

Contents

<i>Preface</i>	xv	
<i>Acknowledgments</i>	xvii	
1	Introduction to the Scope of the Text	1
1.1	Activated Carbon	1
1.1.1	Talking About Porosity	2
1.2	Activated Carbon (Origins): Chapter 2	3
1.3	Porosity in Carbons (Modeling): Chapter 3	4
1.4	Characterization of Porosity: Chapter 4	7
1.5	Activation Processes (Thermal or Physical): Chapter 5	8
1.6	Activation Processes (Chemical): Chapter 6	9
1.7	SEM and TEM Images of Structures in Activated Carbon: Chapter 7	9
1.8	Applications of Activated Carbon: Chapter 8	9
1.8.1	Introduction	9
1.8.2	Adsorptions from Aqueous Solutions	11
1.9	Production of Activated Carbon and Reference Material: Chapter 9	12
2	Activated Carbon (Origins)	13
2.1	Carbon Materials	13
2.2	Parent Materials for Carbons	16
2.3	Carbon Nomenclature	17
2.4	The Element Carbon	22
2.5	Carbons with Industrial Applications	25
2.6	Preparation of Carbons in Solid Phase	27
2.6.1	Introduction	27
2.6.2	Solid-phase Carbonizations	28
2.7	Preparation of Carbons in Liquid Phase: Liquid Crystals	42
2.7.1	Introduction	42
2.7.2	Nematic Liquid Crystals	43
2.8	Preparation of Carbons in Gas Phase	46
2.8.1	Introduction	46
2.8.2	Carbon Black	47
2.8.3	Fullerenes, Nanotubes and Necklaces	49

2.9	Structures Within Carbons	52
2.9.1	Bonding and Structure	52
2.10	The Non-validity of the “Crystallite” (Graphitic Microcrystallite) Concept	54
2.10.1	Introduction	54
2.10.2	Graphitic Microcrystallites in Coal?	57
2.10.3	Causes of Line-broadening in XRD	59
2.10.4	The Graphitic Microcrystallite Theory: Conclusions	62
2.11	Raman Microspectroscopy in Structural Analyses: An Assessment	62
2.11.1	Introduction to the Use of RMS	62
2.11.2	Incorrect Interpretations of RMS Data	63
2.11.3	Definitive Studies Using Pitch (Dumont <i>et al.</i> , 2002)	65
2.11.4	Interpretations of RMS Data	66
2.12	Quantitative Reflectance Microscopy and Carbon Structure	69
2.13	What is Carbon Structure? Concluding Comments	71
2.14	Applications Related to Porous and Chemical Structure	76
2.14.1	The uses of Porous Carbons	76
2.14.2	Take-up of Lithium into Carbons for Batteries	77
3	Porosity in Carbons: Modeling	87
3.1	Introduction	87
3.2	Model Requirements	89
3.3	Why Modeling?	89
3.4	Models to be Considered	91
3.4.1	The Drill-hole Models	91
3.4.2	The Branched-tree Model	91
3.4.3	The Norit Model	91
3.4.4	Carbon from Benzene Hexachloride, Gibson <i>et al.</i> (1946) and Riley (1947)	93
3.4.5	Potato-chip Models	95
3.4.6	Models of Kaneko <i>et al.</i> (1992a, b)	96
3.4.7	Model of Ruike <i>et al.</i> (1994)	98
3.4.8	Falling Card Model of Dahn <i>et al.</i> (1997)	100
3.4.9	Glassy Carbon Model of Yoshida <i>et al.</i> (1991)	101
3.4.10	Model of Porous Microtexture of a Carbonaceous Particle of Oberlin <i>et al.</i> (1980, 1999) and Oberlin (1989)	102
3.4.11	The Model of Virtual Porous Solids of Biggs and Agarwal (1992, 1994) and Biggs <i>et al.</i> (2004a, b)	103
3.4.12	Model of Porous Carbon of Segarra and Glandt (1994)	105
3.4.13	Tight-binding Model of Wang <i>et al.</i> (1996)	107
3.4.14	Computer-generated Models of Acharya <i>et al.</i> (1999)	108
3.4.15	Model of Glassy Carbon of O’Malley <i>et al.</i> (1998)	110
3.4.16	Model of Glassy Carbon of Pikunic <i>et al.</i> (2001, 2002)	111
3.4.17	Model of Porous Carbon of Petersen <i>et al.</i> (2003)	113
3.4.18	Carbon Aerogels of Gavalda <i>et al.</i> (2001, 2002) and Job <i>et al.</i> (2004)	114
3.4.19	Structure of Montmorillonite as shown by Scanning Electron Microscopy	116

