

Contents

Preface to the First Edition	<i>XIII</i>
Preface to the Second Edition	<i>XVII</i>
Preface to the Third Edition	<i>XIX</i>
Preface to the Fourth Edition	<i>XXI</i>

1	Various Aspects of the Energy and Raw Material Supply	1
1.1	Present and Predictable Energy Requirements	2
1.2	Availability of Individual Sources	3
1.2.1	Oil	3
1.2.2	Natural Gas	4
1.2.3	Coal	5
1.2.4	Nuclear Fuels	5
1.3	Prospects for the Future Energy Supply	7
1.4	Present and Anticipated Raw Material Situation	8
1.4.1	Petrochemical Primary Products	8
1.4.2	Coal Conversion Products	11
2	Basic Products of Industrial Syntheses	15
2.1	Synthesis Gas	15
2.1.1	Generation of Synthesis Gas	15
2.1.1.1	Synthesis Gas <i>via</i> Coal Gasification	16
2.1.1.2	Synthesis Gas from Cracking of Natural Gas and Oil	19
2.1.2	Synthesis Gas Purification and Use	21
2.2	Production of the Pure Synthesis Gas Components	24
2.2.1	Carbon Monoxide	24
2.2.2	Hydrogen	26
2.3	C ₁ Units	29
2.3.1	Methanol	29
2.3.1.1	Manufacture of Methanol	30

2.3.1.2	Applications and Potential Applications of Methanol	32
2.3.2	Formaldehyde	37
2.3.2.1	Formaldehyde from Methanol	38
2.3.2.2	Uses and Potential Uses of Formaldehyde	40
2.3.3	Formic Acid	42
2.3.4	Hydrocyanic Acid	46
2.3.5	Methylamines	51
2.3.6	Halogen Derivatives of Methane	52
3	Olefins	59
3.1	Historical Development of Olefin Chemistry	59
3.2	Olefins from Cracking of Hydrocarbons	60
3.3	Special Manufacturing Processes for Olefins	63
3.3.1	Ethylene, Propene	63
3.3.2	Butenes	67
3.3.3	Higher Olefins	75
3.3.3.1	Unbranched Higher Olefins	75
3.3.3.2	Branched Higher Olefins	83
3.4	Olefin Metathesis	86
4	Acetylene	91
4.1	Present Significance of Acetylene	91
4.2	Manufacturing Processes for Acetylene	93
4.2.1	Manufacture Based on Calcium Carbide	93
4.2.2	Thermal Processes	94
4.3	Utilization of Acetylene	98
5	1,3-Diolefins	107
5.1	1,3-Butadiene	107
5.1.1	Historical Syntheses of 1,3-Butadiene	108
5.1.2	1,3-Butadiene from C ₄ Cracking Fractions	109
5.1.3	1,3-Butadiene from C ₄ Alkanes and Alkenes	111
5.1.4	Utilization of 1,3-Butadiene	114
5.2	Isoprene	117
5.2.1	Isoprene from C ₅ Cracking Fractions	118
5.2.2	Isoprene from Synthetic Reactions	119
5.3	Chloroprene	122
5.4	Cyclopentadiene	125
6	Syntheses involving Carbon Monoxide	127
6.1	Hydroformylation of Olefins	127
6.1.1	Chemical Basis of Hydroformylation	128
6.1.2	Industrial Operation of Hydroformylation	131
6.1.3	Catalyst Modifications in Hydroformylation	134

