

CONTENTS

Preface	xxiii
Preface to the First Edition	xxv
Preface to the Second Edition	xxvii
Acknowledgments	xxix
Bryan Godel Reuben 1934–2012	xxxi
List of Acronyms and Abbreviations	xxxiii
Introduction: How to Use <i>Industrial Organic Chemicals, Third Edition</i>	1
I.1 Why This Book Was Written and How It Is Structured	2
I.2 North American Industry Classification System	5
I.3 Units and Nomenclature	5
I.4 General Bibliography	6
I.4.1 Encyclopedias	6
I.4.2 Books	7
I.4.3 Journals	8
I.4.4 Patents	9
I.4.5 Statistics and Internet Sources of Information	10
1. The Evolution of the Organic Chemicals Industry	13
I.1 The National Economy	13
I.2 Size of the Chemical Industry	16
I.3 Characteristics of the Chemical Industry	22
I.3.1 Capital Intensity and Economies of Scale	22
I.3.2 Criticality and Pervasiveness	24
I.3.3 Freedom of Market Entry	26
I.3.4 Strong Regulation	27
I.3.4.1 European Legislation	29
I.3.4.2 Political Factors	30

1.3.5	High but Declining Research and Development Expenditures	34
1.3.6	Dislocations	41
1.4	The Top Companies	43
1.5	The Top Chemicals	44
	Endnotes	46
2.	Globalization of the Chemical Industry	49
2.1	Overcapacity	51
2.1.1	Economic Cycles	55
2.2	Restructuring, Mergers, and Acquisitions	56
2.2.1	SuICIde of a UK Company	60
2.2.2	Private Equity	61
2.3	Participation in International Trade	63
2.4	Competition from Developing Countries	66
	Endnotes	69
3.	Transporting Chemicals	71
3.1	Shipping Petroleum	71
3.2	Shipping Gas	74
3.3	Shipping Chemicals	75
3.3.1	Gases	75
3.3.2	Liquids	77
3.3.3	Solids	85
3.4	Health and Safety	86
3.5	Economic Aspects	87
3.6	Trade in Specific Chemicals	88
3.7	Top Shipping Companies	90
	Endnotes	91
4.	Chemicals from Natural Gas and Petroleum	93
4.1	Petroleum Distillation	97
4.2	Shale Gas	100
4.2.1	Shale Gas Technology	101
4.3	Naphtha Versus Gaseous Feedstocks	102

4.4	Heavier Oil Fractions	103
4.5	Steam Cracking and Petroleum Refining Reactions	104
4.5.1	Steam Cracking	106
4.5.2	Choice of Feedstock	108
4.5.3	Economics of Steam Cracking	110
4.6	Catalytic Cracking	114
4.7	Mechanisms of Steam and Catalytic Cracking	117
4.8	Catalytic Reforming	119
4.9	Oligomerization	122
4.10	Alkylation	124
4.11	Hydrotreating and Coking	125
4.12	Dehydrogenation	126
4.13	Isomerization	128
4.14	Metathesis	128
4.14.1	Metathesis Outside the Refinery	129
4.14.2	Mechanism of Metathesis	131
4.15	Function of the Refinery and the Potential Petroleum Shortage	133
4.15.1	Unleaded Gasoline and the Clean Air Act	134
4.16	Separation of Natural Gas	136
4.17	Oil from Tar Sands	137
	Endnotes	137
5.	Chemicals and Polymers from Ethylene	139
5.1	Ethylene Polymers	141
5.1.1	Discovery of Low and High Density Polyethylenes	142
5.1.2	Low Density Polyethylene	144
5.1.3	High Density Polyethylene	146
5.1.4	Linear Low Density Polyethylene	147
5.1.5	Very High Molecular Weight Polyethylene	148
5.1.6	Metallocene Polyethylenes	149
5.1.7	Very Low Density Polyethylene	149
5.1.8	Bimodal HDPE	149
5.1.9	“Green” Polyethylene	150

