#### а ^

ABS resin 207-208 - synthesis 208 – uses 208 acetaldehyde 6, 210, 221-248, 258 - acetic acid from 244 - chemicals from acetylene 258-259 – condensation 224 conversion to acetic acid 222 - formation by Wacker reaction 235 - history 234-235 - mercuric ion-catalyzed addition of water to acetylene 234 - via oxidation of ethanol 238 - production 150, 234 - reactions of 210 - Wacker reaction 222, 235-238 acetic acid 221-223, 238, 260 - BASF process 244 - conversion to acetaldehyde 222 - by fermentation of carbohydrates 243 - by hydrocarbon oxidation 243 - by methanol carbonylation 244 - modern processes for production 222 parallels to hydroboration 240–241 - synthesis 222 acetone 56, 223, 243 - from cumene 59 - hemiketal from phenol and acetone 62 reaction -- with HCN 139 -- with phenol 56 acetonitrile 207, 213 - byproduct 213 industrial solvent 213 acetylene 6-7, 234-237, 249-260, 268-271 - acidity 252-253 – – role of s-character of C-H bond 253

- boutique use for 254

- 1,4-butynediol 268 - calcium carbide 254 – carbanion, acetylenic 269 -- nucleophilic character 252 - chemicals from 258-260 -- acetaldehyde 258-259 - - acrylic acid from 211-212 -- acrylonitrile 6, 258-259 -- 1,4-butanediol 6, 258-259 -- vinyl acetate 6, 258-264 – – vinyl chloride 6, 258–259 - commercial importance 254 -- uses 259, 268 – complexation with mercuric ion 237 - cost of production 251 - cylinders 250 danger 236, 249–251 - decomposition 256 - derivatives 6 - electric arc process 257 - history 251 - Huels' process 256-257 - hydration 234, 236-238 - instability 259 - lamps 254-255 – – bicycle lamps 255 -- caving lamps 255 - large exotherm 254 - manufacture 256 - mechanism of formation 257 mercuric ion-catalyzed hydration 234 - methylacetylene 152-153 - nucleophilic attack activated by metal ion coordination 259 - orbitals 250

- "over the fence" 251
- oxyacetylene torch 254
- $-\pi$ -bond 214

Organic Chemistry Principles and Industrial Practice. Mark M. Green and Harold A. Wittcoff Copyright © 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-30289-1

– – coordinate bond 214 - positive energy formation 250 production 254–258 – – in Eastern Europe 258 – electric arc 255 -- in Japan 258 – large-scale production 255–258 - reaction with formaldehyde 268, 270 - Reppe, Walter 211, 270, 285 - stability 256-257 - structure 250 -- structural source of instability 250 synthetic preparation 7 - transport 250 - welding 254 acetylide - anion 252-253 – reactive characteristics 253 - dianion 271 - rate constant for reaction with formaldehyde 271 acid of salt (hydrochloric acid) 273 acids / acidity - Brønstead acidity 11-12, 16-17, 52 - carbamic acid 91, 95 - carbon-bound hydrogen 225 - carbon-hydrogen bonds 224 - carbonic acid 96 - carboxylic acid 96 - chloride 96 - conjugate acid 76 - fatty acids (see also there) 81-82, 129, 162 hypochlorous acid (HOCl) 76–78 - organic molecules 123 - phenols, acidity 97-98 Acrilan<sup>TM</sup> 206 acrolein 198, 209-210 - to acrylic acid 214, 243 -- catalysts for 214 -- Mo<sub>12</sub>V<sub>2</sub>W<sub>2</sub>Fe<sub>3</sub> 214 -- Mo<sub>12</sub>V<sub>3</sub>W<sub>1.2</sub>Ce<sub>3</sub> 214  $--Mo_{12}V_{4.6}Cu_{2.2}W_{2.4}Cr_{0.6}$  214 - methacrolein 150 - propylene oxidized to acrolein 213-214 -- catalysts for 214 -- Mo<sub>12</sub>BiFe<sub>2</sub>Co<sub>3</sub>NIP<sub>2</sub>K<sub>0.2</sub> 213 -- Mo<sub>12</sub>BiFeW<sub>2</sub>Co<sub>4</sub>Si<sub>1.35</sub>P<sub>2</sub>K<sub>0.06</sub> 213 typical catalysts 214 acrylic acid 205, 209-217, 221 - from acetylene 211-212 -- acrolein to acrylic acid (see also there) 214, 243

-- air oxidation 209 -- industrial intermediate 210 -- methacrylic acid / methacrylate (see also there) 138, 140, 144, 153 -- oxidations of propylene 212-217 -- poly(acrylic acid) (see also there) 107-108, 204-206 -- polymerization 205 -- produced in the "old days" 209-210 -- Reppe process 270 - esters 204-206 acrylamide 294 acrylate esters (see also there) 139, 204, 206 - Ineos 152 - methyl methacrylate (see also there) 137-156 - poly(alkyl methacrylate) (see also there) 138-139 acrylonitrile 122-125, 133, 205-210, 212-217, 294 - adiponitrile from 124 - from acetylene 258-259 - export 206 - fibers 206 - hydrocyanation 122-123 - polyacrylonitrile (see also there) 206-209 - polymerization 206 – copolymerization with butadiene 208 propylene, conversion to acrylonitrile 212-217 - synthesis, early 209-210 acyl carbon (see also there) 140, 225, 275, 278 - carbonyl, substitution reactions 225 - displacement 80-85 substitution 83–84, 277 transfer reaction 276 addition of reactions - aromatic rings, resistance to addition reactions 71 - 1,3-butadiene (see also there) 120 - carbonyl carbon, nucleophilic addition 139 - chlorine (see also there) 120 - cyanide to carboxyl, catalyzed addition of water 139 - double bond 76 -- 1,2-addition to double bonds 164 - HBr addition (see also there) 129-131 - HCN addition across the double bond in 1,3-butadiene 285 - Markovnikov addition 5, 131, 133, 151 - nucleophilic addition (see also there) 139-141, 227, 275 - polar addition 129

- polymers (see also there) 23-24, 92, 107

- water, addition 201 adipic acid 116-118, 125, 132-133 synthesis of 116–118 adiponitrile electrochemical synthesis 124 – synthesis with HCN 285 aerobic fermentation 243 aircraft wings, de-icing 203 alcohol - aldol, alcohol production 225 - allylic 79, 282 - isocyanate reaction with alcohol 91 pentaerythritol 229 - polyhydric 226 - poly(vinyl alcohol) (see also there) 263-264 - vinyl alcohol (see also there) 234-235, 238 aldehydes 127, 210 - acetaldehyde (see also there) 6, 150, 210, 221-248, 260 - aldol, aldehyde production 225 - butyraldehyde (see also there) 228, 232, 238, 263-264 - formaldehyde (see also there) 107, 210, 226-228, 230, 264, 268, 271 - group 150 -- imine 284 - heptaldehyde 129-130 - isobutyraldehyde (see also there) 150, 228, 231, - propionaldehyde 238-239 aldol - alcohol production 225 - aldehyde production 225 - condensation 210, 222, 224-232 -- n-butanol synthesis 224-226 -- mechanism 225, 227 -- mixed 210, 226 -- problems 226 – single product produced in an aldol 226 alkali carbonates 86 alkane, functionalization 294 alkene 8 alkoxide 76 – anion 202 alkyd resins 80-85, 231, 276 - drying 81 - invention 83 - mechanism of cure 81 - nucleophilic acyl displacement 82-85 - polyester 84, 92 – synthesis 81 alkylate 54 - multialkylation 63

alkyne - carbanion formed with strong bases 252 - terminal 252 allyl/allylic - acetate 79 - alcohol 79, 282 - carbon-hydrogen bond, strength 216 - chloride 76-79, 282 - hydrogens in propylene 204-205 -- advantages 204 - radicals, resonance stabilization 27-28, 147 a-hydroxyisobutyramide 144 a-hydroxyisobutyric acid 144 aluminum trichloride 10, 49, 52 amides - functional group 111-112 - nitriles from amides 117 - polymers from 109 - polyamide (see nylon) 24, 107-136 amines 75 - crosslinked character of amine-cured epoxy resin 69 - curing agents for expoxy resins 75 - quaternary 98 - ratio of methylene units to amide bonds 129 6-aminocaproic acid - attempted polymerization 128, 131 - cyclization 127 11-aminoundecanoic acid 129-130 ammonia / ammonium 142-143 - bisulfate 142-143 -- disposal 143 -- ICI process for recycling 143 - imine formation 284 - sulfate 283-287 -- elimination in caprolactam synthesis 283 -- fertilizer 283 ammoxidation 206, 213 - of propylene 147 amorphous polymers 179 animals, unsaturation in fatty acids 162 anion radical 124 anthracene 6 anti-conformation 158, 162, 167 anti-elastic polymers 177-178 anti-elastomers 177 anti-Markovnikov addition 240-241 antimony, contrast with sodium 215 antioxidants 119 antiozonants 119 aprotic solvents 207 architectural paints 262 ARCO 199, 221

aromatics - electrophilic aromatic substitution 10, 45-65, 204 from steam cracking 5 – rings 71 -- chemical stability 71 – – lend stiffness 82 – molecular rigidity 71 -- resistance to addition reactions 71 Arpe, H.-J. 241 Arrhenius equation, pre-exponential factor A 164 Asahi - process to methyl methacrylate 150 - routes to methyl methacrylate 148 ash/ashes 86 asphalt 4 aspirin 222 Atlantic Richfield Petroleum Co. 293 atoms - pentaerythritol, source of carbon atoms 229 - radical abstracted hydrogen atoms 176 Aztecs 157