6.1.4	Utilization of oxo Products	136
6.1.4.1	Oxo Alcohols	136
6.1.4.2	Oxo Carboxylic Acids	138
6.1.4.3	Aldol and Condensation Products of the Oxo Aldehydes	139
6.2	Carbonylation of Olefins	141
6.3	Koch Carboxylic Acid Synthesis	143
7	Oxidation Products of Ethylene	147
7.1	Ethylene Oxide	147
7.1.1	Ethylene Oxide by the Chlorohydrin Process	148
7.1.2	Ethylene Oxide by Direct Oxidation	149
7.1.2.1	Chemical Principles	149
7.1.2.2	Process Operation	150
7.1.2.3	Potential Developments in Ethylene Oxide Manufacture	152
7.2	Secondary Products of Ethylene Oxide	153
7.2.1	Ethylene Glycol and Higher Ethylene Glycols	154
7.2.1.1	Potential Developments in Ethylene Glycol Manufacture	155
7.2.1.2	Uses of Ethylene Glycol	158
7.2.1.3	Secondary Products: Glyoxal, Dioxolane, 1,4-Dioxane	158
7.2.2	Polyethoxylates	160
7.2.3	Ethanolamines and Secondary Products	161
7.2.4	Ethylene Glycol Ethers	164
7.2.5	Additional Products from Ethylene Oxide	167
7.3	Acetaldehyde	168
7.3.1	Acetaldehyde via Oxidation of Ethylene	169
7.3.1.1	Chemical Basis	169
7.3.1.2	Process Operation	171
7.3.2	Acetaldehyde from Ethanol	172
7.3.3	Acetaldehyde by C ₃ /C ₄ Alkane Oxidation	173
7.4	Secondary Products of Acetaldehyde	173
7.4.1	Acetic Acid	174
7.4.1.1	Acetic Acid by Oxidation of Acetaldehyde	175
7.4.1.2	Acetic Acid by Oxidation of Alkanes and Alkenes	177
7.4.1.3	Carbonylation of Methanol to Acetic Acid	180
7.4.1.4	Potential Developments in Acetic Acid Manufacture	182
7.4.1.5	Use of Acetic Acid	183
7.4.2	Acetic Anhydride and Ketene	185
7.4.3	Aldol Condensation of Acetaldehyde and Secondary Products	189

7.4.4	Ethyl Acetate	191
7.4.5	Pyridine and Alkyl Pyridines	193
8	Alcohols	197
8.1	Lower Alcohols	197
8.1.1	Ethanol	197
8.1.2	2-Propanol	202
8.1.3	Butanols	205
8.1.4	Amyl Alcohols	209
8.2	Higher Alcohols	209
8.2.1	Oxidation of Paraffins to Alcohols	213
8.2.2	Alfol Synthesis	214
8.3	Polyhydric Alcohols	216
8.3.1	Pentaerythritol	216
8.3.2	Trimethylolpropane	217
8.3.3	Neopentyl Glycol	218
9	Vinyl Halogen and Vinyl Oxygen Compounds	221
9.1	Vinyl Halogen Compounds	221
9.1.1	Vinyl Chloride	221
9.1.1.1	Vinyl Chloride from Acetylene	222
9.1.1.2	Vinyl Chloride from Ethylene	223
9.1.1.3	Potential Developments in Vinyl Chloride Manufacture	226
9.1.1.4	Uses of Vinyl Chloride and 1,2-Dichloroethane	227
9.1.2	Vinylidene Chloride	229
9.1.3	Vinyl Fluoride and Vinylidene Fluoride	229
9.1.4	Trichloro- and Tetrachloroethylene	231
9.1.5	Tetrafluoroethylene	233
9.2	Vinyl Esters and Ethers	234
9.2.1	Vinyl Acetate	234
9.2.1.1	Vinyl Acetate Based on Acetylene or Acetaldehyde	234
9.2.1.2	Vinyl Acetate Based on Ethylene	236
9.2.1.3	Possibilities for Development of Vinyl Acetate Manufacture	238
9.2.2	Vinyl Esters of Higher Carboxylic Acids	240
9.2.3	Vinyl Ethers	241
10	Components for Polyamides	243
10.1	Dicarboxylic Acids	245
10.1.1	Adipic Acid	246
10.1.2	1,12-Dodecanedioic Acid	249
10.2	Diamines and Aminocarboxylic Acids	251

10.2.1	Hexamethylenediamine	251
10.2.1.1	Manufacture of Adiponitrile	251
10.2.1.2	Hydrogenation of Adiponitrile	255
10.2.1.3	Potential Developments in Adiponitrile Manufacture	256
10.2.2	ω -Aminoundecanoic Acid	257
10.3	Lactams	258
10.3.1	ϵ -Caprolactam	258
10.3.1.1	ϵ -Caprolactam from the Cyclohexanone Oxime Route	258
10.3.1.2	Alternative Manufacturing Processes for ϵ -Caprolactam	263
10.3.1.3	Possibilities for Development in ϵ -Caprolactam Manufacture	265
10.3.1.4	Uses of ϵ -Caprolactam	266
10.3.2	Lauro lactam	268
11	Propene Conversion Products	273
11.1	Oxidation Products of Propene	274
11.1.1	Propylene Oxide	274
11.1.1.1	Propylene Oxide from the Chlorohydrin Process	274
11.1.1.2	Indirect Oxidation Routes to Propylene Oxide	275
11.1.1.3	Possibilities for Development in the Manufacture of Propylene Oxide	279
11.1.2	Secondary Products of Propylene Oxide	283
11.1.3	Acetone	285
11.1.3.1	Direct Oxidation of Propene	286
11.1.3.2	Acetone from 2-Propanol	287
11.1.4	Secondary Products of Acetone	288
11.1.4.1	Acetone Aldolization and Secondary Products	289
11.1.4.2	Methacrylic Acid and Ester	290
11.1.5	Acrolein	295
11.1.6	Secondary Products of Acrolein	296
11.1.7	Acrylic Acid and Esters	299
11.1.7.1	Traditional Acrylic Acid Manufacture	299
11.1.7.2	Acrylic Acid from Propene	301
11.1.7.3	Possibilities for Development in Acrylic Acid Manufacture	303
11.2	Allyl Compounds and Secondary Products	304
11.2.1	Allyl Chloride	304
11.2.2	Allyl Alcohol and Esters	307
11.2.3	Glycerol from Allyl Precursors	309
11.3	Acrylonitrile	312

