

CONTENTS

Units and Conversion Factors	xxi
Special Units in the Chemical Industry	xxiii
Chapter 0 How to Use Industrial Organic Chemicals	1
0.1 Why this Book was Written and how it is Structured / 1	
0.2 Standard Industrial Classification / 3	
0.3 Units and Nomenclature / 3	
0.4 General Bibliography / 4	
0.4.1 Encyclopedias / 4	
0.4.2 Books / 5	
0.4.3 Journals / 8	
0.4.4 Patents / 9	
0.4.5 Statistics / 10	
0.4.6 CD-ROM and On-Line Data Bases / 11	
Chapter 1 The Chemical Industry	13
1.1 The National Economy / 13	
1.2 Size of the Chemical Industry / 17	
1.3 Characteristics of the Chemical Industry / 18	
1.3.1 Maturity / 18	
1.3.2 Participation in International Trade / 22	
1.3.3 Competition from Developing Countries / 24	
1.3.4 Capital Intensity and Economies of Scale / 26	
1.3.5 Criticality and Pervasiveness / 27	
1.3.6 Freedom of Market Entry / 28	
1.3.7 Strong Regulation / 29	
1.3.8 High Research and Development Expenditures / 31	
1.3.9 Dislocations / 35	
1.4 The Top Chemical Companies / 37	
1.5 The Top Chemicals / 40	
Notes and References / 44	
Chapter 2 Chemicals from Natural Gas and Petroleum	46
2.1 Petroleum Distillation / 50	

2.2	Petroleum Refining Reactions / 55
2.2.1	Steam Cracking / 55
2.2.1.1	Choice of Feedstock / 58
2.2.1.2	Economics of Steam Cracking / 59
2.2.1.3	Mechanism of Cracking / 64
2.2.2	Catalytic Cracking / 65
2.2.3	Catalytic Reforming / 67
2.2.4	Oligomerization / 70
2.2.5	Alkylation / 72
2.2.6	Hydrotreating and Coking / 73
2.2.7	Dehydrogenation / 74
2.2.8	Isomerization / 75
2.2.9	Metathesis / 75
2.2.9.1	Metathesis Outside the Refinery / 76
2.2.9.2	Mechanism of Metathesis / 78
2.3	The Refinery: A Perspective / 79
2.3.1	The Function of the Refinery and the Potential Petroleum Shortage / 80
2.3.2	Unleaded Gasoline and the Clean Air Act / 81
2.4	Separation of Natural Gas / 83
	Notes and References / 84

Chapter 3 Chemicals and Polymers from Ethylene

88

3.1	Ethylene Polymers / 91
3.1.1	Discovery of Low- and High-Density Polyethylenes / 92
3.1.2	Low-Density Polyethylene / 93
3.1.3	High-Density Polyethylene / 94
3.1.4	Linear Low-Density Polyethylene / 94
3.1.5	Very High Molecular Weight Polyethylene / 95
3.2	Ethylene Copolymers / 96
3.2.1	Chlorosulfonated Polyethylene / 96
3.2.2	Ethylene-Vinyl Acetate / 96
3.2.3	Ionomers / 97
3.2.4	Copolymer from "Incompatible" Polymer Blends / 97
3.2.5	Ethylene-Propylene Elastomers / 98
3.2.6	Ultra-Low-Density Polyethylene / 99
3.2.7	Photodegradable Copolymers / 99