## b

backbiting 30 "Badische Anilin und Soda Fabrik" (see BASF) Baizer, Emmanuel 124 bakelite 107-108 Balfour, A.J. 223 Banks, R. 40 Barton reaction 30 BASF ("Badische Anilin und Soda Fabrik") 8, 150, 244, 256, 268, 284-285 - chemical complexes built in Antwerp, Belgium 268 - DuPont/BASF route to caprolactam 284-285, 288-291 - methanol from acetic acid, pioneered by BASF 244 - methyl methyacrylate process 150 battery cases from vulcanized rubber 167 BAYER Co. 92, 99, 187 Bayer, Otto 92 Beckmann, Ernst 127 Beckmann rearrangement 127–128 benzene 6, 45-46, 196 - from coal via coke oven distillate or coal tar 116 - cost 46 - difference from cyclooctatetraene 274 from steam cracking 45 benzoyl peroxide 176 "Bergakademie Clausthal" 59

Berthelot, Pierre E.M. 256  $\beta$ -elimination 237–238  $\beta$ -scissions 14  $\beta$ -sheets 112 biomarkers 1 Bischoff, C.A. 274 bisphenol A 46, 56-59, 71-77, 92, 95-96, 101, 177, 275, 278 – cost 46 - crystallization-based separation 58 - para-para' isomer 58 - preparation 56-59 reaction -- with epichlorohydrin 74 -- with phosgene 96 – salt formation and crystallization 126 - separation of isomers 59 – uses 95–96 block copolymers 181-183 - 1,3-butadiene-derived block 181 – copolymer 181–183 -- temperature dependent behavior 183 relative T<sub>g</sub>'s of the blocks 183 bond energy 250 dissociation energies 195 British British blockade and rubber 171 British Petroleum (BP) 207, 293 Brønstead acidity 11-12, 16-17, 52, 123 Brookhant, Maurice XVII Brunelle, Daniel J. XVI Bruson, Herman 138 Buna, N. 174 Buna, S. 172 Burton, W. 4 1,3-butadiene 118-122, 171, 196, 207-208 - acrylonitrile, copolymerization with butadiene 208 - addition 120-121 -- 1,2 and 1,4 addition products 120 – – of chlorine 120 -- HCN addition 285 -- separation of isomers 121 - carbonylation 286 - 2-chloro-1,3-butadiene 119 - hexamethylene diamine 118, 121 - hydrocyanation 286 polybutadiene rubber 170–171 polystyrene and poly 1,3-butadiene, two phases 182 - separation from 1- and 2-butenes and isobutene 207

- synthesis 118

1,3-butadiene-derived block 181 butane 2 butanol - n-butanol 221-226, 238 – aldol condensation 224–226 – modern processes for production 222 – produced directly from propylene 238 -- synthesis 222, 224-226 - tertiary 199 butene - 1,3-butadiene, separation from 1- and 2-butenes and isobutene 207 - isobutene (see also there) 147-149, 207, 209, 244 butyl - acrylate 221 bromide, relation with methylacetylene 253 - ether, methyl tertiary (see MTBE) 148-150 - hydroperoxide, tertiary 199-200 *n*-butyl -- acetate 221, 224 -- acrylate 221 -- methacrylate 221 - rubber 170-171 – – manufacture 173 1,4-butynediol 6, 268-272 - from acetylene 268 - mechanisms of formation from acetylene 271, 275-276 butyraldehyde 263-264 - acetal, poly(vinyl alcohol) 264 - n-butyraldehyde 228, 232 – produced directly from propylene 238 С Ca (calcium) – Ca carbide 7, 251–253 -- reaction with water 252, 254

- Ca chloride 197
- byproduct from ethylene oxide production 197
  – Ca oxide (lime, CaO) 252

hard water, calcium ions 205

CaCl<sub>2</sub> 197

Ca(OH)<sub>2</sub> 79

– aqueous 229

calcium (see Ca) 7, 79, 197, 205, 251-254

- camphor, plasticizer for cellulose nitrate 233
- Canary, James W. XVII

Cannizzaro, S. 229

- Cannizzaro reaction 229-230

– – mechanism 230

- caprolactam 128-129, 283-287
- DuPont/BASF route 284

- DuPont/DSM route 283-284 - economic consequences of the classical route 284 - elimination of (NH<sub>2</sub>)SO<sub>4</sub> in synthesis 283 - synthesis 283 carbamate/carbamic 91 - carbamic acid 91 from isocyanates 91 carbanion 150, 225 - formed -- at carbon 225 -- at carbonyl 225 - resonance-stabilized 225 carbenium ion 16-17 carbocation 2, 9, 12-13, 15-17, 152, 164-166 difference from free radicals 19 - resonance-stabilized 166 - tertiary stability 164, 166 carbon / carbonic / carbonyl - acid/acidity 96 acyl carbon 140, 225, 275 – – exchange groups 275 - atoms, pentaerythritol source of carbon atoms 229 - electron deficient character of carbonyl carbon 85 - fiber 67, 71, 208 - functional group, situated for nucleophilic attack 225 four carbon branches 31 - groups -- difference in reactivity 227 -- electron-deficient 227 – nucleophilic attack 278 -- reformation 280 - hydrocarbon (see also there) 243 - metal-carbon bond 285 - monoxide 147, 151-152, 238-239 - - addition to methylacetylene 152 -- complexed to nickel 211 – coordination complex with carbon monoxide 239 -- ligand 239 – nucleophilic character 151 -- reaction between carbon monoxide, hydrogen and ethylene 238 – – resonance 239 nickel and carbon/carbonyl -- bond, hydrolysis 212 -- weak bond between 211 - nucleophilic attack 140, 278 -- compare aliphatic and acyl carbons 140

- radicals 168

- reactivity pattern -- of carbonyl compounds 225 -- steric and electronic effects 227 - sp-hybridized carbon 104 transition metal bound to carbon 237 carbonate alkali carbonates 86 - diethyl carbonate (see also there) 99, 275 - dimethyl carbonate 275, 280 - diphenyl carbonate (see also there) 99, 275, 280 - linkage 277 - polycarbonate (see also there) 46-49, 56, 92, 95-102, 177, 225, 274-285 carbon-bound hydrogen, acidity 225 carbon-carbon bonds 13, 225 carbon-hydrogen bond 13, 199 - acidity 224 - adjacent to a carbonyl group 226 - allylic, strength 216 – benzylic 199 - insertion of oxygen from the air 199 - tertiary 199 carboxyl/carboxylic acid 96, 210 - cyanide to carboxyl, catalyzed addition of water 139 - and nitriles, acid groups 210 carcinogen/carcinogenic 122 Carothers', Wallace 70, 82, 93, 107–109, 111–112, 125-126, 231, 263, 280, 284 - Carothers' attempt to synthesize nylon 6 127-129 castor oil - nylon from 115, 129 silk from 129 catalyst / catalyzes / catalytic - acid 9 - antimony 215 - chemists 214 - cracking 2, 10-12, 15-16, 18, 51 – – catalytic 8 -- fluidized 11 -- mechanism 12, 16 – products from 16 -- steam 8-9 -- thermal 6 -- zeolite 10 how do they work 214 - hydrogen / hydrogenation 118 -- catalytic reduction 225 - metallocene 37, 41 - metals, characteristics 214

-- empty orbitals to form  $\pi$ -complexes 214

-- variable oxidation states 214 - nickel 118 phase transfer catalysis 99 - for propylene oxidation 213-216 – – mechanism 215 - reoxidation 216 - single-site 36, 40 – zeolite 52–54 - Ziegler-Natta (see also there) 33-44 ceiling temperature 23 Celanese Corp. 261 cell membranes 86 celluloid 233 cellulose nitrate -- camphor added 233 -- subject to flammability and violent decomposition 233 nitrocellulose 88, 223 chain - cost 46 - curing 46 - destructive action 278 - epoxy resin (see also there) 46-49 - free radical chain reaction 25-26, 59, 77, 124, 168 -- polymerization of ethylene 25 industrial synthesis 47–49 - initiation steps of a free radical chain process 13-14 - mechanism 166-167 -- involving charged entities 166 - stretched chains 159 transfer reactions 17, 28 chemical/chemical industry - bonds 13 - dislocations in the chemical industry 224 - robust process in the chemical industry 224 chemicals - neither "bad" nor "good" 231 – "seven basic chemicals" 196 -- benzene (see also there) 6, 45-46, 196 -- butadiene (see also there) 118-122, 171, 196, 207-208 -- ethylene (see also there) 8, 45-46, 147, 195 - 220-- methane 196 -- p-xylene 196, 222 -- propylene (see also there) 2, 8, 27-28, 45-46, 77-79, 93-94, 122, 147, 195-220 -- toluene (see also there) 6, 92, 196 chemistry

