76-20,922

STADTHERR, Mark Allen, 1950-
A SYSTEMS STUDY OF THE PETROCHEMICAL INDUSTRY

The University of Wisconsin-Madison, Ph.D., 1976
Engineering, chemical

University Microfilms, Ann Arbor, Michigan

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A thesis submitted to the Graduate School of the
University of Wisconsin-Madison in partial fulfillment of
the requirements for the degree of Doctor of Philosophy

BY

Mark Allen Stadtherr

Degree to be awarded: December 19_____ May 19 76 August 19_____

Approved by Thesis Reading Committee:

Major Professor

May 26, 1976
Date of Examination

C. C. Watson

Richard R. Hughes

Dean, Graduate School

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MARK ALLEN STADTHERR

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ACKNOWLEDGMENTS

The author acknowledges the advice of Professor Dale Rudd, the encouragement of family and friends, and the financial support of the National Science Foundation, the Wisconsin Alumni Research Foundation, the University of Wisconsin Graduate School, the University of Wisconsin Mathematics Research Center, and the Exxon Chemical Company.

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1. INTRODUCTION

Over the past few decades this country has made increasing use of chemical technology to satisfy its basic economic needs. Indeed the chemical and allied products industry is now instrumental in producing the high quality food, clothing, and shelter most Americans take for granted. In addition, products of chemical origin are important in many other consumer areas, including transportation, communication, personal and household care, outdoor recreation, and indoor entertainment. A recent American Chemical Society publication[1] details the role of chemical products in our economy.

These products arise from natural resources such as petroleum, natural gas, coal, and various metallic and nonmetallic ores. Primary processing of these resources yields a handful of basic chemical raw materials from which a host of other useful chemicals can be derived. Converting these raw materials into chemicals suitable for eventual consumer use is the task of the industrial chemicals industry. Through a series of chemical transformations, this largely anonymous, but vital industry converts the basic raw materials into the desired chemicals. These chemicals rarely find direct consumer use; instead they are utilized by other industrial sectors whose products ultimately appear on the consumer market. For instance, industrial chemicals may serve as raw materials for the manufacture of plastics, elastomers, or synthetic fibers; or they may be used in other industries as solvents, bleaching agents, or for other auxiliary functions.

Here we focus on the petrochemical industry, the segment of the industrial chemicals industry deriving its products from petroleum and natural gas. The petrochemical industry is a key sector in our economy. One recent study[2] has estimated that products derived from petrochemicals produced in Texas account for thirteen percent of the gross national product and three million jobs. Considering current concerns regarding supplies of petroleum and natural gas, an analysis of this important industry is appropriate.

The petrochemical industry is a large and complex system. Thousands of petrochemicals are made commercially, and hundreds of major companies are engaged in some part of the processing. The many segments of this system interact by competing for raw materials and markets, and by developing and licensing competing process technologies. Thus, if particular segments of the industry are examined in isolation, there is no guarantee that the conclusions reached will be significant when the performance of the overall system is of importance. In such a large, interactive system, the whole is not necessarily made more efficient if one particular part is improved. In fact, local inefficiencies may be necessary if the overall system is to operate at maximum efficiency. Consequently, in this study of the petrochemical industry, we concentrate not on the local economics of individual segments of the industry, but on the performance of the system as a whole. For this purpose a mathematical model of the system is constructed.

Because of the size and complexity of the petrochemical

industry, it is not practical to consider the fine details of its interactive corporate structure when constructing a model of the overall system. Instead we look past the system's organizational structure and model the system by taking advantage of its underlying stoichiometric framework. Accordingly, the petrochemical industry is regarded as a system of chemical reactions that convert crude petrochemical feedstocks into the products consumed by the economy. In this way the system can be described using stoichiometric and yield data characterizing each chemical transformation. These data are generally available in the literature and are the basis for the model described below.

Though this model may overlook locally important technological and economic factors, it effectively approximates the gross behavior of the industry. To study the efficiency with which the industry consumes feedstocks, we use the model to determine technological bounds on the structure of the industry and on the performance of its parts. These results are based on the criterion that the industry as a whole meet the demands of the economy with minimum feedstock consumption and unconstrained by the limits of existing process capacity. Then, by applying the model to the petrochemical industry in decades past, we see to what extent the model is useful in predicting the development of the industry. The model is also used to evaluate the effects of perturbations in feedstock supply, product demand, and process technology. In one such perturbation we determine the structure of the petrochemical industry best suited to the Mexican economy according to the minimum feedstock

consumption criterion. In applications of this sort the model can be used to study technology transfer to other economies. The studies described here are part of a larger study of the industry[3,4].

2. NATURE OF THE INDUSTRY

The basic feedstocks for the petrochemical industry are extracted from natural gas or are produced in petroleum refineries. Coal has largely been replaced as a feedstock source, but may increase in significance in the face of predicted natural gas and petroleum shortages. The petrochemical industry converts its primary feedstocks into a variety of final and intermediate chemical products. The intermediates are consumed within the industry itself; the final products are used elsewhere in the economy, primarily as raw materials for other goods, such as plastics, elastomers, and synthetic fibers.

For the manufacture of a given chemical there are often two or more chemical transformations available, each involving different combinations of feedstocks and coproducts. For example, there are three chemical reactions that have been used commercially to manufacture acrylonitrile: the reaction of acetylene and hydrogen cyanide, the reaction of ethylene oxide and hydrogen cyanide, and the reaction of propylene, ammonia, and air. Some petrochemicals, including ethylene, butadiene, phenol, and acrylic acid can be produced from as many as five different combinations of feedstocks.

Radically different methods of executing a given chemical transformation are not as commonly found, however. The freedom with which chemical processing know-how is licensed world-wide enables all manufacturers to acquire the superior processing methods. Thus, the differences within the industry tend to be dominated by discrete and drastic differences in the feedstocks used, while the

technology used to implement a particular reaction route is relatively uniform. Furthermore, the kind of process technology used to produce the majority of petrochemicals is similar in sophistication and capital intensiveness. One sector of the industry does not differ greatly from any other in the level of technical competence required.

For most petrochemicals, feedstock costs dominate the economics of production. Hahn[5] has estimated production costs for many petrochemical processes; the portion of total production cost attributed to feedstock costs is typically 40 to 80 percent, as shown in Figure 1. This fact, along with the observations made above on the uniformity of process technology, suggests that it is the flexibility with respect to feedstocks and coproducts which dominates the behavior of the petrochemical industry. The details of a particular processing method may alter local economics to some extent, but the prevailing industrial structure is determined by the more primative forces that control the gross production and consumption of materials.

