installed in London and Paris in 1808 and 1815, respectively) and later extended to the residue of the pyrolysis of any carbon-containing substance, thus obtaining petroleum cokes, pitch cokes, etc. After humidification, ground bituminous coal is heated in refractory ovens to 700–1000°C in the absence of air, thereby losing 20–30% of its dry weight by elimination of a gas which, after a complex process of purification, contains mainly H_2 , CH_4 , CO (Partington, 1949). The composition of the residual coke is then close to C 90%, H 1%, (O+N) 4%, ashes 5%, and its calorific power is 29–33 MJ/kg. Metallurgical cokes are obtained from ‘harder’ coals, richer in carbon and with a lower ash content. The cokes or pitches formed as by-products of petrochemistry are particularly prized for their lower ash content. If necessary, the remaining volatile matter can be eliminated by calcination at 1000–1400°C.

Acheson graphite, produced as early as 1896 at Niagara (USA), is a good example of graphitised carbon or artificial graphite: a mixture of sand and pulverised coke or anthracite is heated for 24 hours by passage of thousands of amperes between two electrodes buried in the mass placed under a protective thick layer of sand in a refractory bricks pit. The product, which is practically devoid of SiO_2 , is probably formed by the growth of microscopic graphite crystals in the coke; it is then ground, mixed under pressure with a carbon-rich binder such as pitch, moulded, and finally heated to carbonise the binder at a rate sufficiently low to prevent the formation of cracks due to a contraction of the mass. If necessary, its graphitisation and electrical conductivity can be increased by heating to a high temperature (Bastick *et al.*, 1965).

Coke is the raw material for the manufacture of artificial polycrystalline graphites. After crushing and grinding, the grains are sieved to the size required for the application envisaged and mixed with other carbon powders (natural graphite, carbon blacks, anthracite, ...), agglomerated with a binder such as pitch, extruded or compressed to the appropriate size, then fired at first to 1000–1200°C to carbonise the binder, and finally graphitised at 2500–3000°C. The objects thus obtained – steel oven electrodes can weigh several tons – can, if necessary, be machined to intricate shapes. Depending on the choice of conditions and parameters, the porosity, crystallinity and size of the grains can vary within wide ranges. The physical properties are, evidently, different from those of the graphite single crystal, but they still show a certain anisotropy partly due to the extrusion and/or compression processes which tend to align the grains.

Although the pyrolysis of organic matter gives impure carbons which all finally yield graphite when heated to 3500°C, the chars differ in their propensity to graphitise if the Highest Treatment Temperatures (HTT) is less than 2000°C (cf. Chapter 4). They are all mostly composed of sp^2 hybridised (trigonal) C atoms and all contain Basic Structural Units (BSUs), which are polycondensed aromatic rings of varying sizes, but it is convenient to distinguish between two main groups:

- a) the so-called hard carbons obtained, *inter alia*, by pyrolysis of cellulose and its derivatives and which often contain sizeable amounts of heteroatoms (Hivert *et al.*, 1961); they do not form lamellar intercalation compounds or graphitic oxide, and the average diameters of the BSU are 5 to 10 Å; their transformation into graphite requires catalytic or mechanical constraints;
- b) the soft carbons, obtained by the pyrolysis of organic aromatic compounds or mesophase pitch (Mouraud *et al.*, 1963) and in which the average sizes of the BSU are larger (20–100 Å). They form lamellar intercalation compounds or graphitic oxide and can yield turbostratic (i.e. disorganised) graphite at fairly low HTT.

The graphitisation evoked above is the ultimate step of carbonisation. It is a complex process in which the intermediate steps depend on the initial nature and structure of the organic material and the conditions of pyrolysis, but more particularly on the HTT. Electron Paramagnetic Resonance (EPR) and magnetic susceptibility determinations (cf. Chapter 7) indicate three different stages (Pacault and Uebersfeld, 1965): a) the rather deep minimum of the diamagnetism at about 700°C indicates the presence of a large number of free radicals created by the elimination of heteroatoms leaving behind carbon atoms with unsaturated valences, hence localised paramagnetic Curie centres; b) up to 1000°C, a decrease in the number of paramagnetic centres, followed between 1000 and 1400°C by a slow increase of diamagnetism due to the delocalisation of lone electrons over aromatic structures; c) from 1600 to 2000°C and thanks to thermal agitation, a decrease in the intensity of the EPR signal caused by the migration of defects resulting in the formation of single and multiple carbon bonds as well as in the increase in the average size of the BSU, with a larger delocalisation of π electrons and the stabilisation of the Landau diamagnetism and Pauli paramagnetism.

At this point, the c axes of the graphitic planes are practically parallel. Fujimoto *et al.* (1994) have defined a comprehensive crystallisation index (CCI) which depends on five structural parameters, all easily determined by X-ray diffraction (XRD) and

pycnometry, allowing a good classification of cokes and pyrocarbons as a function of HTT.

The ultrapure graphite used as a moderator in nuclear industry is made from graphitised carbon by eliminating its impurities. The two processes in use (singly or jointly) are thermal purification, and purification by halogenated derivatives (Odening and Bowman, 1958). Thus, heating at 3000°C for 15–50 hours brings the boron content of some American nuclear graphites to less than 0.8 ppm and the ash content down to 700 ppm. In France, the Carbone-Lorraine process yields equivalent results by heating at about 2600°C under Cl₂. By incorporating metallic fluorides (2.5 wt%) into the coke used in the Acheson process prior to heating, the boron content falls to 0.4–0.8 ppm and the ashes to 100 ppm (Des Rochettes, 1961).

Artificial graphites possess a number of valuable qualities: they are refractory, their coefficient of thermal expansion is low ($1\text{--}8 \times 10^{-6} \text{ }^{\circ}\text{K}^{-1}$), their mechanical characteristics improve up to 2500°C, their thermal and electrical conductivity are good ($8\text{--}16 \times 10^2 \text{ S/cm}$ at room temperature), and their specific gravity is low (1.5 to 2).

1.3.2 Flexible graphite

The intercalation of a volatile reagent (such as sulphuric acid) into natural graphite flakes followed by the brutal expulsion of the intercalate by rapid heating yields highly exfoliated ('expanded') graphite with a considerable volume increase, with pore-volumes ranging from 1.0 to 10 ml/g (Shen *et al.*, 1999). The expanded graphite can be agglomerated by compression or rolling, forming flexible sheets of impermeable graphite which can be cut to shape, of low specific gravity (~ 1.1) and good electrical and thermal conductivity.

1.3.3 Carbon blacks

Carbon blacks are constituted by small, generally spherical particles whose size — 10–500 nm — depends on the method of preparation. The first known carbon black was probably the soot produced by the incomplete combustion of a fuel and used by the ancient Chinese and Hindus to make indelible inks. Nowadays, in the 'channel process', (the oldest), 50–350 Å particles are produced by squashing a flame at the tip of burners on the surface of water-cooled steel pipes (Bachman and Berman, 1960). Somewhat akin to this, in the 'lampblack process', the incomplete combustion of aromatic oils produces soot deposited on cones placed above the burners. Because of their low yields (5–10%), these processes have been replaced by the 'furnace process' (the most widely used) consisting in the incomplete combustion of a gaseous or liquid hydrocarbon fed into a turbulent flame (Shearon *et al.*, 1952). By controlling the air/hydrocarbon ratio and the temperature and shape of the burners, a wide variety of characteristics can be obtained for the 200–750 Å particles, with yields of 25–50%. About 80% of the carbon blacks used industrially are now manufactured by this process (Donnet, 1965). In the 'thermal process', carbon black is formed by the thermal (flameless) decomposition of a hydrocarbon, which must have an endothermic heat of decomposition: the hydrocarbon gas is split into two parts, one of which is burnt to heat the oven into which the other passes and is cracked, forming carbon black and H₂ which is recuperated and mixed with the fuel (Moore, 1932). The yield

of 1200–5000 Å particles is about 40%. Because the decomposition of C_2H_2 is exothermal, ‘acetylene blacks’ only require an initial heating of the gas to 800°C (Kaufmann and Hall, 1948).

Carbon blacks are poorly crystallised solids in which the spherical particles are assemblies of microcrystallites, disordered at the centre of the particle but tending towards an ‘onion peel’ framework at the outer border. The interlayer distances are large: 3.50 to 3.6 Å, and never less than 3.40 Å even after thermal treatment at 3000°C. They are therefore non-graphitisable carbons. Their powdery characteristic does not allow the determination of their intrinsic electrical resistivity since their conductance is largely conditioned by the inter-particle contacts. The values given by measurements on compacted powders depend on the pressure applied: for moderate values (a few tens MPa), the resistivities lie between 10^4 and 10^{-1} Ωcm, decreasing with temperature (semi-conducting characteristic). Similarly, the finely divided structure of the carbon blacks, (specific surface of a few tens to a few hundreds m²/g) brings about specific surface properties due to the presence of numerous free radicals and groups (mostly oxygenated), upon which the chemical reactivity depends (Donnet, 1968; Puri, 1970).

The particles of carbon black generally form more or less rigid aggregates (improperly termed ‘primary structures’) whose little understood mechanism of formation is probably connected with the creation of the particles themselves. Acetylene carbon black, sometimes known as ‘chain black’, is particularly prone to give large aggregates.

1.3.4 Pyrocarbons

Pyrolytic carbons, or ‘pyrocarbons’, are massive deposits obtained by the thermal decomposition of hydrocarbons on a substrate (generally polycrystalline graphite) at a closely controlled high temperature (800–2000°C) since the characteristics of the crystalline deposit formed depend on the conditions of formation (nature and flow-rate of the gas, temperature of the surface) and on any following annealing treatments (Tombrel and Rappeneau, 1965). In order to prevent the formation of carbon black, the Vapour Phase Chemical Deposition (VPCD) reaction must be carried out with a low concentration of the active species in the vapour phase, either by maintaining a low pressure or by diluting the active species in an inert carrier gas (H_2 , N_2 , Ar, He). The rate of deposition is therefore low, from 1 μm to 1 mm per hour. The deposit can be separated from the substrate and obtained as plane or curved plates $200 \times 100 \times 8$ mm³.

The growth of the pyrocarbon layer is not epitaxial: cone-shaped formations are observed starting from sites on the substrate, which give to the surface a granular aspect. Nevertheless, the preferred orientation of layers is parallel to the plane of the substrate, and the physical properties of the pyrocarbon are therefore strongly anisotropic: the thermal and electrical conductivities are high parallel to the average plane, and very weak perpendicular to it.

Another interesting property of pyrocarbons is gas-tightness: their permeability is 4 to 10 orders of magnitude smaller than that of artificial graphites. They are therefore used to render these graphites gas-tight and to protect them from corrosion and oxidation by depositing a thin layer of pyrocarbon on their surface. They are also used to form the matrices of fibre-reinforced carbon-carbon composites.

By submitting pyrocarbons to compression at high temperature ($\sim 3000^\circ\text{C}$) followed by annealing, the preferential orientation of the crystallites is considerably improved: the angular misorientation of the c axes is reduced to less than 1° (Moore, 1973), and the size of the crystallites is considerably increased, up to the micrometer rather than the nanometre range in the initial pyrocarbon. Though polycrystalline, the compressed pyrocarbon, which is commercialised under the names HOPG (Highly Oriented Pyrolytic Graphite, from Union Carbide, U.S. of America), and PGCCL (PyroGraphite Comprimé Carbone Lorraine, from Le Carbone Lorraine, France) is very close to monocrystalline graphite and it has therefore been much used in fundamental research since the size of natural single crystals of graphite is seldom larger than one millimetre.