3.4.20	Images Using Scanning Electron Microscopy, Rodríguez-Reinoso (unpublished)	117
3.4.21	Images Using High-resolution, Fringe-imaging Transmission Electron Microscopy, Marsh <i>et al.</i> (1982)	118
3.4.22	Models of Porosity in Activated Carbons as Suggested by Byrne and Marsh (1995)	118
3.4.23	Computer Simulation of Pore-filling Model of Bojan and Steele (1998)	121
3.4.24	Pore-shape Distributions by Davies and Seaton (1998)	121
3.4.25	Nearly Space-filling Fractal Networks of Carbon Nanopores (Micropores) of Pfeifer <i>et al.</i> (2002)	123
3.4.26	Evaluation of Slit-like Porosity by Gun'ko and Mikhalkovsky (2004) and Yang <i>et al.</i> (2002)	127
3.4.27	Star-like Porosity by Py <i>et al.</i> (2004)	131
3.4.28	Is a Definitive Model of Microporosity Possible?	133
3.5	Model Assessments and Criteria for Acceptance	137
4	Characterization of Activated Carbon	143
4.1	Basic Concepts	143
4.1.1	The Adsorption Isotherm	146
4.1.2	Open and Closed Porosity	148
4.1.3	Surface Area: Fact or Fiction?	148
4.1.4	Kinetics and Dynamics	151
4.2	Characterization of Porosity: Gas Adsorption	153
4.2.1	Measurement of the Isotherm	153
4.2.2	Qualitative Interpretation of Isotherms	155
4.2.3	Quantitative Interpretation of Isotherms	155
4.2.4	Quantitative Interpretation of Isotherms Using the t - and α_s - Methods	165
4.2.5	Adsorption of Nitrogen and Carbon Dioxide: A Comparison	166
4.3	Characterization of Porosity: Surface Functional Groups	182
4.3.1	Introduction	182
4.3.2	Formation and Properties of Oxygen Complexes	183
4.3.3	Analyses of Surface Functional Groups	185
4.3.4	Surface Acidity and Basicity	188
4.3.5	Surface Oxygen Complexes: Effects on Adsorption Isotherms	192
4.4	Characterization of Porosity: SAXS and SANS	195
4.5	Characterization of Porosity: Breakthrough Curves	197
4.5.1	Introduction	197
4.5.2	Breakthrough Curves and Times	198
4.5.3	Applications of Breakthrough Curves and Times	200
4.6	Characterization of Porosity: Enthalpies of Adsorption	204
4.6.1	Physical Adsorption and Chemisorption	204
4.6.2	London Dispersion Forces	205
4.6.3	Enthalpies of Adsorption	206
4.6.4	Flow-type Microcalorimetry	207