5.2	Ethylene Copolymers	151
5.2.1	Chlorosulfonated Polyethylene	151
5.2.2	Ethylene-Vinyl Acetate	151
5.2.3	Ionomers	152
5.2.4	Copolymer from “Incompatible” Polymer Blends	152
5.2.5	Ethylene–Propylene Elastomers	153
5.2.6	Polyolefin Elastomers	153
5.3	Oligomerization	154
5.3.1	Dimerization	154
5.3.2	Ziegler Oligomerization of Ethylene	155
5.3.3	Other Ethylene Oligomerization Technologies	156
5.3.4	Shell Higher Olefins Process (SHOP)	158
5.4	Vinyl Chloride	160
5.5	Acetaldehyde	165
5.6	Vinyl Acetate	167
5.7	Ethylene Oxide	169
5.7.1	Ethylene Glycol	171
5.7.2	Proposed Non-Ethylene Oxide Processes for Ethylene Glycol Production	174
5.8	Styrene	177
5.9	Ethanol	181
5.10	Major Chemicals from Ethylene – A Summary	182
5.11	Lesser Volume Chemicals from Ethylene	185
5.11.1	Hydroformylation – Propionaldehyde, Propionic Acid, and <i>n</i> -Propanol	185
5.11.2	Ethyl Halides	186
5.11.3	Acetaldehyde Chemistry	187
5.11.4	Metal Complexes	191
5.11.5	Ethylenediamine and Related Compounds	191
5.11.6	Ethylene Oxide and Ethylene Glycol Derivatives	193
5.11.6.1	Oligomers	193
5.11.6.2	Glycol Ethers and Esters	194
5.11.6.3	Ethylene Carbonate	197
5.11.6.4	Aminoethyl Alcohols (Ethanolamines) and Derivatives	198
5.11.6.5	Ethyleneimine	199

5.11.6.6	1,3-Propanediol	200
5.11.6.7	Ethylene Glycol Derivatives	201
5.11.7	Vinyl Chloride and Ethylene Dichloride Derivatives	203
5.11.8	Vinyl Fluoride and Vinylidene Fluoride	204
5.11.9	Ethylene Dibromide	205
5.11.10	Ethanol Derivatives	206
5.11.11	Vinyl Esters and Ethers	207
	Endnotes	208
6.	Chemicals and Polymers from Propylene	211
6.1	On-Purpose Propylene Production Technologies and Propane Dehydrogenation	214
6.1.1	Propylene Via Enhanced Fluidized Catalytic Cracking	215
6.1.2	Propylene Via Selective C ₄ /C ₅ Cracking	215
6.2	Main Polymers and Chemicals from Propylene	217
6.2.1	Propylene Polymers and Copolymers	217
6.3	Oligomerization	221
6.4	Acrylic Acid	222
6.4.1	Biorenewable Processes to Acrylic Acid	225
6.4.2	Acrylic Acid Markets	226
6.5	Acrylonitrile	227
6.5.1	Uses of Acrylonitrile	230
6.6	Cumene/Phenol and Cumene Hydroperoxide	231
6.7	Acetone and Isopropanol	233
6.7.1	Methyl Methacrylate	235
6.7.2	Methyl Isobutyl Ketone and Other Acetone Derivatives	242
6.8	Propylene Oxide	242
6.8.1	Other Propylene Oxide Processes	247
6.8.1.1	Acetoxylation of Propylene	248
6.8.1.2	Direct Oxidation	249
6.8.1.3	Use of Peracids	249
6.8.1.4	Electrochemical Processes	250
6.8.1.5	Biotechnological Approaches	252
6.8.2	Propylene Oxide Applications	253