- future of chemical industry 293-295

#### 302 Index

 "old-fashioned" 209 - regiochemistry 240 size of chemical industry 293 chemists - Pierre E.M. Berthelot, father of organic chemistry 256 - who develop catalysts of critical importance to industry 214 chirality, synthesis of polypropylene 29-40 children, straw into a glass of milk 95 chloride - acid chloride 96 – addition 78 - allyl chloride 76-79, 282 - aluminum trichloride 10, 49, 52 - calcium chloride (see also there) 197 - chloride anion, loss of 97 - displacement 74 - ethyl chloride 52 - leaving group 101 - methyl chloride 77 - poly(vinyl chloride) PVC 107-108, 196 vinyl chloride 2, 6, 196, 282 chlorine 21, 197, 249, 273-274 addition -- 1,2-addition 120 -- 1,4-addition 120 – – to butadiene 120 - costs 282 - discovery 273 - Dow Chemical Co., chlorine production 201 – history 273 - polyethylene, reaction with sulfur dioxide and chlorine gases 168 - radicals 78 - reaction with propylene 78 - replacement 197 -- by safer chemicals 273-274 – uses 282 - waste, economic penalty 197 2-chloro-1,3-butadiene 119 *m*-chloroperbenzoic acid 198 chloroprene 119-121, 170-171 polychloroprene rubber 171 chorosulfonated polyethylene 168 CIBA Specialties Company 80 cis-1,3-polybutadiene 171 cis-1,4-polyisoprene 170-171 citric acid 273, 295 clays 11 Clostridium acetobutylicum 223 coal - coal tar 6

- energy sources 293 coatings - coil coating 69 – corrosion-resistant 80 – epoxy resin 68–70 coil coating 69 coke 4, 6, 18, 252 – coke oven distillate 6 combustion – analysis 234 - internal combustion engine 2, 8, 10 compact discs 95 competition, profitability impeded by 287 condensation polymerization 84, 111 conformation 158 anti conformation 158, 162, 167 - flexibility, conformational and Tg 181 - gauche conformation 158, 167 - relation to elasticity 158 conjugate acid 76 constitutional isomers 15, 235 coordinate bond 214 -  $\pi$ -bond of propylene and ethylene 214 - covalent bond 236 copolymers 31-32 - block copolymer (see also there) 181-183 - ethylene-propylene 174 - random copolymers, average of the properties of copolymerized units 206 cordite 5, 88, 223 corrosion 68 - coatings, corrosion-resistant 80 - problems solved 262 – unforeseen problems 261 cosmetics 87 costs / production / finance costs (see also economic details) 46, 280-287 - acetylene (high cost of production) 251 - benzene 46 - bisphenol A 46 - cash costs 280 - chlorine 282 - cumene 46 - ethane 46, 260 - ethylene 46 - HCN 286 - methyl methacrylate, cost of production 281 nylon 6 286 - polycarbonate 46, 280-281 - polystyrene 46 propylene / propylene oxide 46 - styrene 46

Courtelle<sup>TM</sup> 206

cracking - catalytic (see also there) 2, 10-12, 15-16, 18, 51 methanol 294 - steam (see also there) 2, 4-6, 8-9, 12, 15, 45, 153, 236 - thermal 4-6 crosslinks / crosslinking / crosslinked 68-70, 74, 161-162, 280 - character of 68-70 - concept of 74 - from crystallization 161 - degree 69-70 -- limit to 70 – different kinds 188 - elastomeric behavior, new approach to crosslinking 177 - EP rubber 175 - epoxy resin 68-70 -- amine-cured 69 - gutta percha, physical crosslinks 162 - Hypalon 167-170 - inability to melt 70 - insolubility 70 - network 82 - physical crosslinking 177-185 - poly(dimethylsiloxane), peroxide crosslinking 176 - polyethylene 168 - rubber-like elasticity 162 - silicone rubber 175-176 - structure, strength 69 - urea linkages 185 crude oil distillation 4 crystalline - regions, hard segments 185 - solid 127 crystallization (see also salt formation) 115, 126 - bisphenol A 126 - crosslinks from crystallization 161 - formation of nylon (see also there) 125-126 hydrogen bonding 185 - polymers 179 – strain-induced 162 crystallization-based bisphenol A separation 58 Cu<sub>2</sub>C<sub>2</sub> 272 - precipitate 272 cumene 46-49 - cost 46 - hydroperoxide (see also there) 59-61 - phenol and acetone from 59 - production 54-56 - synthesis 49 - 2-for-1 process 198

CuOH (cuprous hydroxide) 270 cupric oxide, catalyst in Reppe process 270 cuprous - carbide, catalyst in Reppe process 270 - hydroxide (CuOH) 270 - oxide, unstable in water 270 - salt, reoxidation by air 260 cured epoxy resin 67 Curme, Jr. G.O. 7 cyanide – anion 122 - to carboxyl 139 -- catalyzed addition of water 139 cyanohydrin - conversion to unsaturated carboxylic acid 141 - in methacrylate synthesis 139-142 cyanopyridine 295 cyanosubstituted methanes, acidity 123 cyclohexane 117 cyclohexanol 117 cyclohexanone 117, 127-128 – oxime 127 cyclooctatetraene 274 difference from benzene 274 cyclopentadiene 37

### d

D<sub>2</sub>O (heavy water) 235 Davy family members 274 - Edmund Davy 251 - Sir Humphrey Davy 251, 274 - John Davy 274 Deacon, H. 266 - Deacon reaction / process 267, 273-274 -- and modern oxychlorination 274 depreciation / depreciated 280 - plants 270 Desenex 129 detergents 205 - phosphates 205 - poly(acrylic acid) as detergent builders 205 deterioration - by ozone 167 of rubber 167 Devoe-Raynolds Paint Company 80 di-2-ethylhexyl phthalate 233 diaminoethane in spandex synthesis 187 diapers, superabsorbent polymers 205 diastereotopic 43 1,4-dichloro-2-butene 120-121 3,4-dichloro-1-butene 119, 121 1,2-dichloroethane (see also ethylene dichloride) 196, 266

1,2-dichloro-2-propanol 79 1,4-dicyano-2-butene 121, 123 - cis 121 – trans 121 dicyclopentadiene 174 Diesel fuel 4 diethyl carbonate 99 - for polycarbonate synthesis 99 diethylbenzene 53-54 diglyceride 83, 275 diisocyanate 92 - in spandex synthesis 187 – toluene 273 diisopropylbenzene 49-52 dimethyl carbonate 275, 280 - in polycarbonate synthesis 275 dimethyldichlorosilane 175-176 dimethylformamide 207 2,3-dimethylpentane 17 diphenyl carbonate 99, 280 - in polycarbonate synthesis 275 dipolar / dipole - forces 67 – moment 85 discovery, serendipitous 24 dislocations in the chemical industry 224 distillation - coke oven distillate 6, 116 – of crude oil 4 - molecular 110 – vacuum 202 Distillers Co. 59, 206 double bond - addition 76 -- 1,2-addition to double bonds 164 - importance 2 - reaction with ozone 167 - stability 120 - unsaturated oils, polymerized by double bonds 81 Dow Chemical Co. 80, 201 - chlorine production 201 - hypochlorous route to propylene oxide 201 propylene oxide 201 drying oils - coatings 82 - crosslinking 82 transesterification 83–85 DSM, caprolactam, DuPont / DSM route 283-284 Dubbs' – Carbon 5

- process 5

DuPont exiting from fiber business 286 - DuPont / BASF route, mechanism 285 DuPont / DSM synthesis of caprolactam 283-284 - HCN, DuPont handles 283 dye/dying - fibers 207 - polyacrylonitrile 207 dye-attracting properties 207 dynamite 5, 88-89 - role of glycerol 88-89 e Eastern Europe, acetylene production 258 economic details (see also costs) 280-287 - caprolactam, economic consequences of the classical route 284 - energy / energy sources (see also there) 280, 293-294 - epichlorohydrin economics of manufacture 282 labor and related factors 280 - new technology, more economical and safer 282 - profitability impeded by competition 287 - raw material 280 - reserves 293-294 -- gas 293 -- oil 294 Einhorn, Alfred 274 Elastane<sup>TM</sup> 184 elastic fiber 184-185 elasticity - hug your body elasticity 184-185 - rubber 158-162 -- conformational basis 158-160 -- entropy 159 -- free energy change 160 - rubber-like, crosslinking 163 elastomers / elastomeric 89, 119-120, 157-194 - anti-elastomers 177 behavior, elastomeric -- new approach to crosslinking 177 -- precluded 177 - chemistry 190-194 - deterioration by ozone 167 - ethylene-propylene 159 natural rubber (see rubber) 119-120, 157-194 - oil-resistant elastomer 208