1.3.5 Glassy carbon

The controlled carbonisation of natural or artificial cellulose (viscose) (General Electric Co., 1961) or of various phenol-based or furfurylic resins yields a hard, smooth and shiny non-graphitisable carbon of low open porosity but high closed microporosity, which can be still further decreased by heating at $2500\text{--}3000^\circ\text{C}$. Even though its microstructure is characteristic of a non-graphitisable carbon, its conchoidal fracture has given rise to the name 'glassy carbon'. It cannot be machined, and objects of glassy carbon must be shaped before being fired. Its permeability coefficient K is about 10^{10} less than that of polycrystalline artificial or natural graphite (Yamagushi, 1963). The combination of low specific area ($0.1\text{--}1\text{ m}^2/\text{g}$) and low density ($1.4\text{--}1.5\text{ g/cm}^3$) points to a large proportion of closed cavities. Similarly, the resistance to oxidation — about 3 times that of graphite — indicates a structure in which most C atoms are trigonal, with a reticulation by tetragonal (sp^3 hybridised) carbons and absence of long-range order. Films $200\text{ mm} \times 200\text{ mm}$ of glassy carbon with good resistance to corrosion have been obtained by pyrolysis of Kapton-500H sheets between two highly polished graphite plates; their electrical conductivity is 400 S/cm and the X-ray diffractograms give $d_{002} = 3.353\text{ \AA}$ (Uwai and Inagaki, 1990), in which d_{002} is the mean interlayer distance, as determined by XRD.

1.3.6 Carbon fibres¹

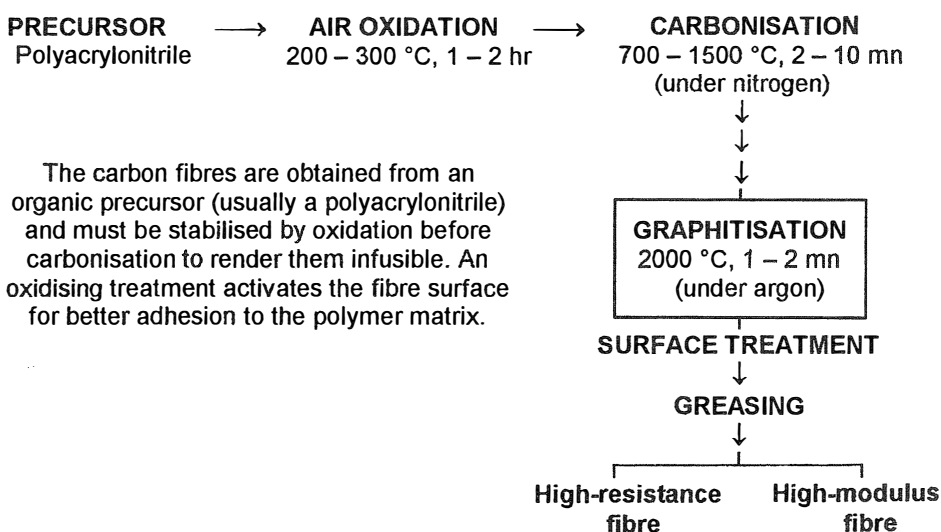
Carbon fibres can be classed into two categories: natural fibres, formed by crystal growth during thermal processes such as cracking of various hydrocarbons on catalysts (Rodriguez, 1993), and synthetic fibres, obtained by pyrolysis of previously spun and twisted textile fibres, or by carbonisation of fluids (the 'precursors') extruded through a die (Cranch, 1962). They can be obtained from a number of precursors in the condensed or gaseous phase (cf. Table 1.1). Starting with a solution of polymer(s) which is spun after passage through a nozzle at room temperature, the yarn is reticulated by partial oxidation at $200\text{--}300^\circ\text{C}$ and thus stabilised for carbonisation at $1000\text{--}1100^\circ\text{C}$. The last treatment at $1300\text{--}3000^\circ\text{C}$ improves the crystallinity and

¹A large part of this Section is due to Serge Flandrois (Centre de Recherche Paul Pascal, C.N.R.S., Bordeaux).

Table 1.1: Principal manufacturing methods for and general characteristics of carbon fibres

<i>Initial phase</i>	<i>Precursor</i>	<i>Method</i>	<i>Graphitizability</i>	<i>Denomination</i>
Condensed	Isotropic pitch	Spinning of molten pitch, then carbonisation	Non graphitisable	ex-pitch
	Solution of polyacrylonitrile	Spinning, then carbonisation	Partially graphitisable	ex-PAN
	Mesophase pitch	Spinning of mesophase, then carbonisation	Graphitisable	ex-mesophase
Gas	Benzene or methane	VPCD in the presence of a catalyst	Highly graphitisable	ex-benzene or ex-methane

fixes the physical properties. The fibres are nearly always elaborated as sketched in the diagram in Fig. 1.1. Although a large number of polymers can be similarly processed, only PAN (polyacrylonitrile) fibres have now been retained as basis of an important industrial production of high-modulus and high-resistance fibres because of their superior characteristics. Among other precursors, mesophases obtained by extraction in a solvent of the discotic phase formed by a thermal treatment of coals or pitches

**Figure 1.1:** Diagram of the manufacturing process of a PAN carbon fibre (Elf-Aquitaine, FILKAR-T300).

(Otani *et al.*, 1969; Chen and Diefendorf, 1983) are important as the 'ex-mesophase pitch' fibres are particularly well adapted to spatial applications (Singer, 1982). It has been shown that the best cross section for this use is in the shape of a three-leaved clover (Stoner and Edie, 1990), which can easily be obtained with the proper nozzle for the extrusion die, and that the mechanical properties improve up to 1300°C (Tanabe *et al.*, 1990). After the thermal treatments appropriate to the nature of the precursor, the following values have been obtained: elastic limit (tension) $\sigma_R = 7$ GPa (steel: 1 GPa); modulus of elasticity: $E = 700$ GPa (steel: 200 GPa); specific gravity ≈ 2 (steel: 7.8) (Martineau and Naslain, 1987).

Other fibres are made from isotropic pitches or from mesophase by processes essentially similar to the one described above. The fibres obtained from isotropic pitches are cheaper, but their mechanical characteristics are not as satisfactory (Johnson *et al.*, 1975) and they are therefore solely used as reinforcement for concrete. In contrast, the mesophase — which can be extracted from certain tars — is composed of highly anisotropic molecules in a nematic liquid crystal phase (Gasparoux, 1984; Lewis, 1984); and the passage through the nozzle of the die plate gives the molecules an orientation parallel to the axis of the draught, thus conferring to the carbon fibres obtained by the subsequent carbonisation quite exceptional performances (Bacon, 1980). The fibres, however, are expensive, principally owing to the cost of extracting the mesophase, which is only present in small concentration in tars or pitches.

The diameter of ex-PAN or ex-mesophase fibres is usually 5–10 μm . The carbon layers are oriented parallel to the axis of the fibre, but the texture (i.e. the organisation of the layers) depends on the precursor and the conditions of preparation: in the cross section of the fibre, the carbon layers can be found to be in a radial, concentric, or random configuration.

Carbon fibres can also be obtained by the thermal decomposition of a hydrocarbon (usually benzene or methane) in the presence of fine particles of a metallic catalyst (such as Fe, Ni, Co). Those obtained by this method ('Endo-type fibres'; Endo *et al.*, 1982), and particularly those obtained by cracking of benzene in the presence of iron particles, are short (a few millimetres to a few centimetres), whereas those obtained by the methods previously described can be kilometres long. It was shown (Oberlin *et al.*, 1976) that carbon from the gas phase is dissolved in the iron particles and crystallises out as coaxial graphitic carbon layers when the particle is saturated. In the process developed by Murayama *et al.* (1990), the growth of the graphitic carbon layers out of Fe_3C particles is perpendicular to the axis of the fibre. After an appropriate thermal treatment, Endo-type fibres are highly graphitised, and their electrical conductivity is large (Ohhashi *et al.*, 1983).

The physical properties of all the fibres also depend on the precursor and the subsequent highest treatment temperature (HTT). Thus, when the HTT is high ($\rightarrow$ graphitic fibres), Young's modulus is larger (high modulus fibres) than when HTT is low ($\rightarrow$ low modulus fibres), but the elastic limit of the latter is generally larger, hence the name 'high resistance fibres'. The electrical conductivity is also very much affected by the HTT, with highest values yielded by markedly semi-metallic vapodeposited carbon fibres heat treated to 3000°C. Ex-mesophase fibres have somewhat similar properties, as seen in Table 1.2.

The possibility of obtaining coiled natural carbon fibres has been demonstrated, and the ones prepared by the Ni- or Mo-activated pyrolysis of acetylene containing

Table 1.2: Physical properties of some typical carbon fibres.

Type	Reference	Density (g/cm ³)	Young's modulus (GPa)	Elastic limit (GPa)	Electrical resistivity ^a (μΩ cm)	Coefficient of thermal dilation ^a 10 ⁶ α (°K ⁻¹)
ex-PAN						
low modulus	T 300	1.76	230	3.5	1800	0.3
medium mod.	T 800	1.81	294	5.6	1400	0.1
medium mod.	T 1000	1.82	294	7.0	1400	
high mod.	M 40	1.81	392	2.7	800	-1.2
	M 50	1.91	490	2.4	800	
	GY 70	1.96	517	1.9	650	
ex-mesophase						
	P-55	2.02	380	2.1		-0.9
	P-75	2.06	500	2.0		
	P-100	2.15	690	2.2		
	P-120		820	3.2	250	-1.6

^aalong the fibre axis

a small amount of a phosphorus compound are particularly striking (Motojima *et al.*, 1995): single or double helical coils (diameter 5–15 μm), usually of circular cross section (~0.5–2 μm) and fairly constant pitch are obtained in good (45%) yield.

1.3.7 Active carbons²

Activated or porous carbons — in the form of carbonised wood — have been utilised for many centuries. Around 1500 BC, the Egyptians used these materials for medicinal and purifying purposes, while the Hindus of India used activated carbon for purifying drinking water. However, production on an industrial scale was not established until the beginning of the 20th century and, even then, these early materials were employed only in very simple processes. Interest in the use of porous carbons for gas separation was stimulated by the need for a durable high adsorption capacity material for use in gas masks during World War I. Since 1918, production techniques have continued to be developed and a range of processes are now available for the production of porous carbons from nut-shells, wood, coal, lignite, peat and coal tar. The range of application of these materials has also increased and porous carbons are now used for the removal of many contaminants from air, gas, water and other fluids. The char obtained by the pyrolysis at rather mild temperatures (< 700°C) of vegetal substances, such as fruit stones, wood, sawdust, copra, lignite, etc., is activated by one (or more) oxidising agent(s) such as steam or CO₂ (*physical activation* or, better, *thermal activation*), or by phosphoric acid, NO₂, nitric acid, ZnCl₂, etc. (*chemical*

² A large part of this Section is due to Roland Pellenq (Centre de Recherche sur la Matière Divisée, C.N.R.S., Orléans).

activation) (Baker, 1992). Industrially, steam activation is preferred for the large-scale preparation of active carbons, as it is considerably faster than activation by CO₂ (Wigmans, 1989). The oxidation creates pores and increases the specific area to 1000–1500 m²/g, forming dangling bonds and active sites by the local elimination of atoms. Depending on the nature of the precursor and their mode of activation, their specific area and pore-size distribution will vary considerably (Bansal *et al.*, 1988). Fairly arbitrarily, a pore is said to be a *micropore* if its average size is <2 nm, or a *mesopore* (2–50 nm), or a *macropore* (>50 nm).

Superactive carbons (AMOCO Corporation, USA; 'MAXSORB', Kansai Coke and Chemicals Company, Japan) have recently been produced, with quite larger specific areas, in the range 2200–3500 m²/g. The Wennerberg and O'Grady (1978) patent and the preparative procedure of Otowa *et al.* (1993) describe the high-temperature treatment of petroleum coke mixed with excess KOH followed by adequate washing to remove all the soluble results of the reactions which finally yield complex structures with a total pore volume in excess of 2.5 cm³/g.

ACF (Activated Carbon Fibres) are increasingly used industrially in purification and recuperation processes, as witnessed by the 200 tons/year used industrially in Japan (Suzuki, 1994). The preparation of CFCMS (carbon fibre composite molecular sieve), its properties and use for the separation of the components in various gas mixtures has been described in detail (Burchell *et al.*, 1997): the macroporous composite made from isotropic pitch-derived CarboflexTM fibres and charred phenolic resin can be moulded into almost any shape, has a minimal resistance to bulk gas flow and routinely develops surface areas above 100 m²g⁻¹. It is electrically conductive so that Joule effect heating can be used to desorb adsorbed gases.