4.7	Characterization of Porosity: Immersion Calorimetry	209
4.7.1	Introduction	209
4.7.2	Immersion Calorimetry: Activated Carbons	214
4.7.3	Immersion Calorimetry: The Activation Process	216
4.7.4	Immersion Calorimetry: Influence of Surface Chemistry	220
4.8	Mesoporosity	224
4.8.1	Definition of Mesoporosity	224
4.8.2	Origins of Mesoporosity	224
4.8.3	Quantitative Assessments of Mesoporosity	228
4.9	Characterization of Mesoporosity: Mercury Porosimetry	234
4.9.1	Principles	234
4.9.2	Mercury Porosimetry: Experimental Results	234
4.9.3	Mercury Porosimetry: Limitations	234
4.10	The Last Word	236
5	Activation Processes (Thermal or Physical)	243
5.1	Thermal Activation: Fundamentals Considerations	243
5.1.1	Carbonaceous Surfaces	245
5.1.2	Thermo-chemistry of Gasification Reactions	248
5.2	Mechanisms of the Carbon-Molecular Oxygen Reaction	249
5.2.1	Intermediate Stages	249
5.2.2	Mobile Surface Oxygen Complexes	251
5.2.3	Use of Isotopic Oxygen: $^{16}\text{O}_2$ and $^{18}\text{O}_2$	252
5.2.4	Variation of the CO/CO ₂ Partial Pressure Ratio in Product Gases	253
5.2.5	Gasification Reactions in Nano-sized Spaces	254
5.2.6	The Energy Profile	256
5.2.7	Temperature Coefficients of Reaction Rates	257
5.3	Rates of Gasification Reactions	258
5.3.1	Diffusion Control of Reaction Rates of Gasification	258
5.3.2	Reactivity of Surfaces During Gasification Reactions	259
5.3.3	Rate Equation for the Carbon-molecular Oxygen Reaction	260
5.3.4	Rate Equations for the Carbon–Carbon dioxide and Steam Reactions	261
5.4	Carbon Structure and Gasification	262
5.4.1	Carbon Structure and Activation Energies of Gasification	262
5.4.2	Catalysis of Gasification Reactions	265
5.4.3	Factors Influencing Rates of Gasification Reactions	267
5.4.4	Topographical Changes During Gasification of Pure Carbons	267
5.4.5	Topographical Changes During Gasification of Impure Carbons	273
5.5	Activation by CO ₂ and H ₂ O: Inhibition by C(O) and C(H)	274
5.5.1	Introduction	274
5.5.2	Direct Addition of Hydrogen: Study of Walker (1996)	275
5.5.3	Modern Approaches to Mechanisms of Activation by CO ₂ and H ₂ O	278
5.5.4	Reactions with Hydrogen and Water (Liquid)	285

5.6	Surface Phenomena During Thermal Activations	285
5.6.1	Introduction	285
5.6.2	Transient States	286
5.6.3	Mechanisms of Desorption of Surface Oxygen Complexes as CO	287
5.7	The Concept of Reactivity	289
5.8	Surface Carbon Atom Migration	292
5.9	Thermal Activation Processes: (Contributions of Rodríguez-Reinoso <i>et al.</i> , 1984)	293
5.9.1	Introduction	293
5.9.2	The Year 1984: Use of Air and CO ₂	294
5.9.3	The Year 1987: Interdependence of N ₂ and CO ₂ Isotherms	294
5.9.4	The Year 1989: Methodologies	296
5.9.5	The Year 1989: Major Review – Adsorption Methodologies	296
5.9.6	The Year 1991: Major Review – Thermal Activation	296
5.9.7	The Year 1995: Use of Different Precursors	298
5.9.8	The Year 1997: Use of Different Experimental Conditions of Activation	299
5.9.9	The Year 2000: Carbon Molecular Sieves	301
5.9.10	The Year 2000: Activation of Carbon Cloths	305
5.9.11	The Year 2001: Carbonization Under Pressure	308
5.9.12	The Year 2001: Review of Immersion Calorimetry	308
5.9.13	The Year 2001: Handbook of Porous Materials	310
5.9.14	The Year 2001: Carbon-sepiolite Pellets	310
5.10	Activation Processes (Thermal): Summary of Effects	312
5.10.1	General Considerations	312
5.10.2	Comparison of Activation by Carbon dioxide and Steam	313
5.10.3	One-step and Two-step Activations	316
5.10.4	Activation with Supercritical Water	317
6	Activation Processes (Chemical)	322
6.1	Chemical Activations	322
6.1.1	Introduction	322
6.1.2	Methodologies and Effects of Impregnations	324
6.1.3	Monoliths made from Activated Carbon via Chemical Activation	332
6.1.4	Density of Adsorbed Methane	335
6.1.5	Summary of Discussions	338
6.2	Chemistry of Activation by H ₃ PO ₄	339
6.2.1	Methodology	339
6.2.2	Porosity Development	340
6.2.3	Analytical Data	341
6.2.4	Morphological and Dimensional Changes	342
6.2.5	Chemistry of Activation by H ₃ PO ₄	344
6.2.6	Summary of Discussions	349
6.3	Chemical Activation: Use of Alkali Metal Salts – K and Na	350
6.3.1	Historical Introduction	350