11.3.1	Traditional Acrylonitrile Manufacture	313
11.3.2	Ammonoxidation of Propene	314
11.3.2.1	Sohio Acrylonitrile Process	315
11.3.2.2	Other Propene/Propane Ammonoxidation Processes	316
11.3.3	Possibilities for Development of Acrylonitrile Manufacture	317
11.3.4	Uses and Secondary Products of Acrylonitrile	318
12	Aromatics — Production and Conversion	321
12.1	Importance of Aromatics	321
12.2	Sources of Feedstocks for Aromatics	322
12.2.1	Aromatics from Coking of Hard Coal	323
12.2.2	Aromatics from Reformate and Pyrolysis Gasoline	324
12.2.2.1	Isolation of Aromatics	327
12.2.2.2	Special Separation Techniques for Non-Aromatic/Aromatic and Aromatic Mixtures	328
12.2.3	Possibilities for Development of Aromatics Manufacture	333
12.2.4	Condensed Aromatics	334
12.2.4.1	Naphthalene	335
12.2.4.2	Anthracene	336
12.3	Conversion Processes for Aromatics	339
12.3.1	Hydrodealkylation	339
12.3.2	<i>m</i> -Xylene Isomerization	341
12.3.3	Disproportionation, Transalkylation, and Methylation	343
13	Benzene Derivatives	347
13.1	Alkylation and Hydrogenation Products of Benzene	348
13.1.1	Ethylbenzene	348
13.1.2	Styrene	351
13.1.3	Cumene	354
13.1.4	Higher Alkylbenzenes	356
13.1.5	Cyclohexane	357
13.2	Oxidation and Secondary Products of Benzene	359
13.2.1	Phenol	359
13.2.1.1	Manufacturing Processes for Phenol	360
13.2.1.2	Potential Developments in Phenol Manufacture	368
13.2.1.3	Uses and Secondary Products of Phenol	370
13.2.2	Dihydroxybenzenes	374

13.2.3	Maleic Anhydride	378
13.2.3.1	Maleic Anhydride from Oxidation of Benzene	379
13.2.3.2	Maleic Anhydride from Oxidation of Butene	380
13.2.3.3	Maleic Anhydride from Oxidation of Butane	382
13.2.3.4	Uses and Secondary Products of Maleic Anhydride	383
13.3	Other Benzene Derivatives	386
13.3.1	Nitrobenzene	386
13.3.2	Aniline	387
13.3.3	Diisocyanates	390
14	Oxidation Products of Xylene and Naphthalene	397
14.1	Phthalic Anhydride	397
14.1.1	Oxidation of Naphthalene to Phthalic Anhydride	397
14.1.2	Oxidation of o-Xylene to Phthalic Anhydride	399
14.1.3	Esters of Phthalic Acid	401
14.2	Terephthalic Acid	404
14.2.1	Manufacture of Dimethyl Terephthalate and Terephthalic Acid	405
14.2.2	Fiber Grade Terephthalic Acid	407
14.2.3	Other Manufacturing Routes to Terephthalic Acid and Derivatives	409
14.2.4	Uses of Terephthalic Acid and Dimethyl Terephthalate	413
15	Appendix	417
15.1	Process and Product Schemes	417
15.2	Definitions of Terms used in Characterizing Chemical Reactions	459
15.3	Abbreviations for Companies	461
15.4	Sources of Information	462
15.4.1	General Literature	462
15.4.2	More Specific Literature (publications, monographs)	464
	Index	487