6.9	<i>n</i> -Butyraldehyde and Isobutyraldehyde	255
6.9.1	Uses for Butyraldehyde, Isobutyraldehyde, and <i>n</i> -Butanol	258
6.9.2	Other Oxo Products	260
6.10	Major Chemicals from Propylene – A Perspective	261
6.11	Lesser Volume Chemicals from Propylene	263
6.11.1	Allyl Chloride and Epichlorohydrin	263
6.11.2	Glycerol	266
6.11.3	Acrylamide	266
6.11.4	Acrolein	268
6.11.5	Acrylonitrile Derivatives	270
	Endnotes	270
7.	Chemicals from the C₄ Stream	273
7.1	Chemicals and Polymers from Butadiene	277
7.1.1	Tires	280
7.1.2	Styrene–Butadiene Elastomers	281
7.1.3	Polybutadienes and Other Elastomers	282
7.1.4	Acrylonitrile–Butadiene–Styrene Resins	283
7.1.5	Hexamethylenediamine	284
7.1.6	Lesser Volume Chemicals from Butadiene	289
7.1.6.1	Cyclization	289
7.1.6.2	Dimerization and Trimerization	291
7.1.6.3	Diels–Alder Reactions	293
7.1.6.4	Adipic Acid	294
7.1.6.5	1,4-Butanediol	294
7.1.6.6	<i>trans</i> -1,4-Hexadiene	295
7.1.6.7	Dimethyl-2,6-naphthalene Dicarboxylate	295
7.1.6.8	Butadiene Monoepoxide	296
7.2	Chemicals and Polymers from Isobutene	296
7.2.1	Methyl <i>tert</i> -Butyl Ether	297
7.2.2	Butyl Rubber	298
7.2.3	Polyisobutenes and Isobutene Oligomers and Polymers	298
7.2.4	<i>tert</i> -Butanol	299
7.2.5	Methyl Methacrylate	299
7.2.6	Lesser Volume Chemicals from Isobutene	299

7.3	Chemicals and Polymers from 1- and 2-Butenes	302
7.4	Chemicals from <i>n</i> -Butane	303
7.4.1	Acetic Acid	303
7.4.2	Maleic Anhydride	303
7.4.3	Succinic, Malic, Fumaric, and Tartaric Acids	306
	Endnotes	307
8.	Chemicals from the C₅ Stream	309
8.1	Separation of the C ₅ Stream	311
8.2	Isoprene	312
8.2.1	Natural Rubber	312
8.2.2	Vulcanization	313
8.2.3	Production of Petrochemical Isoprene	314
8.2.4	Applications of Isoprene	317
8.3	Cyclopentadiene and Dicyclopentadiene	319
8.4	Pentene-1 and Piperylene	321
	Endnotes	321
9.	Chemicals from Benzene	323
9.1	Phenol	326
9.1.1	Phenolic Resins	331
9.1.2	Bisphenol A	333
9.1.2.1	Epoxy Resins	333
9.1.2.2	Polycarbonate Resins	334
9.1.2.3	Lesser Volume Uses for Bisphenol A	337
9.1.2.4	Environmental Problems	340
9.1.3	Cyclohexanone	341
9.1.4	Alkylphenols	342
9.1.5	Chlorinated Phenols	342
9.1.6	2,6-Xylenol/Cresols	343
9.1.7	Aniline from Phenol	344
9.2	Cyclohexane	344
9.2.1	Adipic Acid	344
9.2.1.1	Nylons from Adipic Acid	349
9.2.2	Caprolactam	349

9.3	Aniline	354
9.3.1	4,4'-Diphenylmethane Isocyanate	357
9.4	Alkylbenzenes	361
9.5	Maleic Anhydride	362
9.6	Chlorinated Benzenes	363
9.7	Dihydroxybenzenes	364
9.7.1	Hydroquinone	364
9.7.2	Resorcinol	368
9.7.3	Catechol	369
9.8	Anthraquinone	370
9.8.1	Hydrogen Peroxide	371
	Endnotes	372
10.	Chemicals from Toluene	375
10.1	Hydrodealkylation, Disproportionation, and Transalkylation	375
10.2	Solvents	378
10.3	Dinitrotoluene and Toluene Diisocyanate	378
10.4	Lesser Volume Chemicals from Toluene	380
	Endnotes	382
11.	Chemicals from Xylenes	383
11.1	<i>o</i> -Xylene and Phthalic Anhydride	386
11.1.1	Plasticizers	387
11.1.2	Alkyd Resins	391
11.1.3	Unsaturated Polyester Resin	393
11.2	<i>m</i> -Xylene and Isophthalic Acid	395
11.2.1	Uses of Isophthalic Acid	396
11.3	<i>p</i> -Xylene and Terephthalic Acid/Dimethyl Terephthalate	397
11.3.1	Oxidation of <i>p</i> -Xylene	398
11.3.2	Alternate Sources for Terephthalic Acid	400
11.3.3	Poly(ethylene terephthalate)	400
11.3.4	Lower Volume Polymers from Terephthalic Acid	403
	Endnotes	404