3.3	Oligomerization / 99
3.3.1	Dimerization / 99
3.3.2	Ziegler Oligomerization of Ethylene / 100
3.3.3	Shell Oligomerization of Ethylene / 101
3.3.4	The Shell Higher Olefins Process / 102
3.4	Vinyl Chloride / 104
3.5	Acetaldehyde / 107
3.6	Vinyl Acetate / 109
3.7	Ethylene Oxide / 110
3.7.1	Ethylene Glycol / 112
3.7.2	Proposed Processes for Ethylene Glycol Production / 114
3.8	Styrene / 117
3.9	Ethanol / 120
3.10	Major Chemicals from Ethylene: A Summary / 121
3.11	Lesser Volume Chemicals from Ethylene / 123
3.11.1	Hydroformylation: Propionaldehyde, Propionic Acid, and <i>n</i> -Propanol / 123
3.11.2	Ethyl Halides / 125
3.11.3	Acetaldehyde Chemistry / 126
3.11.4	Metal Complexes / 130
3.11.5	Ethylene Diamine and Related Compounds / 131
3.11.6	Ethylene Oxide and Ethylene Glycol Derivatives / 133
3.11.6.1	<i>Oligomers</i> / 133
3.11.6.2	<i>Glycol Ethers and Esters</i> / 133
3.11.6.3	<i>Ethylene Carbonate</i> / 134
3.11.6.4	<i>Aminoethyl Alcohols</i> (<i>Ethanolamines</i>) and <i>Derivatives</i> / 135
3.11.6.5	<i>Ethyleneimine</i> / 138
3.11.6.6	<i>Ethylene Glycol Derivatives</i> / 139
3.11.7	Vinyl Chloride and Ethylene Dichloride Derivatives / 141
3.11.8	Vinyl Fluorides and Vinylidene Fluoride / 142
3.11.9	Ethylene Dibromide / 143
3.11.10	Ethanol Derivatives / 144
3.11.11	Vinyl Esters and Ethers / 145
	Notes and References / 146

Chapter 4 Chemicals and Polymers from Propylene 149

- 4.1 Propylene Polymers and Copolymers / 152
- 4.2 Oligomerization / 154
- 4.3 Acrylic Acid / 155
- 4.4 Acrylonitrile / 159
 - 4.4.1 Uses of Acrylonitrile / 161
- 4.5 Cumene and Cumene Hydroperoxide/Phenol / 163
- 4.6 Acetone and Isopropanol / 164
 - 4.6.1 Methyl Methacrylate / 165
 - 4.6.2 Methyl Isobutyl Ketone and Other Acetone Derivatives / 170
- 4.7 Propylene Oxide / 170
 - 4.7.1 Propylene Oxide Applications / 174
 - 4.7.2 Projected Propylene Oxide–Propylene Glycol Processes / 175
 - 4.7.3 Other Novel Syntheses of Propylene Oxide / 176
 - 4.7.3.1 *Direct Oxidation* / 176
 - 4.7.3.2 *Use of Peracids or Hydrogen Peroxide* / 176
 - 4.7.3.3 *Electrochemical Processes* / 178
 - 4.7.3.4 *Biotechnological Approaches* / 179
- 4.8 *n*-Butyraldehyde and Isobutyraldehyde / 181
 - 4.8.1 Uses for Butyraldehyde and Isobutyraldehyde / 183
 - 4.8.2 Other Oxo Products / 184
- 4.9 Major Chemicals from Propylene: A Summary / 185
- 4.10 Lesser Volume Chemicals from Propylene / 187
 - 4.10.1 Allyl Chloride and Epichlorohydrin / 187
 - 4.10.2 Glycerol / 188
 - 4.10.3 Acrylamide / 190
 - 4.10.4 Acrolein / 191
 - 4.10.5 Acrylonitrile Derivatives / 192
- Notes and References / 193

Chapter 5 Chemicals and Polymers from the C₄ Stream 196

- 5.1 Chemicals and Polymers from Butadiene / 200
 - 5.1.1 Acrylonitrile–Butadiene–Styrene Resins / 204

7.1.7	Aniline from Phenol /	248
7.2	Cyclohexane /	248
7.2.1	Adipic Acid /	248
7.2.1.1	<i>Nylons from Adipic Acid /</i>	<i>251</i>
7.2.2	Caprolactam /	251
7.3	Aniline /	255
7.3.1	4,4'-Diphenylmethane Diisocyanate /	257
7.4	Alkylbenzenes /	261
7.5	Maleic Anhydride /	261
7.6	Chlorinated Benzenes /	262
7.7	Dihydroxybenzenes /	263
7.8	Anthraquinone /	268
	Notes and References /	269