DuPont Co. 93, 107-108, 111-112, 124, 138,

184, 188, 206, 224, 263, 280, 283-286

- properties 157

- silicone rubber, peroxide crosslinking of elastomers 175 - thermoplastic (Kraton<sup>TM</sup>) 170–171, 181–183, 185, 188-189 - vulcanization 163-164 electrophile / electrophilic - aromatic substitution 10, 45-65, 204 - changed character of ethylene 237 elimination -  $\beta$ -elimination 237–238 - entropy gain by elimination of a small molecule 225 of water 146 Elmer's glue 222, 262 enantiotopic 43 energy 280, 293 - acetylene, positive energy formation 250 bond energy 250 - elasticity of rubber, free energy change 160 - sources of 293 – – coal 293 -- gas 293 engine life, lead oxide 148 entropy 78 - of activation 164 - change, release of HCN and H2O from formamide 145 - gain by elimination of a small molecule 225 - of mixing 182 enzymes 294 - immobilized 294 – technology 294 EP rubber, crosslinked 175 EPDM rubber 174-175 - properties 174 - synthesis 174 – uses 175 epichlorohydrin 71-74, 76-80, 85, 92, 96, 282 - bisphenol A 74 - economics of manufacture 282 - synthesis 76-80 – – Showa-Denko synthesis 79 epoxy resin/epoxides 46-49, 56, 67-77, 80, 92, 95-97.101 - addition of water 201 - adhesives 67 - bonds 72, 201 – bond angle, torsional strain 201 - byproduct formation in electrophilic substitution and in ring opening of epoxides 204

- chain 46–49
- coating 68-70

- crosslinking 68-70 - curing agents 67-68, 75 – – amines 75 -- mechanism 75 - formation 73, 76 - molecular weight 72, 74 - oligomer from epoxides 202 - reactivity 72 - ring openings 75, 94 - strain 201 - structure 67-68 - synthesis 71-72 – uses 67–68 esterification 151 - reaction 231 - transesterification (see also there) 83-85, 99, 202 esters 83 - acrylic/acrylate 204-206 -- uses 206 - difficulties of hydrolysis 231 - exchange reactions 275 methacrylic acid, higher alkyl esters 138 - polycarbonate ester linkage 96 - polyester (see also there) 84, 92, 109-110 polymers from 109 - transesterification of drying oil 83-85 ethane 2 - cost 46 - Saudi Arabia, cheap ethane 244 - vinyl chloride from ethane 294 ethanol 223, 234 dehydrogenated 234 ethyl - acetate 243 - chloride 52 Ethyl Corporation 149 ethylbenzene 6, 199-200, 204 - elimination of H<sub>2</sub> 48 - hydroperoxide 200 production 52–53 ethylene 8, 45-46, 147, 195-220, 222, 236 – π-bond 214 – carbon-hydrogen bond strength 195 - chemical derived from 196 - chemistry 217-220 - cost 46 - dichloride (1,2-dichloroethane) 196, 266 difference from propylene 195 - electrophile, changed character of ethylene 237 glycol 129, 202–204

- giycoi 127, 202-2
- – byproducts 204

– – diethylene glycol 203 - - oligomer from ethylene glycol, expensive separation steps 204 -- oligomer formation on hydration 204 -- toxicity 203 -- uses 203 - diamine 75 - enantiotopic faces 35 - industrial importance 195 - methyl methacrylate, ethylene-based process 150-151 - oxide 2, 198 - - Ca chloride, byproduct from ethylene oxide production 197 -- direct oxidation 197 -- with HCN 209 -- from hypochlorous acid (HOCL) 197-198 – increased proportions of water 204 -- silver-catalyzed oxidation 203 -- uses 201-203 - polyethylene (see also there) 8, 23-43, 107, 196 - polymerization 23, 25 - propionaldehyde from ethylene 239 reaction -- between carbon monoxide, hydrogen and ethylene 238 -- with HBr 237 - steam cracking 45, 236 ethylene-propylene - copolymer 174 - curing 174 - elastomer 159 properties 174 - rubber 170-172 - synthesis 174 ethylene-propylene-diene monomer rubber 170-172 2-ethylhexanol 232-233 - plasticizer from 233 eutrophication 205 exotherm, re-use 203 exposure to light, resistance to yellowing 262 Exxon Mobil Oil Co. 11-12 Faraday, M. 267

*f Faraday, M.* 267 Farbwerke HOECHST 236, 261, 263 fatty acids 81–82, 129, 162 – chains, with methylene groups 82 – unsaturated 81 – – cold and warm-blooded animals 162 ferrocene 37 fertilizer 142 fiber - carbonic 67, 71, 208 - dying fibers 207 - elastic 184-185 - formation 110, 114 FINA 8 Fischer-Tropsch reaction 294 Flory, Paul 70, 82, 93, 280 fluid bed reactor 213 fluidized catalytic cracking 11 fluorosulfonic acid 186 foams / foaming 95, 261 - mass transfer problems associated with 262 - microscopic stirrers, causing foaming 95 - from polyurethane 89, 95 Ford, Henry 224 formaldehyde 107, 226-228, 230 - acetal from poly(vinyl alcohol) 264 - condensation 224 - reaction 210 -- with acetylene 268, 270, 274-275 - susceptible to nucleophilic -- addition 227 – – attack 268 formamide 145 formic acid 270 - byproduct of oxidation 243 5-formyl methylvalerate 284 four-coordinate intermediate 84, 227, 231, 277-278 - steric difficulty in forming 231 fragmentation reactions 9 free radicals 2, 9, 12-14 - chain reaction / mechanisms (see also there) 25-26, 59, 77, 124, 168 difference from carbocations 19 - initiation steps of a free radical chain process 13-14 - polymerization (see also there) 14, 24-27 propagation steps 13 \_ steam cracking 45 - unsaturated oils, polymerized by free radicals 81 Friedel-Crafts reaction 49, 52, 55, 62 fructose corn syrup 294 future - chemical industry 293-295 - petroleum 293

### g

gas – energy sources 293

- gas oil, composition 16

# **308** Index – poison gas 96

- polyethylene, reaction with sulfur dioxide and chlorine gases 168 - polygas 54-55 - reserves 293 stranded gas 294 - synthesis 294 - valorized gas 294 gas-to-liquids (GTL) 294 gasoline - octane number 2, 9 - rationing 173 -- and the rubber in tires 173 gauche conformation 158, 167 General Electric (GE) Co. 81, 83, 96, 99, 175, 274 - chemists 85 - GE process 280 General Mills, Minnesota 25 George, Lloyd 223 German submarine offensive 223 Glasites (Sandemanians) 267 glass / glassy formation -- and conformational motion 181 -- in polymers 179 - polymeric glassy state 177-183 - safety glass 95, 263 - transition temperature (Tg) 179-180 glucose 294 - mutarotation 65 glue 67 - Elmer's glue 222, 262 glycerides - diglyceride 83, 275 - monoglyceride 83, 275 - triglycerides 81 glycerol 80-85, 92-95, 102, 129 absence of toxicity 87 - commercial uses 87 - dynamite 88-89 - history 86-87 - hydrogen bonding 112 - reactions -- with propylene oxide 94 -- with toluene diisocyanate 92 - synthesis 81 - viscosity 87 glycol - diethylene glycol 203 - ethylene glycol (see also there) 129, 202-204 - neopentyl glycol (see also there) 226-228, 231

- propylene glycol (see also there) 202–205

golf club shafts 67 Goodyear, Charles 163 GTL (gas-to-liquids) 294 gutta percha 25, 160–162 – crystalline regions 161 – physical crosslinks 162

# h

H<sub>2</sub>O, entropy change, release of HCN and H<sub>2</sub>O from formamide 145 Haas, Otto (Rohm and Haas) 137-139, 221 halonium ion 77 HBr - addition 129-131 - ethylene reaction with HBr 237 - polar addition and HBr 129 - radical mechanism 131 - undecyclenic acid 129 HCl 266, 268 - history 266 - from isocyanate production 268 - oxidation 266, 270-271 - in oxychlorination 268 HCN (hydrocyanic acid) / hydrocyanation 206, 249-250, 281-285 - acrylonitrile 122-123 - addition across the double bond in 1,3-butadiene 285 - adiponitrile, synthesis with HCN 285 - byproducts 213 - costs 286 DuPont handles 283 - entropy change, release of HCN and H2O from formamide 145 - ethylene oxide with HCN 209 - hexamethylene diamine, hydrocyanation 122 - isobutylene vs. the HCN-acetone route to methyl methacrylate, economics 281 - Nazis, use of HCN 142 - reaction with acetone 139 - replacement 283 - use for adiponitrile synthesis 285 - wool-like fabrics (see also there) 206 – – Acrilan<sup>TM</sup> 206 – – Courtelle<sup>TM</sup> 206 -- Orlon<sup>TM</sup> 206 HCo(CO)<sub>4</sub> 239 HDPE (high density polyethylene) 31 heart - conditions, relieve muscle pain 231 - disease, nitroglycerin 89