12. Chemicals from Methane	407
12.1 Hydrocyanic Acid	408
12.2 Halogenated Methanes	411
12.2.1 Chloromethane	412
12.2.2 Dichloromethane	413
12.2.3 Trichloromethane	413
12.2.4 Fluorocarbons	414
12.2.5 Tetrachloromethane and Carbon Disulfide	414
12.2.6 Bromomethane	416
12.3 Acetylene	417
12.3.1 1,4-Butanediol and 2-Methyl-1,3-propanediol	419
12.3.2 Lesser Uses for Acetylene	423
12.4 Synthesis Gas	424
12.4.1 Steam Reforming of Methane	425
12.4.2 Variants of Steam Reforming	427
12.4.3 Partial Oxidation of Hydrocarbons	428
12.4.4 Solid Feedstocks	428
12.4.5 Hydrogen	429
12.5 Chemicals from Synthesis Gas	429
12.5.1 Ammonia and Its Derivatives	430
12.5.1.1 The Crisis of Nitrogen Depletion	430
12.5.1.2 Ammonia Manufacture	431
12.5.1.3 Urea and Melamine Resins	434
12.5.2 Methanol	435
12.5.2.1 Formaldehyde	438
12.5.2.2 Acetic Acid	439
12.5.2.3 Acetic Anhydride	442
12.5.2.4 Methanol to Gasoline	445
12.5.2.5 Methanol to Olefins	446
12.5.2.6 Lower Volume and Proposed Uses for Methanol	448
12.5.2.7 C ₁ -Based Development Processes	452
12.6 Carbon Monoxide Chemistry	454
12.6.1 Proposed Chemistry Based on Carbon Monoxide	455
12.7 Gas-to-Liquid Fuels	459
12.7.1 Sasol GTL Technology	459
12.7.2 Shell Middle Distillate Synthesis	459

12.7.3 Other GTL Technologies	460
Endnotes	460
13. Chemicals from Alkanes	463
13.1 Functionalization of Methane	464
13.1.1 Methane to Methanol/Formaldehyde	464
13.1.2 Dimerization of Methane	466
13.1.3 Aromatization of Methane	467
13.2 Functionalization of C ₂ –C ₄ Alkanes	468
13.2.1 Oxidation of C ₂ –C ₄ Alkanes	468
13.2.2 Dehydrogenation of C ₂ –C ₄ Alkanes	470
13.2.3 Aromatization of C ₂ –C ₄ Alkanes	471
13.3 Carbon Black	472
Endnotes	473
14. Chemicals from Coal	475
14.1 Chemicals from Coke Oven Distillate	477
14.2 The Fischer–Tropsch Reaction	480
14.3 Coal Hydrogenation	484
14.4 Substitute Natural Gas	485
14.5 SNG and Synthesis Gas Technology	485
14.6 Underground Coal Gasification	488
14.7 Calcium Carbide	488
14.7.1 The Chinese Chemicals to Coal Program	489
14.8 Coal and the Environment	490
Endnotes	491
15. Fats and Oils	493
15.1 Markets for Fats and Oils	495
15.2 Purification of Fats and Oils	497
15.3 Fatty Acids	499
15.3.1 Applications of Fatty Acids	501
15.4 Fatty Nitrogen Compounds	502
15.5 “Dimer” Acid	504