In summary, the petrochemical industry is bounded on one side by sources of primary chemicals derived from crude oil, natural gas, and coal, and is bounded on the other side by the consumer market that requires synthetic materials of great diversity. Within these boundaries the industry is a flexible, interdependent system of commercially proven chemical transformations, the execution of which does not differ greatly around the world. However, the cast of chemical transformations used can vary widely in both time

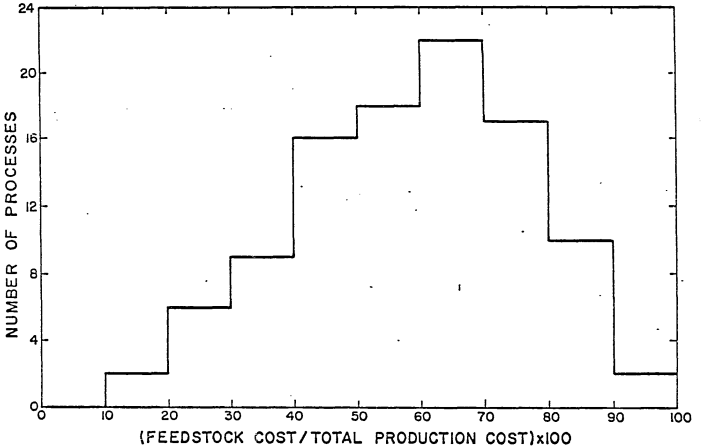

Figure 1. Using data from Hahn[5], the percentage of total production cost due to feedstock cost is estimated for a number of typical petrochemical processes. The graph shows the distribution of the percentages. Note that most frequently feedstock costs account for 40 to 80 percent of total production cost.

and location to meet the needs of an economy. In any case, it is the gross production and consumption of materials that is of primary importance.

Given these views on the nature of the petrochemical industry, we construct a model which effectively accounts for its flexibility and interdependence, and which can be used to study the efficiency with which it produces and consumes materials. This model is described mathematically in the next section.

3. MATHEMATICAL FORMULATION OF MODEL

A useful model of the petrochemical industry must account for the industry's complexity and flexibility, and yet be sufficiently efficacious. Linear programming is a mathematical tool well suited to this problem and is employed in the model formulated below. Several complete treatments of the theory of linear programming are available, including those by Dantzig[6], Hadley[7], and Gass[8]. Discussions of a more practical nature are given by Driebeek[9] and Daellenbach and Bell[10].

We view the petrochemical industry as a system of M chemical transformations that produce or consume N chemicals. To be general, assume that each of the N chemicals is potentially a primary input or final product of the industry. Let p_i be the amount of chemical i used as a primary feedstock; let q_i be the amount of chemical i emerging as a final product; and let x_j be the amount of transformation j used by the industry.

If chemical i is produced by transformation j, let a_{ij} be the amount of i produced per unit of j; if i is consumed by j, let $-a_{ij}$ be the amount of i consumed per unit of j; if i is neither an input or output of j, let $a_{ij} = 0$. The a_{ij} are known as 'input-output coefficients,' and $\underline{A} = [a_{ij}]$ is called the 'technology matrix.'

In these terms, material balances can be written for each chemical as

$$p_i + \sum_{j=1}^{M} a_{ij}x_j - q_i = 0, \quad i = 1, 2, \ldots, N ; \tag{1}$$

or in matrix form

$$\underset{\sim}{p} + \underline{\underline{A}}\underset{\sim}{x} - \underset{\sim}{q} = 0 \ , \tag{1a}$$

where $\underset{\sim}{p} = (p_i)$, $\underset{\sim}{q} = (q_i)$, and $\underset{\sim}{x} = (x_j)$.

In the short-range Equation (1) is constrained by the supply of feedstocks,

$$\underset{\sim}{p} \leq \underset{\sim}{s} \ , \tag{2}$$

by the demand for products,

$$\underset{\sim}{q} \geq \underset{\sim}{d} \ , \tag{3}$$

and by the capacity for each chemical transformation,

$$\underset{\sim}{x} \leq \underset{\sim}{c} \ ,$$

where $\underset{\sim}{s} = (s_i)$ and $\underset{\sim}{d} = (d_i)$ are supply and demand data which might be assembled by functional aggregate studies[3,4], and $\underset{\sim}{c} = (c_j)$ represents industrial capacity.

Equations (1)-(4) form a linear system of constraints within which the industry must function in the short-range. These constraints, together with a linear objective function, form a linear programming problem which can easily be solved to determine the p_i, q_i, and x_j satisfying the given objective.

Linear programming models similar to the one formulated here have been reasonably successful in representing the iron and steel[11,12,13], bituminous coal[14], and petroleum refining[15,16] industries.

4. CONSTRUCTION OF MODEL

The first step in constructing the model formulated above is the selection of the chemicals and chemical transformations which constitute the model.

A list of the chemicals chosen appears in Table 1. The selection is based on volume of production; in general, petrochemicals for which production exceeded 100 million pounds in the United States in 1970 are included, together with the primary feedstocks, organic and inorganic, which may be involved in their production. Chemicals produced in lesser quantities are included if they are potentially an intermediate, coproduct, or major byproduct in the manufacture of one of the larger volume chemicals selected. However, intermediate chemicals which have essentially only one use and for which there is essentially only one manufacturing route are not included explicitly, unless there is significant commercial traffic in that chemical (as in the case of cumene or ethylbenzene, for example). Table 1 also indicates the function of each chemical selected; that is, whether it serves as a primary input, final output, intermediate, or combination thereof. The uses and manufacturing methods for these chemicals are described briefly in Appendix 1.

For each chemical selected, the model includes the chemical transformations currently used to manufacture the chemical, as well as any now obsolete transformations once used on a commercial scale. By accounting for obsolete in addition to current process technology we assure that the model is not biased toward any particular economic

Table 1. A list of the chemicals that constitute the model industry. Also indicated is the potential function of each chemical in the model: I = primary input, M = intermediate, O = final output.