- heavy water (D<sub>2</sub>O) 235
- helicone reactors 275

helmets, safety 95 hemiketal from phenol and acetone 62 hemoglobin 151 heptaldehyde 129-130 *n*-heptane 9 Hermes, Matthew 112, 128 heterogenous catalysis 239 Hevea brasiliensis 160 Hevea rubber 161–163 1,4-hexadiene 174 hexamethylene diamine 116-122, 125, 133, 282, 286 - hydrocyanation 122 - synthesis 116-118 -- from adipic acid 118 -- from 1,3-butadiene 118, 121-122 Hill, J. 110, 114 HOCl (hypochlorous acid) 76-78, 197-198 - Dow Chemical Co., hypochlorous route to propylene oxide 201 - propylene oxide 197-198 HOECHST 236, 261, 263 Hofmann, W.A. 90 - Hofmann reaction 90 - Hofmann rearrangement 95 - polyurethane by Hofmann rearrangement 90-92 Hofmann-Loeffler-Freitag reaction 30 Hogan, P.J. 40 homolytic breaking - carbon-carbon bonds 13 – carbon-hydrogen bonds 13 horse chestnuts 223 Houdry, A. J. 10–11 Hückel, E. 274 – 4n+2 rule 274 Huels' process 256-257 hug your body elasticity 184-185 hydration - of acetylene 238 - of carbonyl containing molecules 227 - glycol oligomer formatation on hydration 204 – ketones 228 hvdride – ion 16 – transfer 165 hydroboration 240-241 - parallels to hydroformylation 240-241 - regiospecificity 240 - steric effects and electron deficiency 241 hydrocarbon oxidation, production of acetic acid 243

hydrochloric acid (acid of salt) 273 hydrocyanic acid/hydrocyanation (see HCN) 122-123, 139, 142, 145, 206, 209, 213, 249-250, 281-285 hydroformylation 222, 238-243, 283 – cobalt catalysis 239 - ligands 243 - mechanism 239, 243-244 - parallels to hydroboration 240-241 - reaction 222 hydrogen - bonding 67, 71, 87, 112-115 -- carbon-hydrogen bonds 13 -- crystallization 185 -- nickel-hydrogen bond 211, 285 -- radical abstracted hydrogen atoms 176 - catalytic reduction / hydrogenation 118, 225 - elimination from ethylbenzene 48 reaction between carbon monoxide, hydrogen and ethylene 238 hydroperoxide / hydroperoxidation 59-61, 198-200 cumene 59-61 - ethylbenzene 200 - mechanism 60-61, 199 - protonated 61 - 2-for-1 process 199 tertiary butyl hydroperoxide 199–200 hydrophilic 87 a-hydroxyisobutyramide 144 a-hydroxyisobutyric acid 144 hydroxyl groups 93 hydroxylamine 127 Hypalon 167–170 - crosslinking 167-170 - manufacture 168 - uses 169-170 hypochlorous acid (see HOCl) 76-78, 197-198 i

I.G. Farben Industrie 128, 172-174 ibuprofen 149 ICI (Imperial Chemical Industries) 24, 29, 138, 143, 261 process for recycling ammonium bisulfate \_ 143 imine, formation from aldehyde and ammonia forms the imine 284 impurities 125 - effect on polymerization 129-130 injection molding 183 Institut fuer Kohlenchemie 59 interfacial polymerization 98

internal combustion engine 2, 8, 10 ionomers (Surlyn<sup>TM</sup>) 188–190 - hydrophilic-hydrophobic conflict 188 - mode of action 189 - synthesis 188 – uses 189 iridium 244 isobutane 54, 199 isobutene / isobutylene 147-149, 244, 281 - 1,3-butadiene, separation from 1- and 2-butenes and isobutene 207 - methyl methacrylate from 147 - oxidation 147 - vs. the HCN-acetone route to methyl methacrylate, economics 281 isobutylene (see isobutene) isobutyraldehyde 150, 228, 231, 240 isobutyric acid 152-153 isocyanate 91-93, 272-273 - carbamates from 91 - diisocyanate 92 - phosgene 272 - source of HCl 273 - synthesis 273 - reactions 91 -- with alcohol 91 -- with amines 91 -- with water 91 - trifunctional 93 isomers / isomeric - butyraldehydes 231 - constitutional 15, 235 isoprene 170-171, 173 isopropanol 5, 8, 241 isopropylbenzene 2, 6, 47-52, 204 - production 54 - synthesis 49 isotope exchange 235 Israel 294

# j

Japan, acetylene production 258

# k

Katzir, E. 294 kerosene 4 ketones 127, 228 – addition of nucleophiles to ketones 228 – hydration 228 – oxime 127 *Kevlar*, uses 178 kieselguhr 88 kinetic control 119–122 Klatte, F. 263 Koch reaction 151 Kraton<sup>TM</sup> (thermoplastic elastomers) 170–171, 181–183, 185, 188–189 krypton, electron configuration 214

# I

lactic acid 273, 295 lamps, acetylene 254 Landau, Ralph 198-199 latex paints 206, 262 - binding agents 206 LDPE (low density polyethylene) 31 Le Chatelier – principle 62 - role of 14 - theorem 121 lead - bromide 148 - oxide lead 148 - tetraethyl lead 148-150 lead-based paints 149 leaving group 96, 277 - best 277 - chloride 101 - competition 280 - nucleophilic -- acyl substitution 142, 280 -- chemistry 142 Lewis, W.K. 11 Liebhafsky, Herman 175 linings 69 linseed oil 81 - paints, linseed oil-based 224 lipophilic 87 lipstick resistance 207 lithium - aluminum hydride 118 - N-diisopropyl amide 270 LLDPE (linear low density polyethylene) 32 Lovell, Wyoming 249 lubricating oil 4 (see also) ucite<sup>TM</sup> 138 "Luftwaffe" 11 Luhansk in Russia 250 Lycra<sup>TM</sup> 184–185

# m

M.I.T. 11 magnesium ions, hard water 205 malic acid 273 *Malthus* (English demographer) 293 manganese dioxide 144

- replaces H<sub>2</sub>SO<sub>4</sub> in synthesis of methacrylic acid 144 Mao Uniforms 264 Markovnikov addition 5, 131, 133, 151 anti-Markovnikov addition 240–241 Marvel, Carl 125, 207 mass transport problems 97 MDI (methylene diphenyl diisocyanate) 273 mechanisms - chain mechanism (see also there) 166-167 - free radical mechanisms of polymerization 171 - improvement 145 - needs 145 - of oxidation catalyst for propylene 216-217 polar mechanism 164 Mellon Institute, Pittsburgh 7 melt/melting point range 112, 127 - crosslinked -- inability to melt 70 -- insolubility to melt 70 - polyester, low melting 110 - polymers 112 and solubility, correspondence between 59 metal-carbon bond 285 metallocene 37 - catalyst 37, 41 - indene-based 39 - racemic mixture, chiral metallocenes 39 metals / metallic catalytic characteristics (see also there) 214 - organometallic chemistry 211 - palladium, expensive metal 236 partially filled orbitals 214 -  $\pi$ -complexes, catalyst metals 214 - transition (see also there) 211-212, 236-243 - variable oxidation states 214 - varies metal oxidation state 216 methacrolein 150 methacrylic acid/methacrylate 153 higher alkyl esters 138 synthesis -- manganese dioxide, replaces H2SO4 144 – nucleophilic attack 140 methanol - acetic acid from 244 -- pioneered by BASF 244 - cracking 294 industrial catalyst competition 244 methyl - acetates 243, 263 - acetylene 152-153

– chloride 77

- ethyl ketone 243 - formate 144 group – hydrophobic character 232 -- more reactive 77 – resonance-activated methyl group in propylene 198 - methyl methacrylate 137-156, 225, 239, 244, 269, 280-283 -- Asahi process 148, 150 -- from acetone 281 – – BASF process 150 – costs of production 281 – ethylene-based process 150–151 -- from HCN 281 – isobutene / isobutylene oxidation 147–148, 281 -- Mitsubishi route 148 -- nucleophilic attack 140 -- polymerization 138 – propylene-based process 151 -- synthesis 139-142 --- Mitsubishi Gas Chemical Co. 144-145 --- Mitsubishi Rayon 147-148 --- NH<sub>4</sub>HSO<sub>4</sub> as by-product 142 – – – without HCN 282 - poly(methyl methacrylate) (see also there) 137 - 138- TERTIARY butyl ether (see MTBE) 148-150 methylacetylene 153 - minor product of steam cracking 153 methylene - diphenyldiisocyanate (MDI) 273 ratio of methylene units to amide bonds 129 microscopic stirrers, causing foaming 95 mines, non-gassy 254 mirror images 35 Mitsubishi - Mitsubishi Gas Chemical Co. 144-145 - Mitsubishi Rayon 147-148 -- methyl methacrylate synthesis 147-148 - Mitsubishi routes to methyl methacrylate 148 mixed oil 117 modulus 207 molecule / molecular disorderly 233 - distillation 110 - entropy gain by elimination of a small molecule 225 epoxy resins – higher molecular weight 74 -- lower molecular weight 74

- fossils 1 - network, three-dimensional 68 resid molecules 4 - rigidity, aromatic rings 71 - sandwich molecules 37 - strained molecules 73 - supermolecule 69-70 weight - - ability to determine molecular weight of molecules 229 -- distribution 70 monoglyceride 83, 275 monomers - proportions, effect on polymerization 126 - vinyl monomers 107 Monsanto Chemical Co. 244 - Monsanto invention 124 Montecatini (Polymeri Europa) 34 montmorillonite clays 11 Morawetz, Herbert 163, 263 motion picture theaters, serious fires 233 MTBE (methyl tertiary butyl ether) 148-150 - human health 149 - synthesis 149 multialkylation 63

#### n

naphtha 4, 14, 207 - full naphtha 14 - heavy 4 – light 4 - oxidation 207 naphthalene 6 National Bureau of Standards 110 Natta, Giulio 24, 32 33-44, 174, - Ziegler-Natta catalysis (see Ziegler) 214 natural rubber (see rubber) 119-120, 157-194 "Nazi Germany" 11 - "Nazis", use of HCN 142 negative charge, stabilization 123 neopentyl glycol 226-228, 231 - commercial niche 231 polyester from 231 - production 231 - steric hindrance 231 neoprene 119-120, 133, 170-171, 173 NEXANT/ Chem systems 286 NH<sub>4</sub>HSO<sub>4</sub> 142–143 - by-product in methyl methacrylate synthesis 142 nickel - carbon/carbonyl 211-212