15.6	Aminoamides and Imidazolines	506
15.7	Azelaic, Pelargonic, and Petroselinic Acids	507
15.8	Fatty Alcohols	508
15.9	Epoxidized Oils	509
15.10	Ricinoleic Acid	510
15.11	Glycerol	512
	15.11.1 Established Glycerol Uses	512
15.12	Alcoholysis of Fats and Oils	513
	15.12.1 Cocoa Butter and Mothers' Milk	513
	15.12.1.1 Mothers' Milk	515
	15.12.2 Trans Fats and Interesterification	515
	15.12.3 Biodiesel and Lubricants	516
	15.12.3.1 Algae	518
15.13	Alkyl Polyglycosides	519
15.14	Non-Caloric Fat-like Substances	519
	Endnotes	520
16.	Carbohydrates	523
16.1	Sugars and Sorbitol	523
	16.1.1 Isosorbide	530
16.2	Furfural	530
16.3	Starch	532
16.4	Cellulose	535
	16.4.1 Miscellaneous Chemicals from Wood	539
	16.4.1.1 Vanillin	541
	16.4.1.2 Levulinic Acid	542
16.5	Gums	543
16.6	Fermentation and Biotechnology	544
	16.6.1 Amino Acids	547
	16.6.1.1 L-Glutamic Acid	547
	16.6.1.2 L-Lysine	547
	16.6.1.3 L-Aspartic Acid	548
	16.6.1.4 L-Cysteine	549
	16.6.2 Polymers	550

16.6.3	Proteins by Recombinant DNA Technology	550
16.6.4	Fermentation and Renewables Scenarios	551
16.6.5	Biofuels	554
16.6.5.1	The Brazilian Experience	554
16.6.5.2	Is U.S. Bioethanol a Renewable Energy Source?	555
16.6.5.3	Biomass as Feedstock	556
16.6.5.4	Catalytic Bioforming	556
16.6.5.5	Biotechnology Versus Synthesis Gas	557
	Endnotes	558
17.	How Polymers Are Made	561
17.1	Polymerization	565
17.2	Functionality	568
17.3	Step Growth and Chain Growth Polymerizations	571
17.3.1	Free Radical Polymerization	573
17.3.2	Chain Transfer	575
17.3.3	Copolymerization	577
17.3.4	Molecular Weight	579
17.3.5	Polymerization Procedures	580
17.3.5.1	Photoinitiation	582
17.3.6	Ionic Polymerization	584
17.3.7	Living Polymers	589
17.3.8	Block Copolymers	589
17.3.9	Graft Copolymers	592
17.3.10	Metal Complex Catalysts	593
17.3.11	Metal Oxide Catalysts	598
17.3.12	Metallocene and Other Single Site Catalysts	599
17.3.12.1	Single Site Nonmetallocene Catalysts	602
17.3.12.2	Late Transition Metal Catalysts	603
17.3.12.3	Commercial Prospects of LLDPEs	604
17.4	Examples of Step Polymerization	605
17.4.1	Phenoplasts and Aminoplasts	605
17.4.2	Polyurethanes	606
17.4.3	Epoxy Resins	611
17.4.4	Dendritic and Hyperbranched Polymers	613
17.4.5	Conducting Polymers	617
17.4.6	Conducting and Semiconducting Inks	621