More recently, techniques have been developed for the production of porous carbon from various cloths and polymers and allowing a degree of control over a range of pore sizes in the final product leading to the development of more sophisticated grades of porous carbons. In most cases, however, and apart from the difference in behaviour due to the difference in type of pores present, physisorption of the adsorbed species on the AC is sought, rather than chemisorption.

1.3.7.1 *Physisorption versus chemisorption*

It is important to distinguish between physisorption, or physical adsorption involving only relatively weak intermolecular forces, and chemisorption, which essentially involves the formation of a chemical bond between the sorbate species and the surface of the adsorbent. The nature of the sorbed species is irreversibly changed during a chemisorption process: catalytic phenomena concern chemisorption processes whilst adsorptive separation processes depend on physical adsorption. Physisorption is characterised by the following general features: (i) a rather low heat of adsorption, of the same order of magnitude as the latent heat of gas liquefaction of the species concerned; (ii) sorbate molecules located at potential minima in the field of the surface atoms; (iii) the possibility of having several layers of adsorbed molecules owing to the non-specific character of physisorption; (iv) the presence of fast diffusion processes characterised by a high value of the diffusion coefficient; (v) no electron transfer although polarisation of the sorbate may occur. In contrast, the characteristics of chemisorption are: the presence of the adsorbate at specific sites which only permit

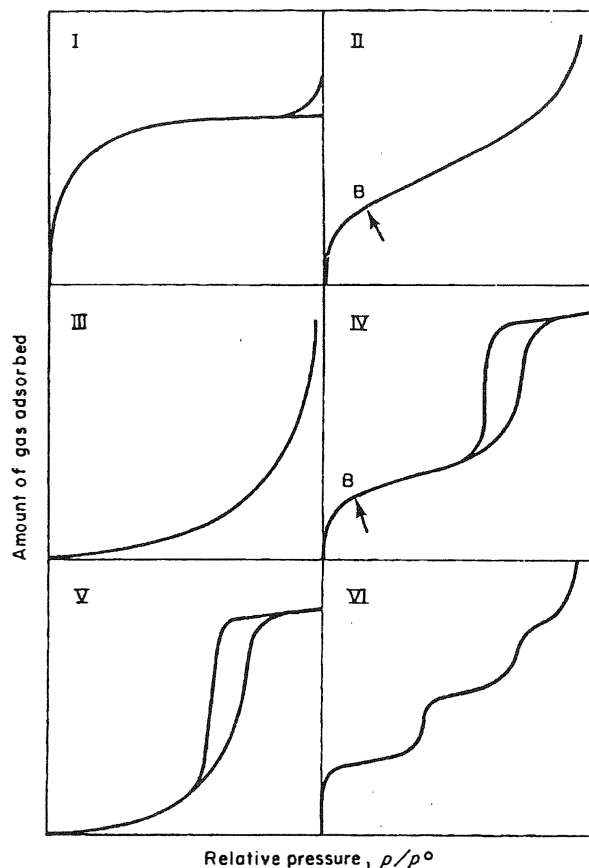


Figure 1.2: Classification of the physisorption isotherms.

the formation of a monolayer, rather slow diffusion processes involving bond formation, and significant overlap of the wave functions of the different species. Moreover, physisorption processes strongly depend on surface geometry and chemical composition, which both govern phenomena such as monolayer phase transitions, layering transitions (on planar surfaces) or capillary condensation (in mesoporous materials).

The type(s) of pore(s) in a given AC is of primordial importance with respect to the use to which the absorbent will be put, and an extremely large number of methods are available for the determination of the absorption characteristics of a given type of AC, most of which largely depend on the study and analysis of the shape of gas adsorption isotherms of the AC.

1.3.7.2 IUPAC classification of the gas adsorption isotherms

Ever since the seminal paper by Brunauer *et al.* (1938), adsorption isotherms have been classified into six types (Fig. 1.2). All the diagrams show the amount of gas

adsorbed at a pressure P plotted as a function of the reduced pressure x , with $x = P/P_0$ in which P_0 is the saturation pressure:

Type I: observed for adsorption in microporous materials; for many years, the steep rise at low pressure followed by the plateau at higher pressure was interpreted in terms of the Langmuir theory of monolayer adsorption, but it is now accepted that this mechanism is not applicable to physisorption in micropores.

Type II, typical of non-porous or macroporous solids, represents unrestricted monolayer-multilayer formation; the sharpness of the 'knee' at B reflects the relative strength of the adsorbate-adsorbent interactions, as compared to the adsorbate-adsorbate interaction.

Type III: this shape of isotherm arises from an adsorption mechanism dominated by adsorbate-adsorbate interactions and reduced strength of the adsorbate-adsorbent interaction.

Type IV: in the low pressure domain, the monolayer-multilayer adsorption is the same as in Type II. At higher pressure, the presence of mesopores in the adsorbent allows capillary condensation — *i.e.* condensation of the confined gas into liquid — and causes an upwards swing in the isotherm ending in a plateau. The condensation occurs at a relative pressure smaller than unity (bulk case).

Type V: the adsorption mechanism at low relative pressure is similar to that of the Type III isotherm and characteristic of weak adsorbate-adsorbent interactions (compared to adsorbate-adsorbate interaction). At higher pressure, the presence of mesopores results in a capillary condensation similar to that of the Type IV isotherm.

Type VI: This uncommon isotherm represents stepwise multilayer adsorption on an energetically uniform non-porous surface; the steps are due to large difference in potential energy between molecular layers.

A number of isotherms do not fit clearly into these categories and many show characteristics of more than one type: thus, adsorbents with micropores and mesopores would exhibit mixed Type I/Type IV isotherms.

1.3.7.3 *Influence of pore size on capillary condensation*

The phenomenon of capillary condensation visible in Type IV and Type V isotherms is a good example of the difference in the thermodynamics of a confined fluid compared to that of the bulk fluid. The desorption branch forms a hysteresis loop attributed to the occurrence of metastable states (capillary condensation is a first order transition, at least in simple pore geometry such as slits and cylinders) and/or to pore blocking phenomena associated with pore connectivity in disordered porous materials (percolation transition): desorption is delayed until there is a percolative gas path from a given pore up to the external surface of the system. Provided that the adsorption experiment be run at a temperature lower than the critical capillary temperature T_{cc} at which the hysteresis loop disappears, the theory for the adsorption on the internal surface of an infinite cylinder predicts a Type IV isotherm characterised by a capillary condensation discontinuity and a hysteresis loop due to the non-superposition of the adsorption and desorption branches: during adsorption, at pressures higher than that corresponding to the hysteresis closure point, and because the system does not have fluctuations of sufficient amplitude to probe and find the equilibrium state (free energy barrier), the adsorbed film (wetting is assumed) is in a metastable state and misses out the transition to its true free energy minimum. By contrast, capillary

evaporation is assumed to occur at equilibrium. At $T > T_{cc}$, the reversible adsorption/desorption isotherm curve increases monotonically with no discontinuity. For a given adsorbate, the smaller the cylinder diameter, the lower the critical capillary temperature. T_{cc} is always lower than that of the bulk homogeneous phase. For pores of diameter less than 15–20 Å, no capillary condensation is observed, whatever the temperature. This limit in pore size in cylindrical geometry is the frontier between the *meso*- and the *micro*-porosity. In a micropore, a fluid cannot undergo a first order capillary transition and is therefore always in supercritical conditions, for the following reasons: (i) the molecules of fluid are confined in the potential field of the solid matrix, stronger compared to the field due to other molecules of its kind; (ii) the small number of neighbours due to reduced confining space prevents any co-operative effect. The adsorption theory has been validated with simulation on simple geometries (slits and cylinders) and experiments on different MCM-41 samples, a commercial mesoporous aluminosilicate characterised by a uniform mesoporosity. For less uniform materials, the condensation/evaporation hysteresis loop can also be explained on the basis of the percolation theory: during desorption, a given pore filled with condensate requires connection to a larger pore already filled with gas in order to undergo its (local) capillary evaporation. Desorption occurs when the set of pores filled with gas constitutes a percolation network connected to the outer surface of the mesoporous sample. The evaporation delay giving rise to the hysteresis loop is then the consequence of pore constrictions and of the geometries of the bottlenecks. There is however no experimental evidence of the percolation process, even though the 'metastable state theory' is found to give a good account of experimental observations in systems such as MCM-41. In the case of disordered mesoporous materials, the determination of the adsorption/desorption mechanism from a simple analysis of isotherms is therefore a difficult task since it may result from 'single tube' behaviours competing with network effects.

1.3.7.4 Determination of the specific surface

Although no single method can be said to be fully satisfactory, gas adsorption has been extensively used for the assessment of the specific surface area (A_s). If a gas can be adsorbed by a known weight of AC under conditions such that a single compact layer of molecules carpets the whole surface of the solid, the determination of the amount n_m of gas thus adsorbed (expressed for instance in cm³/g at STP) and a knowledge of the area occupied by each molecule (a_s in Å²) immediately yields

$$A_s = n_m a_s N_a 10^{-20}/22414 = 0.269 n_m a_s$$

in which N_a is Avogadro's number, 22414 is the molar volume in cm³ of an ideal gas at STP, and A_s is in m²/g. The method most commonly used for the identification of n_m was proposed by Brunauer *et al.*, (1938). The BET adsorption isotherm is written as:

$$\frac{x}{n(1-x)} = \frac{1}{n_m c} + \frac{c-1}{n_m c} x$$

where x is the reduced pressure, n is the amount adsorbed at pressure P and n_m can be found by plotting the quantity $x/[n(1-x)]$ versus x . In many cases, the plot is linear

over a restricted range of reduced pressures and, from the slope and intercept of this linear portion, n_m and c can be evaluated through

$$n_m = 1/(\text{slope} + \text{intercept}) \text{ and } c = 1 + (\text{slope}/\text{intercept}).$$

It is interesting to note that the BET isotherm equation can be derived analytically from statistical thermodynamics. However, the underlying assumptions of the model are drastic and such that it usually is seldom applicable to real cases. The main assumptions are: (i) that adsorption takes place on identical sites (it is a localised adsorption model for energetically homogenous surfaces); this is only true at the low temperature limit even for homogenous surfaces; (ii) that adsorbate-adsorbate interactions are partially taken into account (two adsorbate molecules interact only if they are piled up over an adsorption site, and interactions between adsorbates pertaining to different sites are neglected). The inadequacy of such an approximate theory is not always apparent when it is compared to experiment as the model contains two adjustable parameters, the constants ϵ_1 , the strength of the adsorbate-surface interaction, and ϵ_2 for adsorbate-adsorbate interaction, so that $c = \exp[(\epsilon_1 - \epsilon_2)/kT]$. In particular, the BET model should not be applied to Type I isotherms since the adsorption mechanism in microporous solids is very different from that assumed in the BET model. Even for non porous materials, the BET assumptions are in clear contradiction with the existence of a liquid-like layer wetting the overall surface of the solid phase. In general, the BET specific surface area should be considered as a *qualitative fingerprint* of the adsorption process for a given adsorbate/solid couple. Note that the relative value of the BET c constant can be a useful qualitative guide to the relative strength of the adsorbate-adsorbate and adsorbate-solid interactions. For values close to unity (*i.e.* for isotherms not having a well defined 'knee'), it is often stated that the BET surface area is not accurate. In fact, it has been shown that this situation occurs when the adsorbate does not form a uniform layer on the available surface but rather forms drops in areas of larger surface curvature, in other words when the adsorbate does not wet the surface. This shows a further weakness of the BET surface area calculation which implicitly assumes wetting (which also depends on temperature).

1.3.7.5 Assessment of the microporosity

Type I isotherms are generally associated with microporous solids. The physisorption of gas molecules in very narrow pores such as micropores takes place in the form of volume filling, at low relative pressure. The mechanism of adsorption in micropores is intrinsically different from capillary condensation that characterises adsorption in mesopores. In mesoporous solids, the pores are large enough so that a phase transition such as capillary condensation can occur. In microporous solids, the reduction of space is so important that one approaches the 1-D limit for which it is known that no (first order) phase transition is possible. It is often referred to an enhancement of the adsorption field when considering adsorption in micropores. In other words, in micropores, the adsorbate-solid interaction energy is always much larger than the adsorbate-adsorbate interaction energy. The structure of the adsorbed phase is entirely dictated by the adsorbate-solid potential energy.