6.3.2	Intercalation Compounds	350
6.3.3	Chemistry of Activation using Alkali Salts	353
6.3.4	Summary of Discussions of Alkali Salt Activations	357
6.4	Activation of a Carbon Cloth Using Six Chemical Activating Agents	358
6.5	Information from Selected Publications	359
7	SEM and TEM Images of Structures in Activated Carbons	366
7.1	Introduction	366
7.2	Experimental Microscopy	368
7.3	Selected Micrographs	369
7.3.1	Photography and SEM	369
7.3.2	Transmission Electron Microscopy	373
7.4	Conclusions	378
8	Applicability of Activated Carbon	383
8.1	Liquid-Phase Adsorptions	383
8.1.1	Introduction	383
8.1.2	Adsorption of Iodine and Acetic Acid from Aqueous Solution	384
8.1.3	Adsorption of Inorganic Solutes from Aqueous Solution	387
8.1.4	Adsorption of Organic Solutes from Aqueous Solution	398
8.1.5	Other Studies: Examples	412
8.2	Gas-Phase Applications	414
8.2.1	Introduction	414
8.2.2	Gas Purification	417
8.2.3	Separation of Gas Mixtures: CMS	419
8.2.4	Methane Storage	420
8.2.5	Solvent Recovery	424
8.3	Liquid-Phase Applications	424
8.3.1	Introduction	424
8.3.2	Water Treatment	425
8.3.3	Food and Beverage Processing	428
8.3.4	Chemicals and Pharmaceutical	428
8.3.5	Adsorption of Dyes	428
8.3.6	Other Applications	429
8.4	Porous Carbons in Catalytic Processes	430
8.4.1	Introduction	430
8.4.2	Carbon-Supported Catalysts	431
8.4.3	Effect of Carbon Surface Chemistry	433
8.4.4	Influence of Carbon Inertness	437
8.4.5	Catalysis by Carbon Surfaces	441
8.4.6	Additional Investigations	442
8.4.7	Aerogel Carbons for Catalysis	443
8.4.8	Summary of Carbon in Catalysis	444
8.5	Impregnated Carbons	444
8.6	AC: Worldwide	446
8.7	The Outlook for AC	447

9	Production and Reference Material	454
9.1	Production	454
9.1.1	Introduction	454
9.1.2	Manufacturing Methods	454
9.1.3	Precursors	454
9.1.4	Furnaces	458
9.1.5	Quality Control: Testing	459
9.1.6	Washed Carbons	462
9.1.7	Regeneration	463
9.1.8	Industrial Production	464
9.1.9	Market Consumption	465
9.1.10	Price	467
9.1.11	Conclusions	468
9.2	Reference Information	468
9.2.1	Introduction	468
9.2.2	Keywords from the Journal <i>carbon</i>	469
9.2.3	IUPAC Definitions (Fitzer <i>et al.</i> , 1995)	471
9.3	Surface Chemists: Biographies	501
9.3.1	Irving Langmuir (1881–1957)	501
9.3.2	Brunauer, Emmett and Teller	503
9.3.3	Stephen Brunauer (1903–1986)	503
9.3.4	Paul Emmett (1900–1985)	505
9.3.5	Edward Teller (1908–2003)	505
9.3.6	Mikhail M. Dubinin (1901–2001)	506
<i>Author Index</i>		509
<i>Subject Index</i>		525