Chapter 8 Chemicals and Polymers from Toluene 272

8.1	Hydrodealkylation and Disproportionation /	272
8.2	Solvents /	274
8.3	Dinitrotoluene and Toluene Diisocyanate /	274
8.4	Lesser Volume Chemicals from Toluene /	276
	Notes and References /	278

Chapter 9 Chemicals and Polymers from Xylenes 279

9.1	<i>o</i> -Xylene and Phthalic Anhydride /	281
9.1.1	Uses of Phthalic Anhydride /	282
9.2	<i>m</i> -Xylene and Isophthalic Acid /	286
9.2.1	Uses of Isophthalic Acid /	287
9.3	<i>p</i> -Xylene and Terephthalic Acid/Dimethyl Terephthalate /	288
9.3.1	Oxidation of <i>p</i> -Xylene /	288
9.3.2	Alternate Sources for Terephthalic Acid /	290
9.3.3	Poly(ethylene terephthalate) /	291
9.3.4	Lower Volume Polymers from Terephthalic Acid /	292
	Notes and References /	293

Chapter 10 Chemicals from Methane 294

10.1	Hydrocyanic Acid /	294
10.2	Halogenated Methanes /	297

10.2.1	Chloromethane /	298
10.2.2	Dichloromethane /	299
10.2.3	Trichloromethane /	299
10.2.4	Tetrachloromethane and Carbon Disulfide /	300
10.2.5	Bromomethane /	302
10.3	Acetylene /	302
10.3.1	1,4-Butanediol /	304
10.3.2	Lesser Uses for Acetylene /	307
10.4	Synthesis Gas /	308
10.4.1	Steam Reforming of Methane /	308
10.4.2	Variants of Steam Reforming /	310
10.4.3	Partial Oxidation of Hydrocarbons /	311
10.4.4	Solid Feedstocks /	312
10.4.5	Hydrogen /	312
10.5	Chemicals from Synthesis Gas /	313
10.5.1	Ammonia and its Derivatives /	313
10.5.1.1	<i>Urea and Melamine– Formaldehyde Resins</i> /	315
10.5.2	Methanol /	317
10.5.2.1	<i>Formaldehyde</i> /	318
10.5.2.2	<i>Acetic Acid</i> /	320
10.5.2.3	<i>Acetic Anhydride</i> /	321
10.5.2.4	<i>Methanol to Gasoline</i> /	325
10.5.2.5	<i>Lower Volume and Proposed Uses for Methanol</i> /	326
10.5.2.6	<i>C₁-Based Development Processes</i> /	329
10.6	Carbon Monoxide Chemistry /	331
10.6.1	Proposed Processes Based on Carbon Monoxide /	332
	Notes and References /	335

Chapter 11 Chemicals from Alkanes**338**

11.1	Functionalization of Methane /	339
11.1.1	Methane to Methanol/Formaldehyde /	339
11.1.2	Dimerization of Methane /	340
11.1.3	Aromatization of Methane /	340
11.2	Functionalization of C ₂ –C ₄ Alkanes /	341

- 11.2.1 Oxidation of C_2-C_4 Alkanes / 341
- 11.2.2 Dehydrogenation of C_2-C_4 Alkanes / 342
- 11.2.3 Aromatization of C_2-C_4 Alkanes / 342
- 11.3 Carbon Black / 344
- Notes and References / 345

Chapter 12 Chemicals from Coal 347

- 12.1 Chemicals from Coke Oven Distillate / 348
- 12.2 The Fischer-Tropsch Reaction / 350
- 12.3 Shell Middle Distillate Synthesis / 352
- 12.4 Coal Hydrogenation / 353
- 12.5 Substitute Natural Gas / 354
- 12.6 Calcium Carbide / 355
- 12.7 Coal and the Environment / 356
- Notes and References / 356