It is clear that in the case of purely microporous solids, the microporous volume corresponds to the volume of fluid taken in at the well-defined plateau of the related Type I isotherm. For solids having both micropores and mesopores, the a_s method provides a relatively easy way to the assessment of the microporosity by using the adsorption isotherm data. This method provides a means of comparison of an experimental isotherm with a standard isotherm determined for a non-porous reference material (assuming that both the solid under study and the reference material have the same surface chemistry). The application of the a_s method therefore depends on the availability of a suitable reference adsorbent. The comparison is achieved by plotting the amount adsorbed by the sample at a particular relative pressure against the a_s quantity which is defined as the ratio between the adsorption by the reference material at the same relative pressure and the adsorption by the reference material at an arbitrary state. This reference state is usually taken at $P/P_0 = 0.4$ for nitrogen adsorption at 77K since capillary condensation (i.e. a mesopore filling) occurs at higher relative pressures. A non-porous solid gives a linear plot passing through the origin, and deviations from the straight line can be interpreted in terms of sample porosity. The microporous volume is then evaluated by back-extrapolation at $a_s = 0$. It is often found in the literature with reference to the Dubinin-Radushkevitch equation used to evaluate the microporous volume. In this approach, the microporous volume is obtained from the intercept of the linear region in the plot of the logarithm of the amount adsorbed versus $\log^2(P/P_0)$. Note that both methods presented here for the evaluation of the microporosity are empirical. In particular, the Dubinin-Radushkevitch equation has no theoretical grounds: this is particularly clear when P approaches zero.

1.3.7.6 Assessment of the mesoporosity

The existence in a sample of a range of porosity extending from about 2 nm to a few tens of nm profoundly modifies the shape of the physisorption isotherms. The most obvious modification is the presence of a *hysteresis loop* between the absorption and desorption paths (cf. Fig. 1, Types IV and V) associated with the presence of more-or-less well marked vertical *steps* due to capillary condensation. Another frequent modification is the appearance of *saturation* at high relative pressures of the amount adsorbed, indicating that all the pores whose size can admit the gaseous molecules have been filled. This is easily illustrated by the behaviour of non-porous powder during its compaction which transforms the initial macroporosity into mesoporosity: as compaction increases, the modifications described above progressively appear until sintering eventually eliminates all macroporosity.

The physical origin of capillary condensation lies in the fact that the vapour pressure in equilibrium with a concave meniscus of a liquid is lower than the pressure P_0 found over a plane surface of the same liquid at the same temperature, implying that a gas in a pore and at a pressure P lower than P_0 can condense. The relationship between P and the radius of curvature r_m of the meniscus is:

$$\ln(P/P_0) = 2\gamma V_l / (RT r_m \cos \Phi)$$

in which γ is the surface tension, V_l is the molar volume of the liquid, and Φ is the angle of contact. In actual fact, capillary condensation occurs only in pores whose

internal surface is already covered by an adsorbed film, not in totally empty pores. Since the angle of contact varies with the thickness of the adsorbed film, the exact determination of the size of the pores is quite complex. In practice, it is generally admitted that, at least during desorption, $\Phi = 0$, and the size of the pore is calculated by adding to the 'core' (deduced from the value of r_m) the thickness t of the adsorbed layer. The relationship between r_m and the real size r_k of the core depends of course on the shape of the pore. A number of simple shapes have been considered: cylinders, wedges, slits, packed spheres, etc., but the simplest models are based on cylindrical shapes. The value of t at a given relative pressure is determined from reference isotherms obtained by determinations of the adsorption over non-porous solids.

Among the numerous methods which have been used to determine the distribution of pore sizes dV_p/dr_p (which all imply the choice of a model shape), the one most frequently used is the B.J.H. method (Barret *et al.*, 1951) based on the analysis of the desorption isotherm, starting from the highest relative pressure reached during the adsorption. Discrete intervals $\Delta P/P_0$ are defined, and the quantity of gas desorbed at each decrement is taken to be due to two contributions: (i) that from pores of mean radius r_p whose content is desorbed by capillary evaporation (decondensation) leaving behind an adsorbed multilayer of decreased thickness; (ii) that from pores whose content was only the adsorbed multilayer of decreased thickness. Knowing v_a , t and r_p , and assuming a specific shape for the pores yields, by recursive computation, the area of the walls and the volume of each category of pores. The sum of these values gives the specific cumulated area $a_{s(cum)}$ and the cumulated porous volume $V_{p(cum)}$. The comparison of these values with the specific BET surface and with the volume adsorbed at saturation are indications of the validity of the model adopted for the pores in the solid under study.

The shape of the pores also influences the shape of the hysteresis loop, and De Boer (1958) has identified five types of loops associated with specific shapes of mesopores. During adsorption, condensation is nucleated at the points with the shortest radius of curvature, but, during desorption and when a pore volume is filled, evaporation can only occur over a free surface. Each pore shape therefore leads to a specific behaviour. Cone- or wedge-shaped pores are particular in that they lead to strict reversibility of the evolution of the menisci during adsorption or desorption, hence to the absence of hysteresis. The hysteresis loop due to cylindrical pores open at both ends is characterised by a value of 2 for the ratio of radii relative to adsorption ($r_m = 2 r_k$) and to desorption ($r_m = r_k$). Bottle-shaped pores with a neck and a cylindrical or truncated conical cavity have been most systematically investigated. Pores bounded by two parallel plates at the distance Δ from each other produce a step at $r_m = \Delta$ during desorption but do not show capillary condensation during adsorption for lack of a meniscus. The complex-shaped pores due to the compact stacking of spheres lead to hysteresis, and the radius of curvature connected to the step during adsorption is close to the radius of the inner cavities in the stack but the radius of curvature connected with the step in desorption is close to the radius of the circles inscribed in the gateway to these cavities.

1.4 CARBON AS AN ELEMENT

Even taking into account the ever increasing abundance of known organic compounds, it is clear that elementary carbon is ideally suited to illustrate practically all

aspects of the physics or chemistry of solids: thus, its structure can be perfectly isotropic and three-dimensional (3D) in diamond, or anisotropic and bi-dimensional (2D) in graphite, or even more anisotropic and linear, hence practically uni-dimensional (1D) in the polymers of acetylene and the carbynes. In 1917, Debye and Scherrer showed by XRD that coals have the same structural elements as graphite and are therefore, along with diamond and natural graphite, a possible source of elementary carbon.

Carbon, the first element in the IV A series of the periodic classification, has pronounced non-metallic features and will rather accept than give electrons. However, its $(1s)^2(2s)^2(2p)^2$ electronic structure, corresponding to its atomic number $Z = 6$, enables it to form both CCl_4 by yielding four electrons to the Cl atoms, and CH_4 by accepting four electrons from the H atoms, i.e. to be amphoteric; this characteristic is also encountered — at least in part — in the different allotropic forms of elementary carbon: the ionisation energy of atomic carbon ($E_1 = 11.3$ eV/mole) is quite different from that of graphite for which the experimental value $E_1 \approx 4.00\text{--}4.30$ eV/mole is generally admitted, in agreement with the calculated value $E_1 = 4.07$ eV/mole (André and Leroy, 1969). Similarly, the electronegativity of carbon, viz. $X(\text{C}) = 2.5$ (Pauling, 1960) is different from that of graphite $X(\text{gra}) = 1.83$, calculated from the heat of formation of the alkali metal-graphite compounds (Setton, 1962). Evidently, the reactions or properties of a given allotropic form can only be extrapolated to the other forms within strict and very precise limits.

In line with the definition of allotropy given above, Heimann *et al.* (1997) have drawn up a classification of the various elemental allotropes and molecular forms of carbon. As seen in Table 1.3, besides the ‘usual’ hybridisations (sp^1 , sp^2 , sp^3), structures involving more than a single type of hybridisation (mixed forms) and intermediate hybridisations of type sp^n (with $1 < n < 3$, $n \neq 2$) are included. The former cover mixed short-range order carbon species with more-or-less randomly distributed C atoms, while the latter describe structures in which curvature introduces strains responsible for the admixture of different hybridisations; thus, and as explained in greater detail in Sec. 2.2.1.2, the structure of the fullerene C_{60} leads to attributing to the C atoms a hybridisation intermediate between sp^2 and sp^3 (Haddon, 1993), i.e. $sp^{2.28}$.

1.4.1 The thermodynamic phase diagram of carbon

A phase diagram is a description of the stability domains of the different phases [gas, liquid(s), solid(s)] of a pure species as a function of two intensive variables, such as the temperature T and pressure P . Although the gaseous and liquid phases of any pure compound are usually unique, its solid phase may be polymorphic, as with carbon, of which three solid crystalline phases are presently known, namely diamond, graphite, and the carbynes (cf. Table 1.3). For a chemical element, the different solid phases constitute *allotropic forms*, with each form describable by a specific equation of state and differing by the spatial arrangement of its atoms, (Addison, 1964). In the case of carbon, this definition of allotropy should be completed by ‘and by the type of chemical bonds between the atoms’ lest different polymorphs — such as the cubic and hexagonal forms of diamond (*vide infra*) — be considered as different allotropes.

The thermodynamically stable phase of carbon corresponding to an absolute minimum of free energy (F) and to the stability criteria of Gibbs-Duhem at NTP

Table 1.3: Classification scheme for carbon allotropes, molecular crystals, and derived forms (after Heimann *et al.*, 1997). The Roman numbering scheme for the classification of carbons is due to Whittaker and Wolten (1972). The values in *italics* refer to the empirical classification of carbon forms by Joffe and Regel linking the physical dimension d with the coordination number z , namely $z = d + 1$ (cf. Section 2.2.1.3).

sp^3	sp^2	sp^1
Diamond Cubic (C III) Hexagonal (C IV, Lonsdaleite)	Graphite Hexagonal (C I) Rhombohedral (C II) C VII ^a	Carbyne α -Carbyne β -Carbyne Chaoite (C V) C VI ^b , C VIII ... C XIII
$d = 3; z = 4$	$d = 2; z = 3$	$d = 1; z = 2$
$sp^3 + sp^2 + sp^1$	sp^n (<i>with</i> $3 > n > 1, n \neq 2$)	
Mixed forms of carbon	Intermediate forms of carbon	
Amorphous carbon	$3 > n > 2$	$2 > n > 1$
Glassy carbon	Fullerenes, C _x	Cyclo(N)carbons
Carbon blacks	$x = 60, 70, 84, \dots$	$N = 18, 24, 30, \dots$
Adamantine carbon	(when $x = \infty, n = 2$)	(when $N = \infty, n = 1$)
etc.	Carbon onions	
	Carbon nanotubes	
	etc.	
	$d = 2; z = 3$	$d = 1; z = 2$

^aThis form of carbon corresponds to the $\cdots AA \cdots$ stacking, reported to have been found in meteorites (Sclar and Squiller, 1979); ^bWhittaker and Wolten, 1972.

(normal temperature and pressure) (Bundy, 1989) is hexagonal graphite. Nevertheless, other secondary and local minima of free energy corresponding to perturbations imposed on the system may exist: as exemplified by Hoffmann (1987), the path followed by the system to transit from the stable to any other state may go through a maximum of free energy, in which case a metastable state is reached, or it may be monotonous, in which case the result is an unstable state (Fig. 2.11). A case in point is cubic diamond, which may have an 'infinitely' long life span at NTP, but this information is beyond the reach of thermodynamics. Experimentally, the formation of a metastable phase under conditions far from equilibrium requires an external source of energy. The phase thus prepared is said to be 'kinetic' if or when the time required for its transformation back to the stable state is negligible with respect to the time-scale of observation. This important point is at the basis of the present means of preparation of new varieties of carbon described in Chapter 2.