– – bond, hydrolysis 212 -- carbon monoxide, complexed to nickel 211 -- weak bond between 211 - catalyst 118 nickel-hydrogen bond 211, 285 nicotinamide 295 Nieuwland, J. 119 Ni-H across a  $\pi$ -bond 285 Nippon Shokubai Co. 212 nitrates, organic 88 nitriles - from amides on heating 117 - and carboxylic acid groups, same oxidation state 210 - rubber 170-172, 174 nitrites, organic 88 nitrocellulose 88, 223 nitroglycerin 88-89, 223, 230, 233 - heart disease 89 - synthesis 88 Nitto Corp. 294 Nobel, Alfred 88 - Nobel Prize 5, 24, 29, 70, 88, 108, 230, 274, 280 Norrish type-II photochemical reaction 30 notebook 40 - good chemists 40 Notre Dame University 119 nucleophile / nucleophiles / nucleophilic / nucleophilicity 76, 83, 225 - acyl nucleophilic (see also there) 80-85 -- leaving groups 142 - addition 139-141, 227, 275 -- to carbonyl carbon 139-141, 275 -- four-coordinate intermediate 227, 231, 277-278 -- to ketones 228 - attack 73, 140, 186, 225-227, 268, 280 - - acetylene, activated by metal ion coordination 259 -- at a carbonyl carbon, relative reactivity for aldehydes and ketones 227 -- carbonyl group 225 – compare aliphatic and acyl groups 140 -- formaldehyde susceptible to 268 - carbanion 225 - carbonyl, substitution reactions 225 - differential reactivity 202 character, phenol group 69 - chemistry, leaving groups 142 - displacement 71, 80-85 - in methacrylate synthesis 140 - opening of epoxide rings 76

- reactivity 85 - substitution 101, 140 nylon (polyamide) 24, 107-136 - acrylonitrile (see also there) 122-125, 133, 205-210, 212-217, 294 - artificial silk/silk fiber 112, 129 - castor oil, nylon from 115 - degree of maturity 286 - fiber-forming properties 112 - hydrogen bonding 112 – military uses 112 - nylon 4,6 113, 122-123, 125-126 - - salt formation and crystallization 125-126 - nylon 6 113-114, 127-129, 285-286 -- butadiene carbonylation 286 -- butadiene hydrocyanation 286 -- Carother's attempt to synthesize 127-129 -- intermediates for nylon 6 and nylon 6,6 285-286 -- production costs 286 - - proportions of monomers, effect on polymerization 126 -- route 285, 288-291 - - silk structure compared to nylon 6 114 - nylon 6,6 111-113, 116-118, 125-126, 132 -- intermediates for nylon 6,6 and nylon 6 285-286 -- route 285, 288-291 - - salt formation and crystallization 125-126 -- women's stockings 111 - nylon 6,10 113 - nylon 11 113, 127, 129-132 -- synthesis 132 polyamide – – fibers 113 -- formation 109-110 -- tensile strength 113 - water absorption 113, 115 0 obsolescence 85 octane - improvers 148-150 number gasoline 2, 9 - rating 54 2-octanol 129 oil - castor oil (see also there) 115, 129 - crude oil distillation 4 - drying (see also there) 82-83 - gas oil, composition 16 - linseed 81

- lubricating 4

- mixed 117 - poly(alkyl methacrylate), use for motor oil 138 - reserves 294 – soybean 81 - tung 81 unsaturated (see also there) 81 - and water 189 oil-resistant elastomer 208 olefins 5 oligomer 46 - from ethylene glycol, expensive separation steps 204 - from epoxides 202 - separation 202 Olney Medal 184 OPEC cartel 251 orbitals - of acetylene, hydridization 253 - catalytic metals, empty orbitals to form  $\pi$ -complexes 214 - metals, partially filled orbitals 214 organic - nitrates 88 nitrites 88 organometallic chemistry 211 Orlon<sup>TM</sup> 206 - Orlon carpet 207 oxalic acid 203 oxidation - acrylic acid, air oxidation 209 - ammoxidation (see also there) 206, 213 - antioxidants 119 - carboxylic acids, nitriles, same oxidation state 210 - of ethylene (see also there) 197-198, 207-209 - hydroperoxide / hydroperoxidation (see also there) 59-61, 198-200 isobutylene 147 - metal oxidation state 216 naphtha oxidation 207 \_ - of propylene (see also there) 197-204, 212-217 - reoxidation, catalyst 216 variable oxidation states 215 oxo reaction (see hydroformylation) 222 oxyacetylene torch 254 oxychlorination 267-268 - stoichiometry 268 - vinyl chloride 267 oxygen, discovery 273 oxygen-oxygen bond 60 oxygenates 149

oxymercuration 234

Index

- oxytetramethylene units 184 ozone – double bonds, reaction with ozone
- elastomers, deterioration by ozone 167

167

rubber deterioration 167

### р

paints - architectural paints 262 - latex paints 206, 262 - lead-based 149 - linseed oil-based 224 water-borne paints (see also there) 262 palladium 152, 236-237 - to carbon bond 237 - catalysis 152, 282 conversion to a catalytic process 236 - expensive metal 236 - part of the platinum group 236 - stoichiometric reactant converted to a catalyst 236 Parshall, George W. 236, 272 Pasteur, Louis VI, 25 penicillin production 243 pentaerythritol 226-232 - highly symmetrical polyhydric alcohol 229 - production 230 - propylene 94 reaction with propylene oxide 94 - source of carbon atoms 229 - synthesis 229-232 tetranitrate (see PETN) 230–231, 233 Penzance, England 274 periodic table 215 peroxide 107 - bond, weak 198 - hydroperoxide (see also there) 59-61 - poly(dimethylsiloxane), peroxide crosslinking 176 PETN (pentaerythritol tetranitrate) 230-231, 233 petroleum 1-22, 45 - Atlantic Richfield Petroleum Co. 293 - British Petroleum (BP) 207, 293 - components 3 - fraction / fractionate 3 -- steam cracking of petroleum fractions 236 - future 293 - Phillips Petroleum (see also there) 40 - sources 1-22 – uses 1–22 phase - separation 182 - transfer catalysis 99

phenol/phenolic/phenol group 56, 69, 107, 275 - acidity 98 - bisphenol A (see also there) 46, 56-59, 71-77, 92, 95-96 - consumption 62 - from cumene 59 - hemiketal from phenol and acetone 62 - hydroxyl group, ionization 278 - nucleophilic character 69 - reaction between phenol and acetone 56 - removal 278 phenoxide anion 278 1-phenyl-1-hydroxyethane 200 phenylmethylcarbinol 199 Phillips Petroleum - company 40 - process 40 phosgene 96-97, 249, 272-274 - discovery 274 - history 273 - isocyanates from 272 - polycarbonates from 272 -- synthesis without phosgene 99-100, 274 - reaction with bisphenol A 96 - replacement by safer chemicals 272-274 – uses 272 phosphates 205 - detergents 205 pi -  $\pi$ -bond of acetylene (see acetylene) 214 –  $\pi$ -complexes, catalyst metals 214 - ratio of  $\pi$ - to  $\sigma$ -bonds 250 plants - depreciated 270 - prehistoric 1 plasticizer 232-233 - characteristics 233 - di-2-ethylhexyl phthalate 233 2-ethylhexanol (excellent plasticizer) 233 - internal lubricants 232 Plexiglas<sup>TM</sup> [see poly(methyl methacrylate)] 137-138 poison gas 96 polar - addition and HBr 129 - dipolar / dipole (see also there) 67, 85 - mechanism 164 poly(acrylic acid) 107-108, 204-206 - atactic 205 - capture 205 - as detergent builders 205 - uses 205 - water-loving properties 205

poly(alkyl methacrylate), use for motor oil 138 poly(butylene terephthalate) 269 poly(cis-1,3-butadiene) 173 poly(2,3-dimethyl-1,3-butadiene) 171 poly(dimethylsiloxane) 175-176 glass transition temperature (T<sub>α</sub>) 180 peroxide crosslinking 176 poly(ether imide), uses 178 poly(ethylene terephthalate) 202-203 - preparation 202 poly(lactic acid) 295 poly(methyl methacrylate) / plexiglas<sup>TM</sup> 137-138 – lucite<sup>TM</sup> 138 military use 137–138 Perspex<sup>TM</sup> 138 poly(p-phenylene oxide), uses 178 poly(trimethylene terephthalate) 295 - biosynthesis 295 poly(vinyl acetate) 107, 222, 262-263 - derived by reaction of methanol with poly(vinyl alcohol) 263 glass transition temperature (T<sub>g</sub>) 180 – history 262 - hydrolysis 263 poly(vinyl alcohol) 263-264 - butyraldehyde -- acetal 264 -- reaction with 263 crosslinked formaldehyde acetal 264 - derived by reaction of methanol with poly(vinyl acetate) 263 - formaldehyde acetal 264 tautomerization 264 transesterification 264 – uses 264 poly(vinyl chloride) PVC 107-108, 196, 233, 265 - early synthesis 265 - glass transition temperature (Tg) 180 – uses 265 polyacrylamide 294 polyacrylonitrile (see also acrylonitrile) 206-209 - dying of 207 - fiber formation 207 polybenzimidazole, uses 178 polybutadiene - cis-1,3-polybutadiene 171 - glass transition temperature (Tg) 180 - rubber 170-171 polycarbonate 46-49, 56, 92, 95-102, 177, 225, 274-285 - from bisphenol A 275 - chain function 279