Chemical	Function
Acetaldehyde	MO
Acetic Acid	MO
Acetic Anhydride	MO
Acetone	MO
Acetylene	MO
Acrolein	MO
Acrylic Acid	MO
Acrylonitrile	MO
Adipic Acid	MO
Adiponitrile	MO
Allyl Alcohol	MO
Allyl Chloride	MO
Ammonia	MO
Ammonium Bisulfate	O
Ammonium Chloride	O
Ammonium Sulfate	O
Aniline	O
Benzene	IMO
Benzoic Acid	MO
Bisphenol-A	O
Bromine	I
Butadiene	MO
n-Butane	I
n-Butanol	IMO
s-Butanol	MO
n-Butylenes	IMO
n-Butyraldehyde	MO
Calcium Acetate	O
Calcium Chloride	O
Calcium Formate	O
Calcium Hydroxide	I
Calcium Hypochlorite	I
Caprolactam	O
Carbon	I
Carbon Dioxide	MO
Carbon Disulfide	MO
Carbon Monoxide	IMO
Carbon Tetrachloride	MO
Chlorine	IM
Chlorobenzene	MO
Chloroform	O
Chloroprene	O
Cresylic Acid	O
Crotonaldehyde	MO
Cumene	MO
Cyclohexane	IMO
Cyclohexanol	MO
Cyclohexanone	MO
Dichlorodifluoromethane	O
Diethylene Glycol	MO
Dimethyl Terephthalate	O
Dinitrotoluene	MO
Epichlorohydrin	MO
Ethane	I
Ethanol	IMO
Ethyl Acetate	O
Ethyl Acrylate	O
Ethylbenzene	IMO
Ethyl Chloride	O
Ethylene	MO
Ethylene Dibromide	O
Ethylene Dichloride	MO
Ethylene Glycol	MO
Ethylene Oxide	MO
2-Ethylhexanol	O
Formaldehyde	MO
Fuel Oil	IMO
Gas Oil	I
Glycerin	O
Hexamethylenediamine	O
Hydrogen	IMO
Hydrogen Chloride	IMO
Hydrogen Cyanide	MO
Hydrogen Fluoride	I
Hydrogen Peroxide	IM
Iron	I
Iron(II) Chloride	O
Iron Oxide	O
Isobutane	IM
Isobutanol	O
Isobutylene	IMO
Isobutyraldehyde	MO
Isopentenes	I
Isophthalic Acid	O
Isoprene	O
Isopropanol	MO
Ketene	MO
Maleic Anhydride	O
Methane	IMO
Methanol	MO
Methyl Chloride	MO
Methyl Chloroform	O
Methylene Dichloride	O
Methyl Ethyl Ketone	O

Table 1 (continued)

Chemical	Function
Methyl Isobutyl Ketone	O
Methyl Methacrylate	O
Naphtha	I
Naphthalene	I
Nitric Acid	IMO
Nitrobenzene	MO
Peracetic Acid	MO
Perchloroethylene	O
Phenol	MO
Phosgene	MO
Phthalic Anhydride	MO
Propane	I
Propylene	IMO
Propylene Dichloride	MO
Propylene Glycol	O
Propylene Oxide	MO
Pyrolysis Gasoline	O
Sodium	I
Sodium Chloride	MO
Sodium Hydroxide	I
Sodium Sulfate	O
Sodium Sulfite	O
Styrene	O
Sulfur	IMO
Sulfuric Acid	I
Terephthalic Acid	MO
Toluene	IMO
Toluene Diamine	MO
Toluene Diisocyanate	O
Trichloroethylene	MO
Trichlorofluoromethane	O
Triethylene Glycol	O
Urea	O
Vinyl Acetate	O
Vinyl Chloride	MO
m-Xylene	IMO
o-Xylene	IMO
p-Xylene	IMO

environment and can adapt to radically different patterns of supply and demand. Once obsolete processes could conceivably return to prominence if the appropriate economic environment evolved. Table 2 lists the chemical transformations accounted for by the model.

The heart of the model is the technology matrix. Hence the estimation of the input-output coefficients is a key step in constructing the model. For this purpose yield data for each chemical transformation is required.

Much of the yield data used is taken from the Stanford Research Institute publication, Chemical Conversion Factors and Yields[17]. Most of the yield data reported in this volume was obtained directly from the industry, or was at least subject to industry review. Thus, data drawn from this source can be considered reasonably reliable. The remainder of the yield data used is drawn primarily from surveys of the industry by Brownstein[18], Hahn[5], Goldstein and Waddams[19], and Faith, Keyes, and Clark[20]. Reviews of patent literature[21, 22,23] and various articles in the trade journals have also been consulted; however data drawn from patent literature must be regarded with some skepticism. The estimated values of the input-output coefficients and a complete listing of data sources appear in Appendix 1.

Needed to complete the construction of the model are supply, demand, and capacity data. Since the industry must compete for its feedstocks and markets, supply and demand data are best determined by functional aggregate studies[3,4]. Here, however, supply and

Table 2. A list of the chemical transformations constituting the model industry.

1. Acetaldehyde via oxidation of ethylene
2. Acetaldehyde via dehydrogenation of ethanol
3. Acetaldehyde via oxidation of ethanol
4. Acetaldehyde via oxidation of propane
5. Acetaldehyde via oxidation of n-butane
6. Acetaldehyde via hydration of acetylene
7. Acetic acid via oxidation of n-butane
8. Acetic acid via oxidation of acetaldehyde
9. Acetic acid via carbonylation of methanol (low pressure)
10. Acetic acid via oxidation of naphtha
11. Acetic acid via carbonylation of methanol (high pressure)
12. Acetic anhydride via reaction of ketene and acetic acid
13. Acetic anhydride via oxidation of acetaldehyde
14. Acetic anhydride via reaction of acetylene and acetic acid
15. Acetone via dehydrogenation of isopropanol
16. Acetone via oxidation of isopropanol
17. Acetone via oxidation of propylene
18. Acetone via hydration of acetylene
19. Acetone via hydration of ethanol
20. Acetone via decarboxylation of acetic acid
21. Acetylene via hydration of calcium carbide
22. Acetylene via pyrolysis of methane (arc process)
23. Acetylene via pyrolysis of methane (one-stage partial combustion)
24. Acetylene via pyrolysis of naphtha (one-stage partial combustion)
25. Acetylene via pyrolysis of ethane (regenerative process)
26. Acetylene via pyrolysis of propane (regenerative process)
27. Acetylene via pyrolysis of n-butane (regenerative process)
28. Acetylene via pyrolysis of naphtha (regenerative process)
29. Acetylene via pyrolysis of methane (two-stage partial combustion)
30. Acetylene via pyrolysis of ethane (two-stage partial combustion)
31. Acetylene via pyrolysis of propane (two-stage partial combustion)
32. Acetylene via pyrolysis of n-butane (two-stage partial combustion)
33. Acetylene via pyrolysis of naphtha (two-stage partial combustion)
34. Acrolein via oxidation of propylene
35. Acrolein via reaction of formaldehyde and acetaldehyde
36. Acrylic acid via oxidation of acrolein
37. Acrylic acid via carbonylation of acetylene
38. Acrylic acid via reaction of ketene and formaldehyde
39. Acrylic acid via sulfonation of acrylonitrile
40. Acrylic acid via cyanation of ethylene oxide
41. Acrylonitrile via ammoxidation of propylene
42. Acrylonitrile via cyanation of acetylene
43. Acrylonitrile via cyanation of ethylene oxide
44. Adipic acid via oxidation of cyclohexanone
45. Adipic acid via oxidation of cyclohexanol
46. Adipic acid via oxidation of cyclohexanone with nitric acid
47. Adipic acid via oxidation of cyclohexanol with nitric acid
48. Adiponitrile via reaction of adipic acid and ammonia