Allotropy entails the presence of one or more triple points, each characteristic of a combination of pressure and temperature allowing, at each of these points, the coexistence of three distinct phases. The phase diagram of carbon in Fig. 1.3 is the

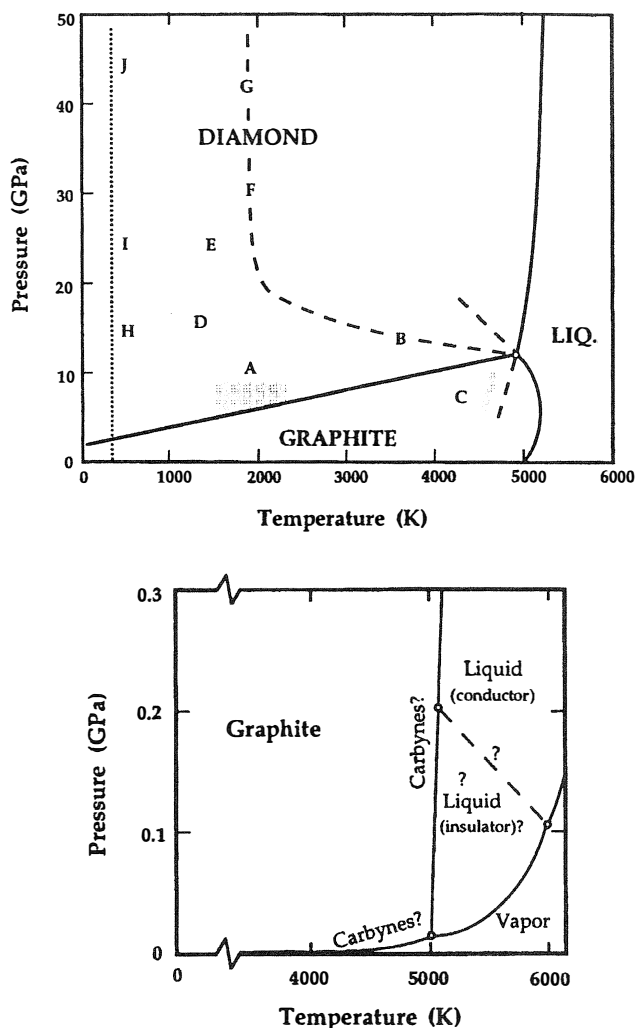


Figure 1.3: *Top:* The P - T phase and transition diagram for carbon (after Bundy *et al.*, 1996) from experimental observations up to 1994. The solid lines represent equilibrium phase boundaries, and the capital letters indicate domains in which various observations were obtained. A: catalysed synthesis of diamond from graphite; B: P - T threshold of very fast (< 1 ms) solid-solid graphite $\rightarrow$ diamond transformation; C: P - T threshold of very fast diamond $\rightarrow$ graphite transformation; D: single-crystal hex. graphite $\rightarrow$ hex. diamond transformation; E: upper ends of shock compression/quench cycles that convert hex. graphite to hex.-type diamond; B, F, G: threshold of fast P - T cycles that convert either type of graphite or hex. diamond to cubic-type diamond; H, I, J: path along which hex.-type graphite single crystals compressed in the c direction at room temperature acquire properties consistent with a diamond-like polytype but slowly reverse to graphite upon releasing the pressure (By courtesy of Pergammon Press).

Bottom: Phase diagram of the lower pressure regions, where the question marks indicate that the existence of carbynes in these regions is controversial. In the liquid phase region, the question marks indicate that the newest experimental results do not support the earlier experimental interpretations that a non-conducting liquid phase exists. The liquid-vapour line probably ends at a critical point estimated to be at ~ 0.2 GPa/6800 K (By courtesy of Pergammon Press).

most recent (Bundy *et al.*, 1996). The melting point of carbon (under Ar, 50 atm) has been found by Togaya *et al.* (1993) about 200 K above the triple point $C_{(liquid)} / C_{(graphite)} / C_{(diamond)}$, itself at ~ 4900 K, 12.3 GPa (Baitin *et al.*, 1990). This triple point should not be confused with the $C_{(gas)} / C_{(graphite)} / C_{(liquid)}$ triple point situated by Baitin *et al.* at 5000 K, 0.012 GPa. The liquid/vapour line should end at a critical point estimated to be at about 6800 K, 0.2 GPa. Measurements of the heat of fusion vary from about 92 to 115 kJ/mole (Togaya *et al.*, 1993), the latter value being probably the most reliable (Bundy *et al.*, 1996), with a slope $1.5 \cdot 10^{-2}$ GPa/K for the solid/solid phase boundary between diamond and the metallic phase.

Theoretical studies by Young and Grover (1988) indicate that a triple point (not shown in Fig. 1.3) corresponding to $C_{(liquid)} / C_{(diamond)} / C_{(BC8, metal)}$ may exist at ~ 10300 K, 1300 GPa and involving a metallic phase known to exist in the phase diagrams of Si and Ge but still unknown for carbon.

Figure 1.3 also gives the melting curve of graphite for pressures between 0 and 130 kbar, with a maximum temperature ~ 5200 K ($P \approx 5.2$ GPa) at which $dP/dT = \infty$, equivalent to a 'critical temperature of fusion' beyond which carbon would always be liquid, whatever the pressure (Bundy, 1963 a; Bundy *et al.*, 1996). Using the results of attempted syntheses of diamond in which both graphite and diamond were found, the melting curves of the two allotropes can be extrapolated, as shown in Fig. 1.3. In this connection, one should remember that the domain of liquid carbon is still somewhat ill-defined: following a suggestion by Bundy (1989), recent theoretical calculations by Van Thiel and Ree (1993) suggest that at sufficiently high temperature and pressure, a liquid-liquid transition could exist and that liquid carbon could therefore be dimorphic, but experimental evidence of this is still unavailable. Measurements of the electrical conductivity of liquid carbon have been performed (with varied and contradictory results) in order to ascertain the validity of a metal-insulator transition, but there appears to be no firm evidence for the existence of an insulating form of liquid carbon: the liquid phase is a semi-metal, and its resistivity is 60–70% of that of solid graphite at the melting point, i.e. 350–600 $\mu\Omega\text{cm}$.

The equation of state of liquid carbon under very high pressure (1 TPa) has been determined and discussed (Sekine, 1993).

In agreement with theoretical calculations (Biswas *et al.*, 1984), the melting line of diamond has a positive slope. As determined from an extremely large number of experiments, the slope dT_m/dP is $\sim +30.6$ K/GPa, for the 20–80 GPa range (Bundy *et al.*, 1996). The stability domain of lonsdaleite (hexagonal diamond) lies entirely within that of cubic diamond. The phase transitions resulting in a change of the coordination number are first order, but the associated enthalpies of transition are not always known. Among them, the graphite-diamond transition has been the subject of a large number of experimental and theoretical studies owing to the economic importance of synthetic diamonds. This 'reconstructive transition' has been analysed by a number of authors (Kertesz and Hoffmann, 1984; Lambrecht *et al.*, 1993). Undoubtedly, the comprehension and control of nucleation are of prime importance for the synthesis of monocrystalline or polycrystalline diamond, as witnessed by the mechanism involving the rhombohedral form of graphite as precursor recently proposed (cf. Chap. 8).

The catalysed synthesis of diamond is performed under the pressure and temperature conditions found in the shaded region noted 'A' in the phase diagram, as also

illustrated by the results of Semchinova *et al.* (1997) who worked at ~ 1500 K and 4.5 GPa: carbon was dissolved by the Mn-Ni catalyst from graphite and reprecipitated as cubic diamond.

Also shown in Fig. 1.3 is the presumed stability domain of carbynes (cf. Sections 1.4.3 and 2.3.1.1). Since the existence of carbynes, nanotubes, C_{60} -type fullerenes and other new species only composed of carbon (cf. Chapter 2) is now well established, the need to include them in the classical carbon phase diagram can legitimately be examined. Apart from carbynes, these forms of carbon are molecular solids in which each molecule contains a finite number of C atoms and has at least one limited spatial dimension, whereas for the other solid forms of carbon (diamond, graphite), it is always possible to increase the size of the solid by tacking on, at the periphery, similarly hybridised C atoms without affecting the phase diagram. This is equivalent to saying that the reaction



is not reversible (from the thermodynamic point of view) for C_{60} , C_{70} , etc., or for the nanotubes (cf. Chapter 5). These molecules should then be considered as distinct species and their mixture with any other single form of carbon must be described by the phase diagram of a two-component system.

The refractory characteristics of carbon rendered the determination of its thermodynamic properties particularly difficult: the long controversy concerning the value of the enthalpy of sublimation L_0 was only settled when Chupka and Inghram (1955) combined mass spectrometry and measurement of the heat of effusion to obtain $L_0 = 169.76$ kcal/mol (710.45 kJ/mol). The variation of the vapour pressure P (in Torr, 1 Torr $\equiv$ 139 Pa) with the temperature T (in K), as given by a semi-empirical relationship due to Nesmeyanov (1963), is:

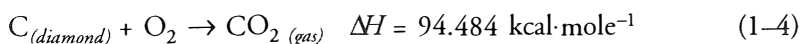
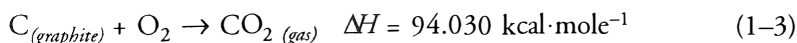
$$\log_{10} P = 16.811 - 37940/T + 9.65 \cdot 10^{-4} T - 1.9500 \log_{10} T \quad (1-2)$$

but the composition of the vapour is complex owing to the presence therein of molecules such as C_2 , C_3 , ... in variable proportions. For the boiling point, the relationship yields $T_{Eb} = 3600$ K for $P = 760$ Torr, a value lower than $T_{Eb} = 4100$ K favoured by Bundy (1963a).

1.4.2 Diamond

1.4.2.1 The graphite $\leftrightarrow$ diamond equilibrium

Rossini and Jessup (1938) determined the following heats of combustion:

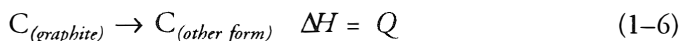


The values of the entropy are known to be $S_{(graphite)} = 1.3608$ and $S_{(diamond)} = 0.5829$ cal/deg/mole (Rossini *et al.*, 1961), hence, for the graphite $\rightarrow$ diamond transition,

under normal pressure and at $T = 298.16$ K:

$$\Delta G = 454 - 298.16 (0.5829 - 1.3608) = 686 \text{ kcal} \cdot \text{mole}^{-1}. \quad (1-5)$$

Graphite is therefore the stable form of carbon, which implies that the variation of energy Q associated with the reaction



is always positive at NTP since it is highly probable that any metastable allotrope which could have been formed during previous geological era under the appropriate physical conditions would, like diamond, have left visible traces, and therefore that these other allotropic forms are less stable than diamond. Nevertheless, this does not exclude the existence of other isolable metastable forms of carbon, as demonstrated by the existence of the group of fullerenes.

1.4.2.2 *The synthesis of diamond*

At the end of the 18th century, Lavoisier and Tennant demonstrated that natural diamond was a dense structural form of carbon. From then on, the synthesis of diamond seemed accessible to the physical-chemists, for all that adequate pressures could be reached. A number of attempts were made during the 19th and the early 20th centuries. As early as 1880, Hannay announced that heating 'an organic oil' with petroleum ether and an AM (Li) to red heat in a thick-walled cast iron tube had yielded positive results in the 3 trials not ending by an explosion, out of more than 70 attempts. The fact that Friedel (1893) had identified microscopic diamonds in the iron-nickel alloy found in the crater of the Diablo Canyon (Arizona) meteorite incited Moissan to attempt the synthesis. The scheme adopted was the saturation of molten iron with carbon, followed by precipitation of the latter by rapid cooling of the molten mass under pressure, and elimination of the iron matrix by dissolution in hydrochloric acid. Moissan (1894) claimed that success had been achieved: some of the grains obtained were apparently identified as diamonds but, unfortunately, none were preserved which could have been characterised by the spectroscopic methods now available. Parsons (1919), who tried both Hannay's and Moissan's techniques, claimed to have obtained diamond in some trials, but later, Bridgman (1955) stated that in 1924, Parsons had been told by Moissan's widow that her husband had been the victim of fraud by one of his assistants who had introduced diamond fragments [...] 'in order to avoid the tedium of long digestions' (Mellor, 1960), and Lonsdale (1962), who had previously identified Hannay's diamonds as being natural (Bannister and Lonsdale, 1943), stated that none of the preparations by Hannay, Moissan or Parson could have yielded diamond. It seems therefore that Moissan's claim was groundless, although he undoubtedly was on the right track. The results of Rossini and Jessup (1938) clearly show that diamond is metastable at all temperatures if the pressure is less than 1.3 GPa.