17.5	Polymer Properties	622
17.5.1	Crystallinity	622
17.5.2	Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature	626
17.5.3	Molecular Cohesion	628
17.5.4	Stress–Strain Diagrams	628
17.6	Classes of Polymers	630
17.7	Plastics Fabrication Techniques	631
	Endnotes	635
18.	Industrial Catalysis	637
18.1	Catalyst Choice	637
18.1.1	Reaction Velocity and Selectivity	638
18.1.2	Recovery of Unchanged Catalyst	641
18.1.3	Catalyst Deactivation	642
18.1.4	Access to Nonequilibrium Products	642
18.2	Homogeneous and Heterogeneous Catalysis	643
18.2.1	Reactors for Heterogeneous Catalysts	644
18.2.2	Immobilization of Homogeneous Catalysts	646
18.3	Catalyst Markets	647
18.4	Catalysis by Acids and Bases	651
18.5	Dual Function Catalysis	654
18.6	Catalysis by Metals, Semiconductors, and Insulators	655
18.6.1	Catalysts for Automobile Emission Control	656
18.7	Coordination Catalysis	657
18.7.1	Catalysts for Stereoregular Compounds	658
18.7.2	Asymmetric Synthesis	660
18.8	Enzymes	661
18.8.1	Catalytic Antibodies	663
18.9	Shape-Selective Catalysts	664
18.10	Phase-Transfer and Fluorous Biphase Catalysis	669
18.11	Nanocatalysis	670
18.12	Catalysts of the Future	673
18.12.1	Catalyst Design	673
18.12.2	Higher Selectivities	673

18.12.3	Catalysts with Greater Activity	674
18.12.4	Pollution Problems	675
18.12.5	Catalysts for New Reactions	675
18.12.6	Catalysts that Mimic Natural Catalysts	676
18.12.7	Catalyst Discovery Via High Throughput Experimentation	676
	Endnotes	677
19.	Green Chemistry	681
19.1	The Decline of Acetylene Chemistry	683
19.2	Nylon	683
19.3	Replacement of Phosgene	684
19.4	Monomethylation by Dimethyl Carbonate	685
19.5	Liquid and Supercritical Carbon Dioxide and Water	685
19.6	Ionic Liquids	687
19.7	Photocatalysts	690
19.8	Paired Electrosynthesis	691
19.9	“Green” Pharmaceuticals	692
19.9.1	Ibuprofen	692
19.9.2	Sertraline	694
19.9.3	Pharmaceuticals from “Renewables”	696
19.10	Catalytic Dehydrogenation of Diethanolamine	698
19.11	Genetic Manipulation	698
19.12	Biodegradable Packaging	698
19.12.1	Polyhydroxyalkanoates	701
19.13	The Presidential Green Chemistry Challenge Program	703
	Endnotes	704
20.	Sustainability	707
20.1	Climate Change	708
20.2	Resource Depletion	712
20.2.1	Food, Water, and People	713
20.2.1.1	Food	713
20.2.1.2	Water	714
20.2.1.3	People	715

20.3	Energy Sources	717
20.3.1	Wind Power	719
20.3.2	Wave Power	720
20.3.3	Solar Power	721
20.3.3.1	Concentrated Solar Power	721
20.3.3.2	Photovoltaic Cells	721
20.3.3.3	Dye-Sensitized Solar Cells	722
20.3.3.4	Artificial Photosynthesis	724
20.3.4	Nuclear Energy	726
20.3.5	Methane Hydrate	727
20.3.6	The Hydrogen Economy	728
20.3.7	Fuel Cells	729
20.3.8	Electric Vehicles	735
20.4	Pollution	736
20.4.1	The Ozone Layer	738
20.4.2	Trace Chemicals	742
20.4.2.1	Pesticides	742
20.4.2.2	Nonpesticide Lipophiles	743
20.4.3	Air Pollution	744
20.4.3.1	Sulfur Dioxide Particulates	745
20.4.3.2	Automobile Exhaust Emissions	748
20.4.4	Water Treatment	750
20.4.5	Solid Wastes	752
20.4.5.1	Waste Prevention	753
20.4.5.2	Recycling	754
20.4.5.3	Combustion/Incineration	755
20.4.5.4	Sanitary Landfill	756
20.4.6	Petrochemical Industry Wastes	758
20.4.7	Other Environmental Problems	759
20.5	Valediction	759
	Endnotes	761
	Appendix A: A Note on Cost Calculations	765
	Appendix B: Units and Conversion Factors	771
	Appendix C: Special Units in the Chemical Industry	773
	Appendix D: The Importance of Shale Gas and Shale Oil	775
	Index	779