49. Adiponitrile via chlorination of butadiene
50. Adiponitrile via hydrodimerization of acrylonitrile
51. Allyl alcohol via reaction of acrolein and isopropanol
52. Allyl alcohol via isomerization of propylene oxide
53. Allyl alcohol via hydrolysis of allyl chloride
54. Allyl chloride via chlorination of propylene
55. Ammonia via reaction of hydrogen and nitrogen
56. Aniline via hydrogenation of nitrobenzene
57. Aniline via reaction of chlorobenzene and ammonia
58. Aniline via reaction of phenol and ammonia
59. Aniline via reduction of nitrobenzene with iron
60. Benzene via hydrodealkylation of toluene
61. Benzene via disproportionation of toluene
62. Benzoic acid via oxidation of toluene
63. Benzoic acid via decarboxylation of phthalic anhydride
64. Benzoic acid via chlorination of toluene
65. Bisphenol-A via reaction of phenol and acetone
66. Butadiene via dehydrogenation of n-butylenes
67. Butadiene via dehydrogenation of n-butane
68. Butadiene via reaction of ethanol and acetaldehyde
69. Butadiene via dimerization of acetaldehyde
70. Butadiene via reaction of acetylene and formaldehyde
71. Butadiene via dehydration/dehydrogenation of ethanol
72. Butadiene via chlorination of n-butylenes
73. n-Butanol via hydrogenation of n-butyraldehyde
74. n-Butanol via hydrogenation of crotonaldehyde
75. n-Butanol via carbonylation of propylene
76. s-Butanol via sulfonation of n-butylenes
77. n-Butylenes via dehydrogenation of n-butane
78. n-Butyraldehyde via oxonation of propylene
79. n-Butyraldehyde via hydrogenation of crotonaldehyde
80. n-Butyraldehyde via dehydrogenation of n-butanol
81. Caprolactam via reaction of cyclohexanone and hydroxylamine
82. Caprolactam via reaction of cyclohexanone and peracetic acid
83. Caprolactam via nitrosation of cyclohexane
84. Caprolactam via hydrogenation of benzoic acid
85. Caprolactam via nitration of cyclohexane
86. Carbon disulfide via reaction of methane and sulfur
87. Carbon disulfide via reaction of charcoal and sulfur
88. Carbon tetrachloride via chlorination of methane
89. Carbon tetrachloride via chlorination of carbon disulfide
90. Carbon tetrachloride via chlorinolysis of propane
91. Carbon tetrachloride via chlorinolysis of propylene dichloride
92. Carbon tetrachloride via chlorination of methyl chloride
93. Carbon tetrachloride via chlorinolysis of ethane
94. Carbon tetrachloride via chlorinolysis of propylene
95. Chlorine via electrolysis of sodium chloride
96. Chlorobenzene via chlorination of benzene
97. Chlorobenzene via oxychlorination of benzene
98. Chloroform via chlorination of methane

99. Chloroform via reaction of acetone and bleaching powder
100. Chloroform via reaction of ethanol and bleaching powder
101. Chloroform via chlorination of methyl chloride
102. Chloroform via reduction of carbon tetrachloride
103. Chloroprene via chlorination of butadiene
104. Chloroprene via dimerization of acetylene
105. Cresylic acid via methylation of phenol
106. Cresylic acid via reaction of toluene and propylene
107. Crotonaldehyde via dimerization of acetaldehyde
108. Cumene via reaction of benzene and propylene
109. Cyclohexane via hydrogenation of benzene
110. Cyclohexanol via oxidation of cyclohexane
111. Cyclohexanol via hydrogenation of phenol
112. Cyclohexanol via oxidation of cyclohexane (boron-assisted)
113. Cyclohexanone via dehydrogenation of cyclohexanol
114. Cyclohexanone via hydrogenation of phenol
115. Dichlorodifluoromethane via reaction of carbon tetrachloride and hydrogen flouride
116. Diethylene glycol via reaction of ethylene glycol and ethylene oxide
117. Dimethyl terephthalate via esterification of terephthalic acid
118. Dimethyl terephthalate via reaction of methanol and p-xylene
119. Dinitrotoluene via nitration of toluene
120. Epichlorohydrin via chlorohydration of allyl chloride
121. Epichlorohydrin via chlorination of allyl alcohol
122. Ethanol via hydration of ethylene
123. Ethanol via sulfonation of ethylene
124. Ethyl acetate via esterification of acetic acid
125. Ethyl acetate via dimerization of acetaldehyde
126. Ethyl acrylate via esterification of acrylic acid
127. Ethylbenzene via reaction of benzene and ethylene
128. Ethyl chloride via hydrochlorination of ethylene
129. Ethyl chloride via chlorination of ethane
130. Ethyl chloride via hydrochlorination of ethanol
131. Ethylene via pyrolysis of ethane
132. Ethylene via pyrolysis of propane
133. Ethylene via pyrolysis of n-butane
134. Ethylene via pyrolysis of naphtha (low severity)
135. Ethylene via pyrolysis of naphtha (high severity)
136. Ethylene via pyrolysis of gas oil (low severity)
137. Ethylene via pyrolysis of gas oil (high severity)
138. Ethylene via hydrogenation of acetylene
139. Ethylene via dehydration of ethanol
140. Ethylene dibromide via bromination of ethylene
141. Ethylene dichloride via chlorination of ethylene
142. Ethylene dichloride via oxychlorination of ethylene
143. Ethylene glycol via hydration of ethylene oxide
144. Ethylene glycol via carbonylation of formaldehyde
145. Ethylene oxide via oxidation of ethylene
146. Ethylene oxide via chlorohydration of ethylene