After these unsuccessful experimental trials, a theoretical thermodynamic study of the problem was undertaken. Equilibrium curves separating the graphite and diamond domains were proposed by Rossini and Jessup (1938) and Prosen *et al.* (1944) but Bridgman (1947) did not obtain the transformation of graphite into diamond even

at 4 GPa, thus demonstrating that a second necessary condition was that the activation free energy of the transformation must itself be favourable. Because the curve was only valid to 1300 K, Berman and Simon (1955) proposed two extrapolations to high temperatures based on the coefficient of expansion of diamond. On the basis of this curve and of the values of P and T , it was clear that the former trials could not have succeeded. Bridgman then built equipment enabling him to carry out tests on pure carbon at 4.5 GPa and 2500°C, which however did not lead to the formation of diamond.

During the same period, a third approach was developed by Leipunskii (1939) who undertook the task of reproducing the natural conditions (silicates, molten metals) likely to favour the formation of diamond, but the pressure (300 MPa) was not sufficient to yield diamond. On the basis of an analysis of the work of Rossini and Jessup (1938), he concluded that a pressure of the order of 6 GPa and a temperature of 2000 K were required for the synthesis in the solid state of diamond from graphite. Nevertheless, he suggested that these conditions could be reduced insofar as an adequate solvent for carbon — perhaps iron? — could be found.

Work on the synthesis of diamond was carried out in Sweden at *Allmanna Svenska Elektriska Aktiebolaget* (ASEA), as a possible means of extending the use of high-pressure technology. After a large number of trials, diamond was finally obtained (1953) at 10 GPa and 4300 K, but only in the presence of a solvent of carbon such as iron (Liander, 1955; Liander and Lundblad, 1960). In 1955, Bundy *et al.*, at the *General Electric Company* (GEC) (USA), announced the successful synthesis of industrial grade diamonds obtained by maintaining 'carbonaceous materials' at about 3000°C and $P \approx 10$ GPa over relatively long periods of time. Later, Bovenkerk *et al.* (1959), after having perfected the 'belt' (Hall, 1958), a new high-pressure apparatus capable of maintaining simultaneously high pressures and high temperatures, disclosed that a molten metal (Cr, Fe, Ni, Fe/Co alloys, Ta, ...) served as a flux and catalyst, as suggested by Moissan. In South Africa and since 1955, De Beers Consolidated Mines Ltd. also synthesise and sell industrial diamonds. Working at 12.5 GPa and 3000 K, without catalyst but with the addition of about 71 kJ/mole of energy, Bundy (1963b) obtained the direct and nearly quantitative transformation of graphite into diamond. Honda *et al.* (1964) discharged about 4000 J of electrical energy between two Ni or Fe electrodes immersed in kerosene under pressure and obtained 0.5 mm diamonds at ~ 104 K and 15–20 GPa (estimated).

In 1960, the annual production of industrial diamonds by the GEC was of the order of $3.5 \cdot 10^6$ carat ($7 \cdot 10^2$ kg; Mellor, 1960). The total annual production in 1995 was of the order of $4 \cdot 10^8$ carat ($8 \cdot 10^4$ kg).

This brief historical analysis clearly underlines three important points:

- if a material has a major economical importance (owing to its physical properties and/or its potential applications), the necessary means for its synthesis are found;
- in the realm of high-pressure synthesis of materials, technological developments have been of prime importance;
- a thorough analysis of previous work is always beneficial: if Bridgman had used the principle of dissolving carbon in an appropriate solvent as suggested by Leipunskii and by Moissan, his trials might have been successful as early as 1947–1948.

The synthesis of diamond, which at first tended to be considered mainly as a success of Science insofar as this mythical material had finally been synthesised by Man, eventually turned out to be an essential step in the development of high-pressure equipment and in the acceptance of the 'exotic' pressure parameter in sundry disciplines.

1.4.2.3 Cubical diamond

Natural diamonds are found in Siberia, India and Pakistan, in Brazil, Guyana and Arkansas, in Zaire and South Africa, and in Australia. The main centre of production is at Kimberley (South Africa), where the diamonds are found dispersed (average: 0.1 g/ton, but the 'Cullinan' diamond weighs about 0.6 kg) in mineral mixtures rich in olivine or embedded in kimberlite, a silica-poor volcanic lava.

Natural diamond is cubic, space group $Fd\bar{3}m$, with $a_c = b_c = c_c = 3.5597 \text{ \AA}$ (where $a_c = \text{lal of the cubic cell, etc.}$), with 8 atoms per unit cell and density = 3.51 g/cm^3 (cf. Fig. 1.4 and Chapter 13). The purest, colourless diamonds are said to be Type II, while those containing impurities (metals or nitrogen, in traces) are Type I. An important property of diamond is its optical transparency, which is greater than 10% for all wavelengths between 80 and $0.22 \text{ }\mu\text{m}$ (Type I) or $0.30 \text{ }\mu\text{m}$ (Type II) for a 2 mm-thick plate (AIP Handbook, 1963a). The thermal conductivity is greater than that of copper at room temperature, and that of Type II diamonds is 2–8 times larger than that of Type I diamonds in which the presence of impurities partially blocks the transmission of phonons. The high transparency and thermal conductivity are explicable by the small mass of the C atoms, the symmetry of the crystal lattice, and the strong interatomic covalent bonds in the solid (Bundy, 1974), as confirmed by the particularly large value of the Debye temperature, viz. $\theta_D = 2200 \text{ K}$ (AIP Handbook, 1963b; cf. Chapter 9).

The hardness of diamond is assigned the value 10 (the highest value) on the Mohs scale, and 7,000 on the Knoop scale (Bundy, 1974). Table 1.4 gives some of its mechanical characteristics.

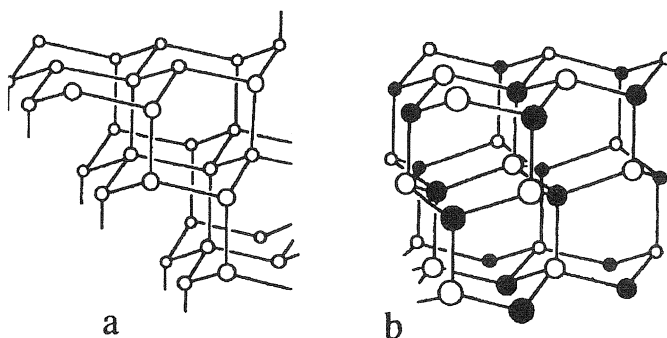


Figure 1.4: (a): Cubical diamond; (b): wurtzite (ZnS), or hexagonal diamond when all the Zn and S atoms are replaced by C atoms and all bond lengths are equal. In a direction parallel to the vertical axis, the conformation of the C atoms are "chair" for cubical diamond, and "boat" for hexagonal diamond.

Table 1.4: Elastic parameters C_{ij} and their derivatives, and linear compressibilities Λ of diamond, graphite and C_{60} .

i,j	1,1	1,2	1,3	3,3	4,4	$\Lambda_c \text{ (GPa)}^{-1}$	$\Lambda_a \text{ (GPa)}^{-1}$
Diamond						$75.4 \cdot 10^{-2} \text{ }^b$	$= \Lambda_c$
$C_{ij} \text{ (GPa)}^a$	1076	125			576		
Graphite						$5 \cdot 10^{-2} \text{ }^b$	$-0.25 \cdot 10^{-2} \text{ }^b$
$C_{ij} \text{ (GPa)}$	1060 ^c	180 ^c	15 ^c	36.5 ^c	4.5 ^d		
	1160 ^e	290 ^e	109 ^e	46.6 ^e	2.3 ^e		
$\partial C_{ij} / \partial P \text{ }^f$	39	11	9.6	3.1	0.0023		
$\partial C_{ij} / \partial T \text{ (GPa/}^\circ\text{K)} \text{ }^g$	1.1	0.26	0.046	0.8	0.01		
C_{60} ^h						$-2.3 \cdot 10^{-2} \text{ }^i$	$= \Lambda_c$

^aMcSkimin and Bond, 1957; ^bBasset, 1941; ^cBlasklee *et al.*, 1970; ^dSoule and Nezbeda, 1968; ^eGmelins, 1967; ^fat 295 K, Gauster and Fritz, 1974; ^gat 1 bar, Gauster and Fritz, 1974; ^hfor C_{60} , simple cubic phase below 261 K (at $P = 1$ bar) and above 0.5 GPa (at $T = 293$ K). ⁱFischer *et al.*, 1993; the value of Λ_a probably corresponds to the simple cubic phase

1.4.2.4 Hexagonal diamond (Lonsdaleite)

Some lines in the X-ray diffractograms of synthetic diamonds obtained at $P > 130$ GPa — i.e. beyond the graphite / diamond / $C_{(liq)}$ triple point — by Bundy (1963b) were later indexed (Bundy and Kasper, 1967): after releasing the pressure, a new hexagonal phase was found among the crystals of cubical diamond, with parameters $a_h = 2.52 \text{ \AA} = a_c / \sqrt{2}$, $c_h = 4.12 \text{ \AA} = 2 c_c / \sqrt{3}$, and for which the space group would be $P6_3/mmc$. The density 3.51 g/cm^3 was the same as that of cubical diamond, but the position of the atoms was that of the atoms in wurtzite (Fig. 1.4). This phase is best obtained from pyrocarbons, in which the c axes of the layers are already fairly parallel, when submitted to a compression perpendicular to the layers followed by annealing at $T > 1300$ K. The transformation cubical diamond $\rightarrow$ hexagonal diamond does not seem to be possible.

1.4.2.5 Other homologous forms of diamond

Since 1950, techniques for the vapodeposition of carbon layers — more or less doped and more or less cubical — on various substrates have been elaborated to put to good use the mechanical properties (low friction coefficient, hardness) of this ‘adamantine carbon’. Thus, studies (Yarborough, 1990) have revealed that organic molecules in the vapour play an important rôle by configuring the carbon to precipitate as diamond, and the deposition of carbon clusters with a selected size distribution around C_{20} has been reported to yield diamond-like layers with nearly pure sp^3 bonds (Paillard *et al.*, 1994).

Theoretical considerations by Fahy and Louie (1987) point to the possibility of explaining certain experimental observations made by Vereshchagin *et al.* (1972) by the existence of a simple cubic phase which, however, has not yet been isolated. A superdense semiconducting diamond phase (‘supercubane’, 16 atoms per centred

cubic unit cell, density 4.1 g/cm³) may have been obtained by Matyushenko *et al.* (1979) via reactive plasmas; if it exists, this phase, less stable than diamond, would have a large band gap (cf. Chapter 2).

1.4.3 Carbynes

The existence of carbynes was questioned for a long time, probably because the samples which were prepared or examined were always of microscopic size, and because these samples were often — but not always — associated with impurities (K, Fe, SiO₂, ...) (Smith and Busek, 1982, 1985) which may even have acted as stabilisers (Whittaker and Wolten, 1972). Even if these allotropic forms of carbon could be stable at about 2600 K under some tens GPa (Whittaker, 1979), their stability would be much inferior to that of diamond (Fahy and Louie, 1987) since they are metastable with respect to hexagonal graphite (Fig. 2.4).

Korshak *et al.* (1961) suggested that it might be possible to prepare linear chains such as $(=C=C=)_n$ and $(-C\equiv C-)_n$ by chemical reactions which would preserve the linear characteristics of the carbon skeleton: thus, heating to 1000°C the amorphous carbon obtained by the oxidation of acetylene (Korshak *et al.*, 1961) or by the dehydrochloridation of poly(vinylidene chloride) (Sladkov *et al.*, 1968) yields carbon partially crystallised as a white powder which, by IR spectroscopy, X-ray and electron diffraction (Kasatoshkine *et al.*, 1967) was shown to have bonds already met in the sp^2 hybridised cumulenes and the sp hybridised (digonal) acetylene derivatives. The presence of these 'carbynes' in meteorites (El Goresy and Donnay, 1968) and even in natural graphite (Whittaker, 1979) was later announced and attributed to the effect of shock waves on graphite or diamond — for which evidence has recently been found (Rinzler *et al.*, 1995) — which implies that carbynes could be prepared both by chemical and by physical methods.