Chapter 13 Fats and Oils 358

- 13.1 Fatty Acids / 362
- 13.2 Fatty Nitrogen Compounds / 366
- 13.3 "Dimer" Acid / 368
- 13.4 Aminoamides and Imidazolines / 369
- 13.5 Azelaic, Pelargonic and Petroselinic Acids / 370
- 13.6 Fatty Alcohols / 371
- 13.7 Epoxidized Oils / 373
- 13.8 Ricinoleic Acid / 373
- 13.9 Glycerol / 375
- 13.10 Alcoholysis of Fats and Oils / 375
 - 13.10.1 Cocoa Butter / 376
- 13.11 The Future of Fat and Oil Chemistry / 377
 - 13.11.1 Noncaloric Fat-Like Substances / 377
 - 13.11.2 Alkyl Polyglycosides / 377
 - 13.11.3 Fatty Acid-Based Fuels and Lubricants / 378
- Notes and References / 379

Chapter 14 Carbohydrates 382

- 14.1 Sugars and Furfural / 382
 - 14.1.1 Furfural / 386
- 14.2 Starch / 389

- 14.3 Cellulose / 391
- 14.4 Gums / 399
- 14.5 Fermentation and Biotechnology / 396
 - 14.5.1 Amino Acids / 398
 - 14.5.2 Polymers / 400
 - 14.5.3 Proteins by Recombinant DNA Technology / 401
 - 14.5.4 A Fermentation Scenario / 402
- Notes and References / 403

Chapter 15 How Polymers Are Made **404**

- 15.1 Polymerization / 408
- 15.2 Functionality / 410
- 15.3 Step Growth and Chain Growth Polymerizations / 414
 - 15.3.1 Free Radical Polymerization / 416
 - 15.3.2 Chain Transfer / 418
 - 15.3.3 Copolymerization / 420
 - 15.3.4 Molecular Weight / 422
 - 15.3.5 Polymerization Procedures / 424
 - 15.3.6 Ionic Polymerization / 426
 - 15.3.7 Living Polymers / 432
 - 15.3.8 Block Copolymers / 432
 - 15.3.9 Graft Copolymers / 435
 - 15.3.10 Metal Complex Catalysts / 435
 - 15.3.11 Metal Oxide Catalysts / 440
 - 15.3.12 Metallocene Catalysts / 441
- 15.4 Examples of Step Polymerization / 445
 - 15.4.1 Phenoplasts and Aminoplasts / 445
 - 15.4.2 Polyurethanes / 447
 - 15.4.3 Epoxy Resins / 450
- 15.5 Polymer Properties / 452
 - 15.5.1 Crystallinity / 452
 - 15.5.2 Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature / 456
 - 15.5.3 Molecular Cohesion / 457
 - 15.5.4 Stress–Strain Diagrams / 458
- 15.6 Classes of Polymers / 460
- Notes and References / 462

Chapter 16 Industrial Catalysis**468**

- 16.1 Catalyst Choice / 468
 - 16.1.1 Reaction Velocity and Selectivity / 470
 - 16.1.2 Recovery of Unchanged Catalyst / 472
 - 16.1.3 Catalyst Deactivation / 473
 - 16.1.4 Access to Nonequilibrium Products / 474
- 16.2 Homogeneous and Heterogeneous Catalysis / 474
 - 16.2.1 Reactors for Heterogeneous Catalysts / 475
 - 16.2.2 Immobilization of Homogeneous Catalysts / 476
- 16.3 Catalyst Markets / 477
- 16.4 Catalysis by Acids and Bases / 480
- 16.5 Dual Function Catalysis / 483
- 16.6 Catalysis by Metals, Semiconductors, and Insulators / 484
 - 16.6.1 Catalysts for Automobile Emission Control / 486
- 16.7 Coordination Catalysis / 486
 - 16.7.1 Catalysis to Stereoregular Products / 487
 - 16.7.2 Asymmetric Synthesis / 490
- 16.8 Enzymes / 491
 - 16.8.1 Catalytic Antibodies / 493
- 16.9 Shape-Selective Catalysts / 494
- 16.10 Phase-Transfer Catalysis / 497
- 16.11 Catalysts of the Future / 498
 - 16.11.1 Artificial Photosynthesis / 500
- Notes and References / 503

Index**509**