147. 2-Ethylhexanol via dimerization of n-butyraldehyde
148. Formaldehyde via oxidation of methanol
149. Formaldehyde via oxidation/dehydrogenation of methanol
150. Glycerin via hydrolysis of epichlorohydrin
151. Glycerin via reaction of allyl alcohol and hydrogen peroxide
152. Glycerin via reaction of allyl alcohol and peracetic acid
153. Hexamethylenediamine via hydrogenation of adiponitrile
154. Hydrogen via water-gas reaction
155. Hydrogen via steam reforming of methane
156. Hydrogen via steam reforming of ethane
157. Hydrogen via steam reforming of propane
158. Hydrogen via steam reforming of n-butane
159. Hydrogen via steam reforming of naphtha
160. Hydrogen via partial oxidation of methane
161. Hydrogen via partial oxidation of ethane
162. Hydrogen via partial oxidation of propane
163. Hydrogen via partial oxidation of n-butane
164. Hydrogen via partial oxidation of naphtha
165. Hydrogen via partial oxidation of gas oil
166. Hydrogen via partial oxidation of fuel oil
167. Hydrogen via water-gas shift reaction
168. Hydrogen cyanide via ammoxidation of methane
169. Hydrogen cyanide via reaction of sodium cyanide and sulfuric acid
170. Hydrogen cyanide via decomposition of formamide
171. Hydrogen cyanide via reaction of methane and ammonia
172. Hydrogen cyanide via reaction of propane and ammonia
173. Hydrogen cyanide via reaction of naphtha and ammonia
174. Hydrogen peroxide via oxidation of isopropanol
175. Isobutane via isomerization of n-butane
176. Isobutanol via hydrogenation of isobutyraldehyde
177. Isobutanol via reaction of hydrogen and carbon monoxide
178. Isobutylene via dehydrogenation of isobutane
179. Isobutylene via pyrolysis of isobutane
180. Isophthalic acid via oxidation of m-xylene
181. Isoprene via dehydrogenation of isopentenes
182. Isoprene via dimerization of propylene
183. Isoprene via reaction of formaldehyde and isobutylene
184. Isoprene via reaction of acetylene and acetone
185. Isopropanol via sulfonation of propylene
186. Isopropanol via hydration of propylene
187. Ketene via pyrolysis of acetic acid
188. Ketene via pyrolysis of acetone
189. Maleic anhydride via oxidation of benzene
190. Maleic anhydride via oxidation of n-butylenes
191. Methanol via hydrogenation of carbon monoxide
192. Methanol via hydrogenation of carbon dioxide
193. Methyl chloride via chlorination of methane
194. Methyl chloride via hydrochlorination of methanol
195. Methyl chloroform via chlorination of ethylene dichloride
196. Methyl chloroform via hydrochlorination of vinyl chloride

Table 2 (continued)

197. Methyl chloroform via chlorination of ethane
198. Methylene dichloride via chlorination of methane
199. Methylene dichloride via chlorination of methyl chloride
200. Methyl ethyl ketone via dehydrogenation of s-butanol
201. Methyl ethyl ketone via oxidation of n-butylenes
202. Methyl ethyl ketone via oxidation of n-butane
203. Methyl isobutyl ketone via dimerization of acetone
204. Methyl methacrylate via cyanation of acetone
205. Methyl methacrylate via oxidation of isobutylene
206. Nitric acid via oxidation of ammonia
207. Nitrobenzene via nitration of benzene
208. Peracetic acid via oxidation of acetaldehyde
209. Perchloroethylene via chlorination of trichloroethylene
210. Perchloroethylene via chlorinolysis of propane
211. Perchloroethylene via chlorinolysis of propylene dichloride
212. Perchloroethylene via chlorination of ethylene dichloride
213. Perchloroethylene via oxychlorination of ethylene dichloride
214. Perchloroethylene via chlorinolysis of ethane
215. Perchloroethylene via chlorinolysis of propylene
216. Perchloroethylene via pyrolysis of carbon tetrachloride
217. Phenol via oxidation of cumene
218. Phenol via decarboxylation of benzoic acid
219. Phenol via dehydrochlorination of chlorobenzene
220. Phenol via alkaline hydrolysis of chlorobenzene
221. Phenol via sulfonation of benzene
222. Phosgene via reaction of chlorine and carbon monoxide
223. Phthalic anhydride via oxidation of o-xylene
224. Phthalic anhydride via oxidation of naphthalene
225. Propylene dichloride via chlorination of propylene
226. Propylene glycol via hydration of propylene oxide
227. Propylene oxide via chlorohydration of propylene
228. Propylene oxide via oxidation of propylene with t-butyl hydroperoxide
229. Propylene oxide via oxidation of propylene with ethylbenzene hydroperoxide
230. Styrene via dehydrogenation of ethylbenzene
231. Styrene via oxidation of ethylbenzene
232. Terephthalic acid via oxidation of p-xylene
233. Terephthalic acid via disproportionation of benzoic acid
234. Terephthalic acid via oxidation of p-xylene with nitric acid
235. Toluene diamine via hydrogenation of dinitrotoluene
236. Toluene diisocyanate via phosgenation of toluene diamine
237. Trichloroethylene via chlorination of acetylene (catalytic dehydrochlorination)
238. Trichloroethylene via chlorination of acetylene (alkaline dehydrochlorination)
239. Trichloroethylene via chlorination of ethylene dichloride
240. Trichloroethylene via oxychlorination of ethylene dichloride
241. Trichlorofluoromethane via reaction of carbon tetrachloride and hydrogen fluoride

242. Triethylene glycol via reaction of diethylene glycol and ethylene oxide
243. Urea via reaction of ammonia and carbon dioxide
244. Vinyl acetate via reaction of acetylene and acetic acid
245. Vinyl acetate via reaction of ethylene and acetic acid
246. Vinyl acetate via reaction of acetaldehyde and acetic anhydride
247. Vinyl chloride via dehydrochlorination of ethylene dichloride
248. Vinyl chloride via hydrochlorination of acetylene
249. Vinyl chloride via alkaline dehydrochlorination of ethylene dichloride
250. p-Xylene via isomerization of m-xylene

demand are estimated using observed values of production and observed usage patterns. Production data is taken primarily from U. S. Tariff Commission and U. S. Bureau of Mines reports[24,25] and from the Stanford Research Institute's Chemical Economics Handbook[26]. Usage patterns for most of the chemicals of interest are compiled by Brownstein[18], Hahn[5], Waddams[27,28,29], and Faith, Keyes, and Clark[20,30,31,32]. Estimated supply and demand data for the United States in 1940, 1950, 1960, and 1970, as well as a complete listing of sources, appears in Appendix 1. Capacity data is not required for the studies described below and so its collection is not considered here.

The model constructed here is a slightly revised and expanded version of the model used by this author previously[33]. The changes made are discussed in the introduction to Appendix 1.

5. EFFICIENT FEEDSTOCK CONSUMPTION

In this section we use the model described above to study the efficiency with which the industry consumes feedstocks. We seek to establish a bound on the structure of the petrochemical industry by finding the industrial structure that minimizes feedstock consumption. In addition, we look for bounds on the efficiency of feedstock consumption by the various parts of the industry, and measure the contribution of each chemical transformation toward achieving minimum feedstock consumption.