Care should be taken to distinguish between the α and β forms (cf. Fig. 1.5) of this allotrope of carbon (Sladkov and Kudryavtsev, 1969; Kudryavtsev *et al.*, 1993); the crystal parameters of both forms were determined by Kasatoshkine *et al.* (1973) and found to be hexagonal:

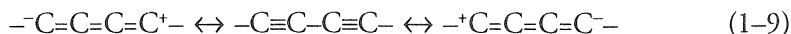
- α carbyne $(-C\equiv C-C\equiv C-)_n$, with poly-yne links of bond-lengths ~ 1.20 Å (for $C\equiv C$) and ~ 1.38 Å (for $C-C$) (also known as chaoite when found native, as in meteorites) (Whittaker and Watts, 1980), and parameters:

$$a = 8.92 \text{ Å}; c = 15.36 \text{ Å}; \text{density: } 2.68 \text{ g/cm}^3; \quad (1-7)$$

- β carbyne $(=C=C=C=C=)_n$, with cumulene links, a resonant form of a carbyne, with a single bond-length ~ 1.28 Å. and parameters

$$a = 8.24 \text{ Å}; c = 7.68 \text{ Å}; \text{density: } 3.13 \text{ g/cm}^3. \quad (1-8)$$

The conformation of the chains has been studied by Heimann *et al.* (1984) and by Kudryavtsev *et al.* (1992) who worked on monocrystalline layers deposited on a KBr substrate. Thus,



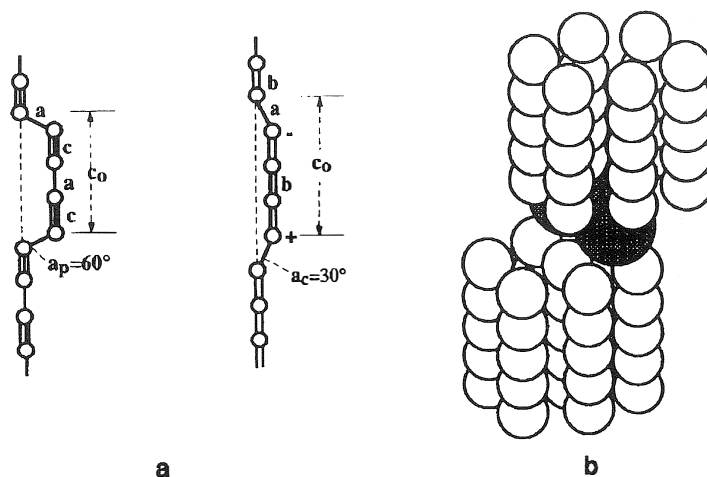


Figure 1.5: (a): Carbyne chains, after Heimann *et al.*, (1984); (b) stack of carbyne chains, after Kudryavtsev *et al.*, (1992); only the bottom stack is compact, the top is only 2/3 filled. The large atom between the top and bottom stacks is an impurity stabilising the structure. (By courtesy of Persimmon Press)

The number of C atoms in the chains must therefore be even. The presence of charges at the ends of the chains forces the single bonds to form an angle $a_c = \pm 60^\circ$ (or $\pm 30^\circ$) (Jansta and Dousek, 1980; Heimann *et al.*, 1984), so that the axes of successive chains are staggered laterally (cf. Fig. 1.5a). Random signs for a_c would create ‘paracrystals’ (Hoseman, 1973) of fixed identity periods along c but statistical fluctuations of the a parameter. According to Heimann *et al.*, the unit cell of a carbyne corresponds to a compact packing of 12 linear and cylindrical cumulene-type chains with radius $r = 1.28 \text{ \AA}$, with their principal axis parallel to c and with 12 C atoms (or 6 C atoms for β carbyne). This description of the unit cell differs from that given by Kudryavtsev *et al.*, (1992; 1993) for whom there are two types of packing along the c axis for the polyenic (rather than polyyenic) chains, the first compact along one half of its length whereas the second half involves vacancies in 1/3 of its sites (Fig. 1.5b).

Many physical and chemical syntheses of these phases have been tried (Kudryavtsev *et al.*, 1993); at the present time, it seems that oligomers with 20 to 30 C atoms can be obtained (Lagow *et al.*, 1995). Their physical properties, which still require extensive research, cannot yet be said to be well-known (Smith and Busek, 1982). The need for further research in this field is illustrated by the results presented by Kavan *et al.* (1995) whose electrochemical reduction of perfluorinated hydrocarbons by alkali-metal amalgams yielded 16-atom long polyyenic chains (as ascertained by Raman spectroscopy) which decomposed spontaneously if the alkali-metal fluoride was extracted by leaching out with water.

1.4.4 Graphite

Natural graphite has been found in the five continents. The mines of graphite at Passau

(Germany) and Cumberland (England) were exploited in the Middle Ages. The variable and sometimes low content of graphite in the extracted mineral (10–50%) explains the importance acquired by the manufacture of artificial graphite, or rather of more or less well graphitised carbon.

As will be seen below, the structure of graphite is a highly anisotropic, a feature affecting all its physical properties and making graphite to be a quasi 2D solid (Delhaès, 1985).

1.4.4.1 Structural characteristics

The unit graphite lattice is hexagonal [2(h)-graphite, space group $P6_3/mmc$], with $a = b = 2.461 \text{ \AA}$, $c = 6.708 \text{ \AA}$ (with $a = |a|$, etc.), 4 atoms per cell, theoretical density = 2.26 g/cm^3 . In graphite, two-dimensional (2D) sheets of carbon are stacked along the c axis at $3.354 \text{ \AA}$ from each other, with each atom in a layer symmetrically bonded to three other atoms at $1.421 \text{ \AA}$, thus forming a honeycomb of sp^2 hybridised C atoms (Bacon, 1948). The relative position of two successive layers is determined by two translation vectors (Fig. 1.6): the first, of modulus $|c|/2$, is parallel to c whereas the second, $\Delta = \pm(2a/3 + b/3)$ is of length equal to the distance between any two adjacent C atoms in the layer and is perpendicular to c . A constant sign of this second vector — say, positive — would yield rhombohedral graphite, i.e. a stack described by the sequence ...ABCABC... since $3\Delta = 2a + b$, whose components are integral multiples of a and b . In perfect natural graphite, the successive values of Δ have opposite sign, i.e. $+\Delta - \Delta + \Delta - \Delta \dots$, which yields the sequence ...ABAB... in which one C atom out of every two in each layer is in a potential well, with no other C atom directly above or below it. The ...AA... form, with no translation vector Δ , seems to have been found in meteorites (Sclar and Squitter, 1979) in spite of its lower stability with respect to the ...ABAB... sequence in natural graphite.

Random stacking defects may occur, giving rise to sequences such as ...ABACBCA... and forming partially disordered carbons in which the long distance order along c is destroyed but the interlayer distance is still $3.354 \text{ \AA}$. As a result, natural graphite sometimes contains small proportions of the rhombohedral variety [3(r)-graphite, space group $R\bar{3}m$; Laves and Baskin, 1956], and grinding can bring this value up to 30% (Boehm and Hofmann, 1955). The interlayer distance of graphite is a function of the number and type of defects: in turbostratic carbons, all the graphitic carbon layers are parallel to each other but are randomly oriented (Biscoe and Warren, 1942), with $3.44 \text{ \AA}$ as interlayer distance. Méring and Maire (1965a) defined a parameter g given by

$$g = (3.44 - d_{002}) / (3.44 - 3.354) \quad (1-10)$$

equal to 0 for turbostratic carbons, and to 1 when the carbon is fully graphitised. [The value $3.44 \text{ \AA}$ in Eq. (1–10) is valid for soft carbons, but the mean interlayer distance in hard carbons is closer to $3.7 \text{ \AA}$ (Méring and Maire, 1965b). In view of this discrepancy and of the fact that the value 3.354 in Eq. (1–10) is sometimes replaced by 3.35 , the CCl index of Fujimoto *et al.* (1994) seems more appropriate (cf. Sec. 1.3.1 above)].

Other lattice defects can exist, between and/or in the graphitic carbon layers: thus, recent field effect microscope observations have highlighted coordination defects in

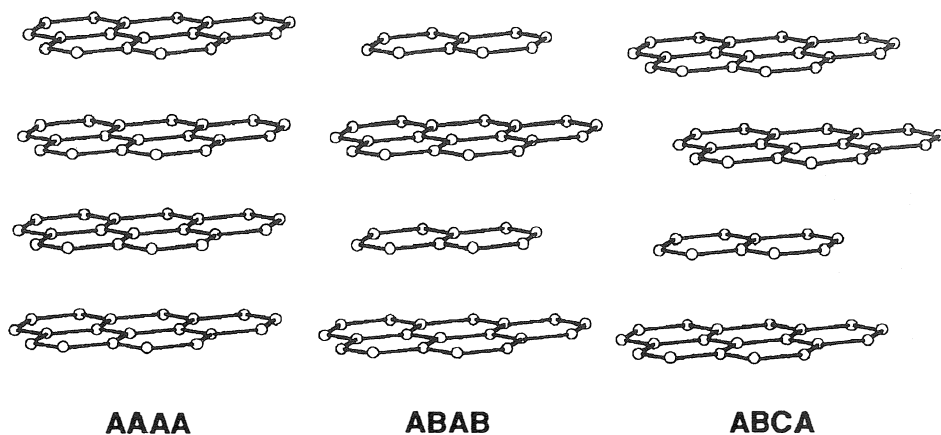


Figure 1.6: Stacking of graphitic layers: (a) AAAA type, with no translation vector parallel to the layers; (b) ABAB type, with translation vectors $+\Delta$ and $-\Delta$; (c) ABCA type, with a single translation vector Δ .

certain C atoms of a single crystal of hexagonal (kish) graphite extracted from carbon-rich cast iron (Biensan *et al.*, 1991), in which the presence of tetracoordinated C atoms creates non-planar seven- and three-membered carbon cycles.

The structural relationships between graphite and the two forms of diamond are shown in Figs. 1.4 and 1.6. Neglecting the difference in bond lengths between sp^2 and sp^3 C bonds, and after cutting all the bonds parallel to c in the diamond structures, flattening the corrugated layers of C atoms yields a rhombohedral (...ABCABCA...) stack from cubic diamond and hexagonal graphite (...ABABABA...) from hexagonal diamond.

The remarkable properties of graphite are due to its crystal structure, in which layers form stacks bound to each other by weak van der Waals interactions, with each layer constituted by a honeycomb of strongly bonded C atoms in sp^2 configuration (cf. Chapter 6). In general, all the physical properties are highly anisotropic, and the electronic characteristics are due to the presence of a more or less delocalised quasi 2D gas of π electrons (Delhaès, 1985). As a consequence, all the physical properties are also anisotropic, as reflected in the band structure of the solid. The band structure of the ...ABCABCA..., ...ABABABA... and ...AAA... stacks have been studied by Samuelson *et al.* (1980) who showed that the weak interplane interactions are sufficiently important to create large differences in the π bands at the Fermi level. This was confirmed by the more recent and very complete work by Charlier *et al.* (1994).

1.4.4.2 Thermal properties

Graphite is highly refractory and thermally exceptionally stable (in non-oxidising atmospheres). Its vapour pressure is only $1.8 \cdot 10^{-3}$ bar at 3000 °C (Nesmeyanov, 1963). It sublimes without melting at 3600°K (Jones and Weltner, 1959). Its thermal expansion

is peculiar: the coefficient of expansion $\alpha_a = \alpha_b$ measured along the carbon layers is weak and negative ($-1 \cdot 10^{-6}/^\circ\text{K}$) at room temperature, becoming zero at $\sim 700^\circ\text{K}$, then weak, positive and constant ($+1 \cdot 10^{-6}/^\circ\text{K}$) from 1000 to 3000°K (Morgan, 1972); the thermal dilation measured perpendicularly to the layers is $\alpha_c = +27 \cdot 10^{-6}/^\circ\text{K}$, constant till 1000°K , then steadily increasing to $+35 \cdot 10^{-6}/^\circ\text{K}$ at about 2500°K (cf. Sec. 1.4.4).