complex of reactions 279

- cost of production / financial aspects 46, 280-281 diphenyl carbonate process 280 – ester linkage 96 - high molecular weight 275 - history 274 industrial synthesis 47–49 - manufacturers 96 phase transfer process 100 - phenoxide group addition 279 – chain breaking 279 -- chain growth 279 phosgene 272, 275 – phosgene process 281 - production, savings in replacing phosgene 281 - resins 95 - shape of 57 - synthesis 96-97, 276-285 -- diethyl carbonate for 99 -- via ester exchange, mechanisms 277, 280-285 -- with diphenyl carbonate 276 – via transesterification 275 -- without phosgene 99-100, 274 - uses 95-96, 178 polychloroprene rubber 171 polyester 109-110 alkyd resin 84, 92 - easily soluble 110 - from diols 109 - from dicarboxylic acids 109 - formation 109-110 low melting 110 - steric and hydrophobic effects 232 polyether polyols 93-94, 226 polyethylene 8, 23-43, 107, 196 - branching 30 - chlorosulfonated 168 - crosslinking 168 \_ discovery 24 - high density (HDPE) 31 - linear low density (LLDPE) 32 low density (LDPE) 31 - Philip's petroleum process (see also there) 40 - reaction with sulfur dioxide and chlorine gases 168 - types 29-32 – uses 25 polygas 54-55

polyhydric alcohol 226

cis-1,4-polyisoprene 170–171

Polymeri Europa (Montecatini) 34 polymers / polymerization acrylic acid 205 - acrylonitrile 206-209 addition polymers 23–24, 92, 107 – thermodynamics 23–24 advance polymerization process 277 - aggregates or colloids 263 - from amides 109 - of 6-aminocaproic acid, attempted 128, 131 amorphous polymers 179 - anti-elastic polymers 177-178 biodegradable 295 - bonding forces 108-109 - condensation polymerization 84, 92, 111 - copolymers (see also there) 31-32, 181 - crystallization 179 - diapers, superabsorbent polymers 205 - from esters 109 - ethylene 23, 25 – free radicals 14, 24–27 -- initiation 24-27 – – mechanism 171 -- propagation 24-27 -- termination 24-27 glass formation in polymers 179 glassy state, polymeric 177–183 - impurities (see also there) 125, 129-130 - interfacial 98 - melting points 112 methyl methacrylate 138 - miscible/miscibility 181-182, 194 - nature 263 polymer science 190 proportions of monomers 126 - propylene 27 rigid polymers 177–178 - rubber, individual polymer chains 158 - stereochemistry 23-43 - synthetic polymer, biological analog 112 - under increasingly high vacuum 275 vinyl acetate 262 vinyl-based synthetic polymers 107 - Ziegler-Natta polymerization 212 polyolefins 196 polyoxymethylene, glass transition temperature (T<sub>g</sub>) 180 polypropylene 2, 23-43, 107, 196 - atactic 34, 37, 41 - cryptochirality 33 34 - diastereomers – discovery 29 - glass transition temperature (T<sub>g</sub>) 180

helical arrangement 32 - isotactic 33-34, 41 patents 40 stereochemistry 32–33 - syndiotactic 34, 41 X-ray analysis 33 polystyrene 46-49, 107-108 – cost 46 - glass transition temperature (Tg) 180 - industrial synthesis 47-49 with a poly 1,3-butadiene, two phases 182 Polytechnic University, Brooklyn 250 polyurethane 85, 89-97, 184, 226 – crosslinked 91–94 - foams from 89, 95 -- structure 91 - by Hofmann rearrangement 90-92 - stiffness 93 – uses 89–90 pot life 68 potassium carbide 251 prehistoric – animals 1 - life 45 - plants 1 production costs 46 profitability, impeded by competition 287 propane 2 - vinyl chloride from propane 294 1,3-propanediol 295 propanol 150 - 1,2-dichloro-2-propanol 79 - isopropanol 5, 8, 241 *n*-propanol 241 propionaldehyde 238-239 - from ethylene 239 propionic acid, byproduct of oxidation 243 proportions of monomers, effect on polymerization 126 propyl acetate 79 propylene 2, 8, 27-28, 45-46, 77-79, 93-94, 122, 147, 195-220 -  $\pi$ -bond 214 *n*-butanol and *n*-butyraldehyde, produced directly from propylene 238 - carbon-hydrogen bond strength 195 chemicals, derived from 196 - chemistry 217-220 – chirality 36 - copolymer 174 - cost 46 - difference from ethylene 195

- ethylene-propylene, elastomers 159

- enantiotopic faces 35 - glycol 202-205 -- allylic hydrogens 204-205 -- mechanism of formation 202 -- toxicity 203 - hydroformylation 240 - identical 35 - industrial importance 195 - methyl methacrylate process, propylenebased 151 - oxide / oxidation 197-204, 212-217, 221 -- to acrylic acid (see also there) 212-217 - - allylic methyl group 212 -- ammoxidation 147 -- catalyst in key/catalyst mechanism 212-217 -- conversion to acrylonitrile 212-217 -- direct oxidation 197 -- Dow Chemical Co., propylene oxide 201 -- increased proportions of water 204 -- by hydroperoxide oxidation 198-199 -- from hypochlorous acid (HOCl) 197-198 -- oxidized to acrolein 213 -- resonance-activated activity 198 – – uses 201–203 - polymerization 27 - polypropylene (see also there) 2, 23-43, 107, 180, 196 reaction -- with chlorine 78 -- with glycerol 94 -- with pentaerythritol 94 -- with sucrose 94 - resonance-activated methyl group in propylene 198 - steam cracking 45 protonated hydroperoxide 61 prussic acid 273 PVC [poly(vinyl chloride)] 107-108, 196, 233, 265

### q

quaternary amines 98

#### r

racemic mixture 36 – chiral metallocenes 39 radicals – allylic radicals 27–28, 147

- anion radical 124
- carbon radicals 168
- chlorine radicals 78
- free radicals (see also there) 2, 9, 12–14, 19, 24–27, 45, 59, 77, 124, 168

- resonance-stabilized 27-28, 78 random copolymers, average of the properties of copolymerized units 206 rearrangements 9, 15, 17, 60-62 redox reaction 236 regiochemistry 240 Reppe, Walter 211, 270, 285 - Reppe ingenuity, production of acrylic acid 270 - Reppe process 211-212, 214, 221, 239 – synthesis of acrylic acid from acetylene 285 -- thick-walled stainless-steel towers 272 resid molecules 4 resonance - hybrids 50 - theory 49 resonance-activated methyl group in propylene 198 resonance-stabilized / resonance stabilization 62, 77 - carbanion 225 - carbocation 166 - intermediate 195 - radicals 27-28, 78, 147 ricinoleic acid 129-130 rigid polymers 177-178 ring - aromatic rings (see also there) 71, 82 - eight-membered sulfur rings 167 - formation, dependence on ring size 132 - opening of epoxide rings 76, 94 - - byproduct formation in electrophilic substitution and in ring opening of epoxides, parallel solutions 204 - six-membered ring transition state 30 - ten-membered ring 164 - three-membered ring 73 Roelen, Otto 150, 238, 240 Rohm, Otto 137-139, 221 Rohm and Haas Co. 137-139 Rubber Reserve Co. 172 rubber - battery cases from vulcanized rubber 167 - and the British blockade 171 - butyl rubber (see also there) 170-171, 173 - characteristics 157 - discovery and early history 157 - elasticity (see also there) 158-162 - EP rubber, crosslinked 175 - EPDM rubber (see also there) 174-175

- ethylene-propylene rubber 170-172, 174
- ethylene-propylene-diene monomer rubber 170–172

- Hevea rubber 161-163 - individual polymer chains 158 - natural (see also elastomers) 119-120, 157-194 – glass transition temperature (T<sub>g</sub>) 180 – – synthetic 170–171 - nitrile rubber 170-172, 174 - ozone, rubber deterioration 167 - polybutadiene rubber 170-171 - polychloroprene rubber 171 - silicone rubber (see also there) 175-177 - stretching 157 – structure 160–162 - styrene-butadiene rubber (SBR) 170-171, 173 rubber-like elasticity, crosslinking 162 Ruhrchemie 150, 238 Russian tanks, motor oil 138

### S

safety – glass 95 - helmets 95 salt - acid of salt (hydrochloric acid) 273 -- dephlogisticated 273 - formation -- bisphenol A 126 -- nylon (see also there) 125-126 SAN 208 Sandemanians (Glasites) 267 sandwich molecules 37 saponification 86 Saudi Arabia, cheap ethane 244 SBR (styrene butadiene rubber) 170–171 Scheele, C.W. 273 - discoveries by 273 Scientific Design 198  $\beta$ -scissions 14 segregated structure 182 serendipitous discovery 24 seven basic chemicals (see chemicals) 196 SHELL Chemical Company 80, 183, 199 1,2-shifts 17 ship transporting, insulate ship 89 Shivers, Joseph C. 184 Showa-Denko - process 79-80, 282 - synthesis of epichlorohydrin 79 shutdown economics 221-222, 244  $\sigma$ -bond 14 silicone rubber 175-177 - applications 176 - crosslinked 176