Since carbon atoms form the backbone for most petrochemical molecules, we choose to measure feedstock in terms of carbon content. Thus, if $\omega_{C,i}$ is the weight fraction carbon in feedstock i, the problem is to find the p_i, q_i, and x_j which minimize $\sum_i \omega_{C,i} p_i$, and which satisfy Equations (1)-(3). This represents an optimization problem which is easily solved using linear programming. Note that the capacity constraint, Equation (4), is not used, since this would impose the current industrial structure on the solution. By relaxing the capacity constraint a bound independent of any particular economic setting can be obtained. This bound thus represents the ultimate performance of the industry with respect to feedstock consumption. Also note that the consumption of carbon to provide process energy is not considered in the objective function, since most of the fuel used by the industry is for the generation of steam or electricity[34], and thus in the long-range is not necessarily tied to feedstock carbon.

The structure of the bounding industry found by solving the

given linear programming problem for 1970 is compared with the predominant structure of the actual industry in Figure 2. The optimal values of the p_i, q_i, and x_j are listed in Appendix 2. Each number in Figure 2 represents a commercially proven process technology listed in Table 2. The current technology and that chosen by the model are marked to identify the technology that is common and that which differs. The details of the bounding industry shown here and that reported earlier[33] differ slightly (see discussion in introduction to Appendix 1), but the conclusions to be drawn are the same. It is evident from Figure 2 that the model reproduces much of the dominant structure of the industry.

In 1970 two or more routes were available to 60 of the chemicals included in the model. The bounding industry uses 64 processes to manufacture these 60 chemicals. Of these 64 processes, 42 are dominant in the actual industry. In 16 of the 22 cases in which the actual and bounding industries differ, the processes used by the bounding industry are the subject of current interest and could someday come to predominate. For example, the production of acetic acid from methanol is already nearing predominance. Only in the manufacture of six chemicals, acetone, ethylene oxide, ethylene glycol, phenol, hydrogen cyanide, and aniline does the bounding industry use obsolete processes. In the case of ethylene oxide, the bounding industry prefers the chlorohydrin process to the direct oxidation of ethylene. This is not surprising since the chlorohydrin process offers a much higher yield. However, this is offset by the need to consume chlorine, which was not accounted for in finding the

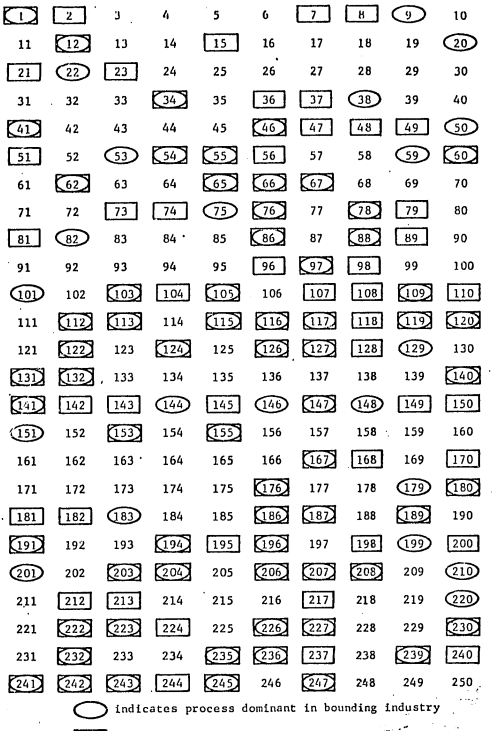

Figure 2. A comparison of the processes dominant in the actual industry in 1970 and those in the bounding industry for that year. Each number corresponds to a process listed in Table 2.

bounding industry. In the case of phenol, the bounding industry prefers the chlorobenzene route to the cumene route. The yield of phenol from chlorobenzene is higher than from cumene, but in practice this is offset by the coproduction of acetone when cumene is used. In the bounding industry, however, acetone is produced from acetic acid, which is very efficiently produced from methanol and synthesis gas. Thus there is no need for the coproduct acetone and the cumene route is rejected. Similar arguments explain the use in the bounding industry of the other obsolete processes.

The bounding industry and the actual industry are strikingly similar. This leads us to two important conclusions. First, it indicates that the petrochemical industry in its current form is a quite efficient user of its feedstocks, and in fact approaches rather closely the configuration in which feedstock consumption is mimimized. Second, it implies that an underlying driving force in the development of the petrochemical industry has been the minimization of feedstock consumption. This is particularly interesting because it suggests that industrial planning can be based, at least in its preliminary stages, on studies of raw material consumption using simple technological models of the type described above. The extent to which the minimum feedstock consumption criterion is useful in predicting the development of the industry is considered in the next section.

Associated with each constraint in a linear programming problem is a dual variable, or 'shadow price,' which is essentially the partial derivative of the objective function with respect to the

right-hand-side coefficient of the constraint. Thus, in the linear programming problem being considered here, the shadow prices associated with Equation (3) represent the marginal increase in overall feedstock consumption as the demand for a given chemical increases. By comparing the shadow prices with theoretical feedstock requirements one can determine the efficiency with which individual chemicals are produced. The theoretical carbon requirement for the manufacture of a given chemical is simply its weight fraction carbon. We define the ratio of the theoretical carbon requirement for a chemical to its shadow price as its 'feedstock efficiency index.' This represents a measure of the ultimate performance of each part of the industry when totally integrated.

Table 3 lists, for the bounding industry, the feedstock efficiency indices for the final and intermediate products modeled. Note that a chemical's feedstock efficiency index may exceed unity if it can be manufactured from byproducts of other processes. For example, in the bounding industry acetic acid is derived from carbon monoxide, which is contained in or can be manufactured from the off-gases from various processes. The feedstock efficiency indices provide insight into the strengths and weaknesses of the industry and suggest areas in which further development is possible. Thus, they may be useful parameters in a dynamic model of the industry such as that proposed by Rudd[3,4], in which the impact of new technological developments is considered.

The contribution of a chemical process toward minimizing feedstock consumption can be measured by fixing its capacity at zero and

Table 3. Feedstock efficiency indices for the bounding industries for 1940, 1950, 1960, and 1970.