The thermal conductivity along the layers ($\lambda_a = \lambda_b \approx 20 \text{ W/cm } ^\circ\text{K}$) is comparable to that of diamond (Smith and Rasor, 1956), and much higher than the one perpendicular to the layers since $\lambda_a/\lambda_c = \sim 200$. The very large difference in thermal conductivities measured across or along the planes led Magnus (1923) to ascribe two Debye temperatures to graphite, namely $\theta_{D\perp} = 760 \text{ K}$ and $\theta_{D\parallel} = 2280 \text{ K}$ to obtain an adequate description of the modes of vibration respectively perpendicular and parallel to the planes. This large anisotropy is particularly useful in thermal shields. Similarly, the mean thermal expansion coefficients between 15 and 800°C are $\alpha_\perp = 28.3 \cdot 10^{-6}$ and $\alpha_\parallel = 1.5\text{--}0.9 \cdot 10^{-6}$ (Matuyama, 1955, 1968).

1.4.4.3 Mechanical properties

Table 1.4 gives the elasticity parameters determined by various authors on graphite single crystals (Kelly, 1981). The particularly high value of C_{11} is noteworthy: it reflects the strength of the intralayer sp^2 C–C bond (by way of comparison, C_{11} for a cubic crystal like Fe is five times smaller). Similarly, the very low value of C_{44} is characteristic of the weak interlayer forces, hence a low resistance to shearing stresses perpendicular to the crystallographic c axis, at the basis of the use of graphite as a lubricant.

1.4.4.4 Electronic properties

The presence of π electrons (one per C atom) confers a particular structure to the energy bands of the solid. Phenomenological models based on the symmetry of graphite and giving the dispersion relationships of the bands (cf. Chapter 7) have been developed by Slonczewski and Weiss (1958) and by McClure (1960). According to these models, the valence and conduction bands slightly overlap ($\sim 0.04 \text{ eV}$) at the Fermi level, where the electron density is slight, giving to graphite semi-metallic characteristics. Although the concentration of charge carriers is small ($\sim 10^{-4}$ per C atom), the electrical conductivity of graphite along the layers is high because of the exceptional mobility of these carriers (10^4 to $10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$): the electrical resistivity ($\rho_a = \rho_b = 40 \mu\Omega\cdot\text{cm}$, about 20 times that of Cu at room temperature) is metal-like, i.e. it increases with temperature. Parallel to the c axis, and as could be expected, the resistivity is much higher: $\rho_c/\rho_a \approx 10^4$ (also at room temperature).

Another noteworthy property — which, however, does not seem to have been exploited — is the exceptional diamagnetism of graphite: the room temperature values are $\chi_a = -0.4 \cdot 10^{-6} \text{ emu/g}$ (H parallel to the layers), and $\chi_c = -21 \cdot 10^{-6} \text{ emu/g}$ (H perpendicular to the layers), reaching the value $\chi_c = -30 \cdot 10^{-6} \text{ emu/g}$ at the temperature of liquid He (Maaroufi *et al.*, 1982). Graphite is thus the most highly diamagnetic substance after the superconductors. These large values, as well as the temperature variation, have been quantitatively interpreted by means of the Slonczewski-Weiss-McClure model (Sharma *et al.*, 1974).

1.4.4.5 Chemical properties

Graphite can undergo two types of chemical reactions: those in which the 'normal' valence rules compatible with the hybridisation of the C atoms are followed, and the topochemical reactions of intercalation.

Examples of the first type of reaction are the formation of carbides with most metals (Nightingale *et al.*, 1962), and the reaction with hydrogen at high temperatures to give light hydrocarbons (mainly methane; Walker *et al.*, 1959). Oxidation reactions are quite numerous: by air as from 500 °C, with vaporised S or H₂S to yield CS₂ (Sykes *et al.*, 1953). The reactions with O₂, H₂O and CO₂, which limit the use of carbon materials at high temperatures, have been particularly well studied, and the catalytic influence of metallic impurities (alkali metals, Fe, Mn, ...) is now well established. On the other hand, coatings of borates (McKee, 1986) or of silicon carbide (Balat *et al.*, 1993) provide an appreciable — even if only partial — protection against oxidation of the underlying carbon substrate.

In all the reactions described above, the carbon layers are completely destroyed but other reactions merely modify the hybridisation of the C atoms in the layers without breaking the C–C intralayer bonds. Thus, Brodie (1855, 1859) showed that graphite is oxidised by a liquid and concentrated solution of potassium chlorate in fuming nitric acid at 60 °C to yield, after many hours, an electrically insulating, light brown hygroscopic powder known as 'graphitic oxide'. Later preparations (Hummers *et al.*, 1958) yielded a composition C₈O_{1.6}(H₂O)_{0.6} (as determined by titration of the acid hydroxyl functions, IR, and ¹³C NMR spectroscopy), close to the formula C₈O₂(OH)₂ of the ideal structure attributed to the oxide (Fig. 1.7; Mermoux *et al.*, 1991). The presence of oxygen bridges and hydroxyl groups forces a chair configuration for some of the previously plane hexagonal cycles of the graphitic carbon layers; both trigonal and tetragonal carbons now coexist, with the *sp*³ carbons out of the mean plane. As with clays, considerable swelling of the structure may occur if water is absorbed between the layers.

Similarly, the reaction of gaseous F₂ on graphite at temperatures greater than 300 °C yields compounds with covalent C–F bonds on *sp*³-hybridised C atoms (Rüdorff and Rüdorff, 1947), with compositions between C₂F and CF and which have found interesting applications as cathodes in electric batteries with lithium anodes (Watanabe *et al.*, 1988).

1.5 LAMELLAR COMPOUNDS OF GRAPHITE³

Reactions in which the structure and hybridisation of the carbon layers are preserved are the true intercalation reactions, rendered possible by the lack of interlayer bonding

³ Among all the general review articles which could supplement Section 1.5.1, those of Rüdorff (1959), Dresselhaus and Dresselhaus (1980), Selig and Ebert (1980), Legrand *et al.* (1988), Zabel and Solin (1990) will be found to be particularly useful. Rather more specialised and centred on some specific aspect are: Hérol (1979), on the crystallochemistry of graphite intercalation compounds (GICs); Fischer (1979), on the electronic properties of GICs; Dresselhaus and Dresselhaus (1979), on the molecular dynamics of GICs; Setton (1990) and Lagrange and Setton (1990), on ternary GICs; Setton (1988 a and c), on the use of GICs in preparative chemistry; Setton (1988 b), for a list of patents (1977–1985) featuring GICs for various uses; Inagaki (1989) for the relationship between the properties of GICs and the use to which they are put.

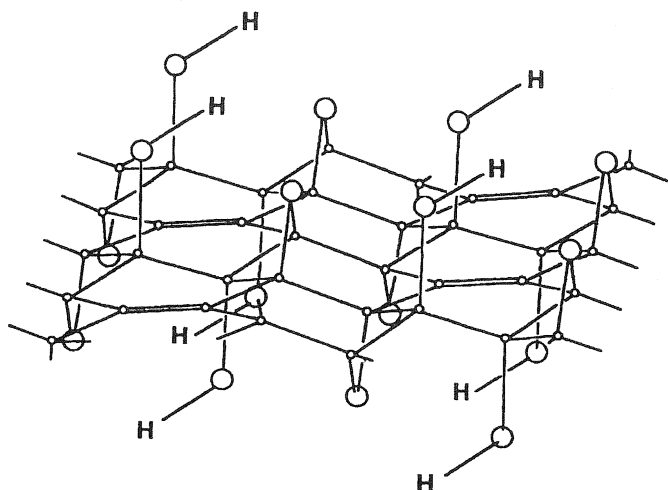


Figure 1.7: Structure of graphitic oxide, after Mermoux *et al.*, (1991). (By courtesy of Pergamon Press)

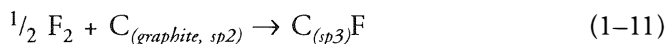
between the individual graphitic layers of the structure (cf. Sec. 1.51 and Chapter 11): an extremely large number of intercalation compounds can be formed, with electro-positive (electron donor) as well as electronegative (electron acceptor) species (Hérol, 1987). Intercalation can be obtained of reagents initially in the gaseous or liquid phase, or *via* electrochemistry. Alkali metals, alkaline earths, halogens (except iodine), halides, oxyhalides, oxides, acids, nitrates, have all been intercalated, forming compounds with original structural and physical properties intensively studied during the last 20–40 years. Although the fundamental interest of this research is undeniable, the applications of these compounds are limited, with the exception of their ever increasing use in lithium batteries, to be discussed in Sec. 14.3.2.

1.5.1 General features

The exact value of the interlayer energy of cohesion due to the interlayer interaction in graphite is unknown but certainly rather weak, since estimates vary from 0.97 (Girifalco and Lad, 1956) to 5.0 kcal/mole (Setton, 1960) (4.1 to 21 kJ/mole, or 42 to 220 meV), while calculation by the density-functional theory (DFT) approach fixes the value at 20 meV (Charlier *et al.*, 1994a and b) to 25 meV (Schabel and Martins, 1992) (0.46–0.58 kcal/C atom). The absence of covalent bonds between the planes facilitates the invasion of the interlayer space by various chemical species whose presence between the layers creates a GIC. Depending on the type of interaction between graphite and the invading species, the reaction results either in the formation of a covalent compound, with consequent lengthening of the C–C bonds which then tend towards sp^3 hybridisation, or of an ionic lamellar or intercalation compound in which the original trigonal bonding of the C atoms is conserved without deformation

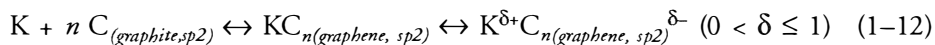
of the aromatic layers or major modification of the in-layer C–C bond length. The formation of covalent bonds is irreversible, whereas the formation of a true intercalation compound is at least partially reversible. In both cases, the separation of the graphitic carbon layers [now called ‘graphene’⁴ layers since the solid is no longer graphite (Boehm *et al.*, 1994)], is greater than $\sim 3.35 \text{ \AA}$, but no rigid tridimensional structures is known to have been created by the formation of bonds between a single intercalated species and the graphene layers on either side.

The synthesis of the fluoride CF is a good example of the formation of a covalent compound with modification of the trigonal hybridisation of carbon:



in which the π electrons no longer exist as such and the white product formed is an electrical insulator.

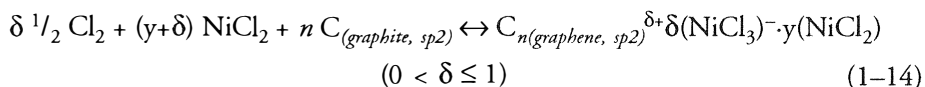
Intercalation – which is a topochemical reaction only possible in the solid state – also involves a redistribution of the electric charges. Its stoichiometry depends on geometrical and steric factors, namely on the interlayer space available between the graphene layers, and the size of the intercalated moiety (the ‘intercalate’). It produces important modifications in the physical properties associated with the bulk structure of the solid intercalate, such as the disappearance of its melting point (Mazières *et al.*, 1961). The composition of the product(s) corresponds to formulas such $\text{C}_4\text{I}_{0.45}\text{Cl}_{0.55}$ which obviously do not follow the usual valence rules, as seen also in the reaction with the electron donor K resulting in the formation of KC_8 :



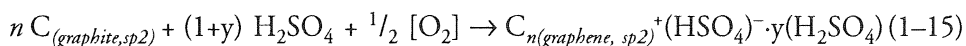
or with bromine Br_2 , a molecule which, after dissociation, yields two atoms which can accept electrons from the graphene and act as oxidisers:



or with ‘neutral’ halides in the presence of an oxidiser:



Acid salts of graphite can be obtained from strong acids with a chemical oxidiser or using the electric current as oxidising agent:



⁴ Although ‘graphene’ was chosen to designate a single plane layer of sp^2 hybridised carbon atoms in the intercalation compounds of graphite (Boehm *et al.*, 1994), its use to designate this type of assemblage of C atoms in other cases is still under consideration. It will, however, be used henceforth to replace other more cumbersome locutions, such as ‘polyaromatic and polyconjugated assembly of sp^2 –hybridised C atoms’.