- flexibility at very low temperatures 177 - peroxide crosslinking of elastomers 175 silk 112 - artificial silk (see also nylon) 112, 129 - structure, compared to nylon 6 114 Silliman, B. 4 silver-catalyzed oxidation of ethylene 203 single-site catalysts 36, 40 six-membered ring transition state 30 skateboard wheels 89 ski boots 89 smokeless powder 223 S<sub>N1</sub> reaction / mechanisms 21, 77 S<sub>N2</sub> reaction / mechanisms 21, 73-74, 131, 186 soap production / manufacture 86-87 Sobrero, Ascanio 88-89 Socony Vacuum Oil Co. 11 sodium - hydride 270 - sebacate 129 SOHIO 206, 212 solubility and melting point, correspondence between 59 solvents 207 - aprotic 207 - inventing new ones 207 soybean oils 81 space shuttle 89 spandex 89, 91, 184-188 - ability to stretch 185 - chain 91 - flexible segment 184 - hard segment 185 - properties 184 - soft segment 185 - stiff segment 184 - structure 184 - synthesis 186–188 tetrahydrofuran for spandex 186–187 sp-hybridized carbon 104 spinneret 114 spiro compound 61 Stalingrad, tank battle 138 Standard Oil – of Indiana 4 - of New Jersey 5, 172 Staudinger, Herman 108 steam cracking 2, 4-6, 8-9 - aromatics from 5 - benzene 45 - development 4-5, 8 - ethylene 45, 236 - free radicals 45

#### 318 Index

- mechanism 12 - methylacetylene, minor product of steam cracking 153 - of petroleum fractions 236 - products from 5, 15 - propylene 45 - steam and catalytic cracking 8-9 stereochemistry of polymers 23-43 steric hindrance 73 - neopentyl glycol 231 stockings, nylon 111-112 stoichiometry in oxychlorination 268 strain / strained 72-73 - crystallization, strain-induced 162 - epoxides 72, 201 - molecules 73 – state 72 stranded gas 294 styrene 46, 48, 107, 200 - cost 46 - polystyrene (see also there) 46-49, 107-108, 182 production 48 styrene-butadiene rubber (SBR) 170-171, 173 succinic acid, byproduct of oxidation 243 succinonitrile 123 sucrose 93-94 - reaction with propylene oxide 94 sulfonamide 168 sulfur / sulfuric - acid, role in methacrylate synthesis 141 - eight-membered sulfur rings 167 - polyethylene, reaction with sulfur dioxide and chlorine gases 168 - trioxide 143 - vulcanization with 164-167, 170 sulfur-sulfur bonds 164 Sun Oil Co. 11 supermolecule 69-70 surfactant 87 Surlyn<sup>TM</sup> (see ionomers) 188–190 synthesis - ABS resin 208 adipic acid 116–118 - adiponitrile 124, 285 - alkyd resins 81 - butadiene 118 - caprolactam 283 – cumene 49 - EPDM rubber 174-175 – epichlorohydrin 76–80 - epoxy resin 71-72 - ethylene-propylene 174

– gas 294 - glycerol 81 - hexamethylene diamine 116-118 - ionomers (Surlyn<sup>TM</sup>) 188–190 - isocyanate 273 - isopropylbenzene 49 - methyl methacrylate 139 - MTBE (methyl tertiary butyl ether) 149 - nitroglycerin 88 - nylon 4,6 122, 125 - nylon 6 127-129 - nylon 6,6 116 - nylon 11 132 - pentaerythritol 229-232 - polycarbonate (see also there) 96-97, 276-285 - polystyrene 47-49 spandex 186–188

#### t

tartaric acid 273 tautomerism 235 - deuterium exchange 235 - mechanism 235 tear resistance 208 teflon 67 temperature - ceiling 23 - chlorine 282 - glass transition temperature 179-180 - silicone rubber, flexibility at very low temperatures 177 ten-membered ring 164 terephthalic acid 222 tetraethyl lead 148-150 tetrahydrofuran for spandex 186-187 tetramethylene diamine 122-123, 125 thermal cracking 4-6 thermodynamic - addition polymers 23-24 – control 119–122 thermoplastic elastomers (Kraton<sup>TM</sup>) 170–171, 181-183, 185, 188-189 thiokol 170, 172-173 - uses 173 three-membered ring 73 tires - failure potential 157 - gasoline rationing and the rubber in the tires 173 – life 174 - run-flat 89 TNT (trinitrotoluene) 233

toiletries 87 toluene 6, 196 - diisocyanate 273 glycerol reaction with toluene diisocyanate
 92 toothpaste 87 transesterification 83-85, 99, 202 - chemistry 99 - of drying oil 83-85 - polycarbonate, synthesis via transesterification 275 transition - glass transition temperature (Tg) 180 - metals / metal catalysis 211-212, 236-243, 283 -- bound to carbon 237 -- early example 211-212 -- magic 212 six-membered ring transition state 30 triethylbenzene 53-54, 204 triglycerides 81, 86, 129 triisopropylbenzene 49-52 trimethylolpropane 226-228, 231 - production 231 2,2,4-trimethylpentane 9 trinitrotoluene (TNT) 233 tung oils 81 Turin (ITALY) 89 2-for-1 process 198-201, 286 - cumene 198 - Dow Chemical Co. 201 hydroperoxide 199 - tyranny-associated 201

#### и

undecyclenic acid 129-130 - HBr addition 129 Union Carbide 5, 7, 197 University - of Chulalongkon XVII - of Illinois 107 - of Manchester 223 - of Tuebingen 139 unsaturated oils 81 double bonds 81 - polymerized by free radicals 81 uranium 212 urea 91 - bonds 184 - crosslink-associated with urea linkages 185 urethane 91 - bonds 184 - polyurethane (see also there) 85, 89-95, 184 uric acid 273

#### ν

vacuum distillation 202 - multiply vacuum-vented extruders 275 - polymerization under increasingly high vacuum 275 - Socony Vacuum Oil Co. 11 vacuum-vented extruders 275 valorized gas 294 vandalism 95 vinyl - acetate 258-264 – from acetylene 258–259 -- from ethylene 260 -- polymerization 262 -- uses 262 - alcohol 234-235, 238 -- conversion 235 -- rearrangement to acetaldehyde 235 - chloride 2, 6, 196, 258-259, 265-268, 282, 294 -- from acetylene 265 – – from ethane 294 -- from ethylene 265 -- by oxychlorination 267 -- poly(vinyl chloride) (see also there) 107-108, 196, 233, 265 -- production from ethylene 258-259, 265 -- from propane 294 -- synthesis from acetylene 265 - monomers 107 - poly(vinyl acetate) 107 vinyl-based synthetic polymers 107 vinylacetylene 119 vinylpyridine 207 viscosity - control agents 205 – glycerol 87 vitalism 256 vitamin C process 295 von Liebig, Justus 234 vulcanization 69, 163-171 battery cases from vulcanized rubber 167 - discovery 163 - elastomers 163-164 - mechanism of 164, 169-171 - with sulfur 164-167, 170

Wacker process / reaction 153, 222, 235-238, 244, 260-261 insight via isotope exchange experiments 238 - mechanism 238

 shuts down all older industrial methods to acetaldehyde 236–238

Wacker-Chemie 236

water

- aldol, loss of water 150
- calcium chloride, reaction with water 252, 254
- cyanide to carboxyl, catalyzed addition of water 139
- cuprous oxide, unstable in water 270
- elimination 146
- epoxides, addition of water 201
- ethylene or propylene oxide, increased proportions of water 204
- hard water, calcium and magnesium ions 205
- heavy water (D<sub>2</sub>O) 235
- hydrophilic (water-loving) 87
- isocyanate, reactions with water 91
- nylon, water absorption 113, 115
- and oil 189
- poly(acrylic acid), water-loving properties 205
- zeolite, water-absorbing 146
- water-borne paints 262
- acrylic 262
- esters 262
- poly(vinyl acetate) 262 Weissermel, K. 241 Weizmann, Chaim 223
- Weizmann-process 223
- Wilkinson, John 6
- Willstätter, Richard 274

wiped film evaporators 275 Woehler, Friedrich 251, 256 Woodward-Hoffmann rules 19 wool-like fabrics 206 World War I. 137, 170, 223–224 World War II. 11, 138 – turning point 138 Wright, Gilbert 176

#### X

p-xylene 196, 222

#### z

Zentel, Rudolf XVII zeolite / zeolytic 10-12, 15, 54-56 - catalysts 52-54 - catalytic cracking 10 - channels, size selectivity 54 - structure 10 - water-absorbing 146 - Zeolite Socony Mobil (see ZSM) Ziegler, Karl 24, 29, 32 Ziegler-Natta - catalysts 33-44, 174, 214 -- chirality 36 - - mechanisms of polymerization 38-40 -- stereochemical hypothesis 39 - polymerization 212 Zionism 223 ZSM (Zeolite Socony Mobil) 5, 11-12 Zyklon B 142, 249