Chemical	Feedstock Efficiency Indices for 1940	1950	1960	1970
Acetaldehyde	.31	.78	.90	.86
Acetic Acid	.30	1.11	1.38	1.67
Acetic Anhydride	.27	1.00	1.24	1.52
Acetone	.41	.83	.98	1.22
Acetylene	.33	.61	.64	.65
Acrolein			.83	.83
Acrylic Acid	.32	.70	1.00	1.11
Acrylonitrile	.30	.60	.64	.64
Adipic Acid	.60	.62	.63	.60
Adiponitrile	.45	.57	.58	.58
Allyl Alcohol		.70	.75	.70
Allyl Chloride		.78	.78	.78
Aniline	.86	.88	.86	.79
Benzene	1.00	1.00	1.00	.91
Benzoic Acid			.91	.91
Bisphenol A			.81	.77
Butadiene		.82	.67	.67
n-Butanol	.27	.76	.78	.82
s-Butanol	.84	.79	.65	.65
n-Butylene	1.00	.95	.77	.77
n-Butyraldehyde	.28	.85	.88	.88
Caprolactam			.49	.57
Carbon Dioxide	∞	5.40	∞	∞
Carbon Disulfide	.50	.94	.94	.94
Carbon Monoxide	4.30	2.39	4.30	4.30
Carbon Tetrachloride	.94	.94	.94	.94
Chlorobenzene	.85	.85	.85	.77
Chloroform	.97	.95	1.00	1.00
Chloroprene	.26	.48	.50	.51
Cumene			.99	.78
Crotonaldehyde	.30	.87	.85	.81

Table 3 (continued)

Chemical	Feedstock Efficiency Indices for 1940	1950	1960	1970
Cresylic Acid				.79
Cyclohexane		.91	1.00	.81
Cyclohexanol	.73	.74	.77	.73
Cyclohexanone			.77	.73
Dichlorodifluoromethane	.77	.77	.77	.77
Diethylene Glycol	∞	.65	.69	.67
Dimethyl Terephthalate			.97	.97
Dinitrotoluene			.75	.75
Epichlorohydrin		.62	.62	.62
Ethanol	.35	.85	.88	.84
Ethyl Acetate	.31	.90	1.00	1.04
Ethyl Acrylate	.31	.71	.88	.92
Ethylbenzene	.68	.94	.96	.88
Ethyl Chloride	.34	.82	.84	.80
Ethylene	.38	.91	.94	.90
Ethylene Dibromide	.37	.87	.93	.87
Ethylene Dichloride	.36	.86	.89	.86
Ethylene Glycol	.26	.83	.89	.89
Ethylene Oxide	.32	.76	.78	.75
2-Ethylhexanol	.25	.73	.76	.76
Formaldehyde	1.04	.98	1.04	1.04
Glycerine		.60	.67	.64
Hexamethylenediamine	.41	.53	.52	.52
Hydrogen Cyanide	1.16	1.02	1.16	1.16
Isobutanol	.90	18.00	14.10	14.10
Isobutylene	1.00	1.00	1.00	1.00
Isobutyraldehyde		∞	∞	∞
Isophthalic Acid			.79	.78
Isoprene			.83	.86
Isopropanol	.44	.82	.97	.97
Ketene	.27	1.00	1.24	1.54
Maleic Anhydride	.45	.42	.41	.37

Table 3 (continued)

Chemical	Feedstock Efficiency Indices for 1940	1950	1960	1970
Methanol	1.13	1.06	1.13	1.13
Methyl Chloride	1.02	.96	1.02	1.02
Methyl Chloroform			.82	.78
Methylene Dichloride	.97	.93	.97	.97
Methyl Ethyl Ketone	.78	.73	.59	.67
Methyl Isobutyl Ketone	.38	.75	.88	1.07
Methyl Methacrylate	.43	.67	.78	.87
Nitrobenzene	.91	.94	.91	.84
Peracetic Acid				.80
Perchloroethylene	.82	.82	.88	.82
Phenol	.85	.84	.85	.77
Phosgene			4.00	4.00
Phthalic Anhydride	.66	.68	.66	.71
Propylene	.54	1.00	1.00	1.00
Propylene Dichloride			1.03	1.00
Propylene Glycol	.37	.68	.71	.71
Propylene Oxide	.41	.77	.79	.79
Styrene	.63	.87	.88	.81
Terephthalic Acid			.95	.95
Toluene	1.00	1.00	1.00	1.00
Toluene Diamine			.62	.62
Toluene Diisocyanate			.65	.65
Trichloroethylene	.29	.58	.86	.82
Trichlorofluoromethane	.78	.78	.78	.78
Triethylene Glycol	∞	.58	.60	.59
Urea	1.11	1.11	1.11	1.11
Vinyl Acetate	.30	.75	.88	1.12
Vinyl Chloride	.34	.83	.78	.81
m-Xylene			.99	.99
o-Xylene		.95	.92	1.00
p-Xylene			1.00	1.00

observing the increase in optimal carbon consumption. For each process used in the bounding industry we define the ratio of the increase in optimal carbon consumption caused by its deletion to its optimal activity as its 'feedstock conservation index.' This is a measure of the overall amount of feedstock carbon saved per unit of process used. Table 4 lists the feedstock conservation indices for the processes in the bounding industry. The relative values of the feedstock conservation indices may be useful in evaluating investment alternatives in a dynamic model of the industry. For instance, of the processes dominant in the bounding industry but not in the actual industry, the processes with relatively high feedstock conservation indices may be the more likely candidates for future expansion. Of the processes dominant in both the bounding industry and the actual industry, the processes with relatively high feedstock conservation indices may be the least likely candidates for obsolescence. These ideas are explored further in the next section.

Table 4. Feedstock conservation indices for processes in the bounding industries for 1940, 1950, 1960, and 1970. The indices are given in units of thousands of pounds of carbon per unit of process. Processes for which removal from the industry is infeasible are denoted by 'nf.'

Process	Feedstock Conservation Indices for 1940	1950	1960	1970	Process	Feedstock Conservation Indices for 1940	1950	1960	1970
1			48	53	59	272	58	82	80
2		17			60				74
3	13				62			127	127
6	72				65			nf	nf
8	nf				66		329	302	281
9				51	67			9	52
11		130	84		73		138	72	
12	560	250	174	278	74	nf			
15	121				75				36
20		86	32	140	76	nf	nf	nf	nf
21	nf				78		217	146	59
22	1579	119	152	172	79	177			
23		88			81			nf	
34			47	212	82				180
37		82			86		148	148	148
38			144	193	87	nf			
40	nf				88	2	7	2	2
41				8	97	93	91	93	84
43	nf	29	1		98		5		
46			42	7	101	2		2	2
47	nf	13			103				11
48	nf				104	nf	nf	nf	
49		280			105				8
50			190	190	107	nf			
51			44		109		nf		nf
53		45		42	111	nf	155		
54		nf	nf	nf	112				46
55	nf	nf	nf	nf	113				32

Table 4 (continued)

Process	Feedstock Conservation Indices for 1940	1950	1960	1970	Process	Feedstock Conservation Indices for 1940	1950	1960	1970
114			49		177	nf			
115	nf	nf	nf	nf	179				55
116	nf	nf	nf	nf	180			nf	nf
117			122	122	181			nf	
119			nf	nf	183				76
120		68	25	60	185	nf	nf		
122		19	12	19	186			94	112
123	nf				187	906	344	216	161
124		91	65	114	188	1139			
125	42				189		266	217	103
126	nf	nf	nf	nf	190	104	62		
127	nf	nf	nf	nf	191	33	31	32	33
128	22				194	36	58	36	43
129		11		1	196			1	1
130			4		198	5	5		
131	1468	146	148	244	199			4	4
132	1459	64	38	73	200	nf	nf	36	
140	nf	nf	nf	nf	201				124
141	nf	nf	9	9	203	nf	nf	nf	nf
143	nf				204	nf	nf	372	363
144		92	100	105	206	nf	nf	nf	nf
146	530	182	102	226	207	nf	nf	nf	nf
147		nf	nf	nf	208				187
148	10	11	10	10	210			9	3
150		nf			216	358	102		
151			58	27	220	84	77	84	84
153	nf	nf	nf	nf	222			nf	nf
155	4285	496	452	527	223		50	76	nf
167	5418		1855	1683	224	nf	nf	nf	
170	214	156	18	82	226	nf	nf	nf	nf
176		728	671	243	227	nf	nf	nf	371

Table 4 (continued)

Process	Feedstock Conservation Indices for 1940	1950	1960	1970
230	nf	211	223	111
232			140	150
235			nf	nf
236			nf	nf
237		15		
238	nf			
239			11	11
241	nf	nf	nf	nf
242	nf	nf	nf	nf
243	nf	nf	nf	nf
244	nf	nf		
245				103
246			44	
247	36	7	1	2

6. MODELING INDUSTRIAL DEVELOPMENT

The model described above is essentially a static model of resource allocation. When considering the projection of industrial development the static model can be used with the criterion of minimum feedstock consumption to gain some insight into the future of the industry, as is demonstrated below. However, it is likely that a dynamic model of the industry could provide sharper perception of future developments. One approach to the formulation of a dynamic model is recursive programming[3,4,35].

In a recursive programming model a series of static models, each representing a single time period, is solved sequentially. The exogeneous parameters in the static models are interrelated by a set of recursive relations that give the parameters for a particular period in terms of parameters derived from solutions of models for previous periods. The basic premise is that, because of uncertainties about the future, industrial managers are compelled to reoptimize production plans periodically, and thus industrial development is best modeled by a progression of optimization problems. The static model constructed here is the first step in the construction of a recursive programming model of industrial development.

To account for changing industrial capacity, investment activities must be considered in the dynamic model. Some means of evaluating investment alternatives is necessary. The fact that the bounding industry minimizing feedstock consumption strongly resembles the actual industry suggests that an underlying force in the development of the industry has been the minimization of feedstock

consumption. Thus, processes appearing in the bounding industry may be more likely candidates for investment than those not appearing. This hypothesis is tested by finding the bounding industries for 1940, 1950, and 1960 and comparing them with the industry as it actually developed.

Figures 3, 4, and 5 show the bounding industries and actual industries for 1940, 1950, and 1960. The optimal values of the p_i, q_i, and x_j are listed in Appendix 2. Numbers not appearing in these figures are processes that were not yet commercialized on a large scale. The x_j for these processes are fixed at zero using capacity constraints.

In 1940 there were two or more routes available to 25 chemicals in the model. Of the 30 processes used in the bounding industry to manufacture these 25 chemicals, 17 were dominant in the actual industry. Of these 17, all retained their dominant position in the actual industry for one decade, 14 retained this position for two decades, and 11 for three decades. Another 17 processes were dominant in the actual industry but do not appear in the bounding industry. Of these 17, only 14 retained their predominant position in the actual industry for one decade, only ten retained this position for two decades, and only seven for three decades. These results are summarized in Table 5, along with the results of similar analyses for 1950 and 1960. It is evident that processes dominant in the actual industry are less likely to become obsolete and more likely to attract continued investment if they appear in the bounding industry.

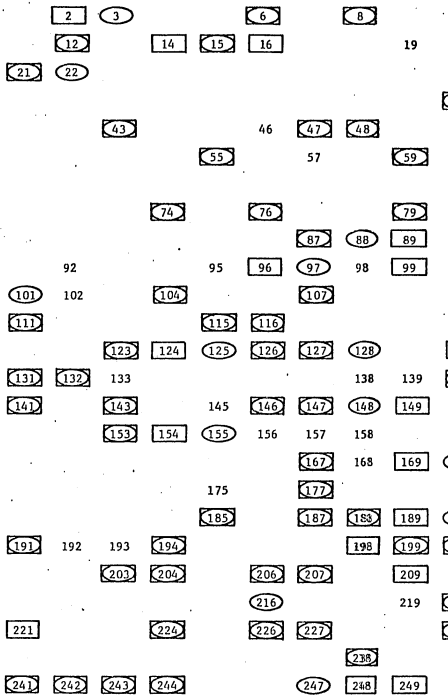

Figure 3. A comparison of the processes dominant in the actual industry in 1940 and those in the bounding industry for that year. Each number corresponds to a process listed in Table 2. Numbers not appearing represent processes not commercialized on a large scale as of 1940.

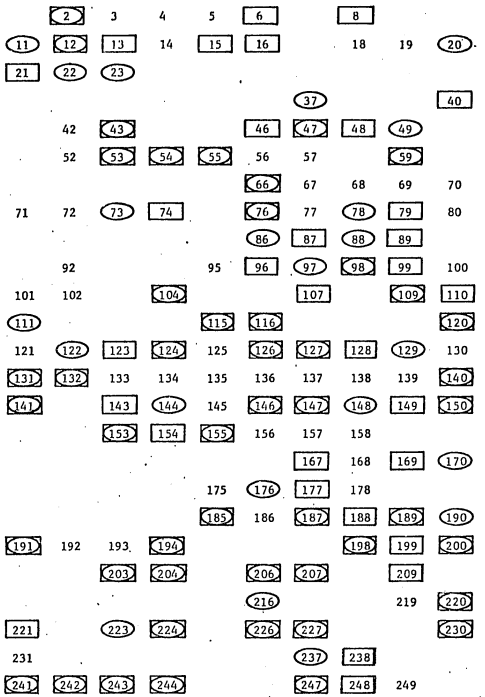

Figure 4. A comparison of the processes dominant in the actual industry in 1950 and those in the bounding industry for that year. Each number corresponds to a process listed in Table 2. Numbers not appearing represent processes not commercialized on a large scale as of 1950.

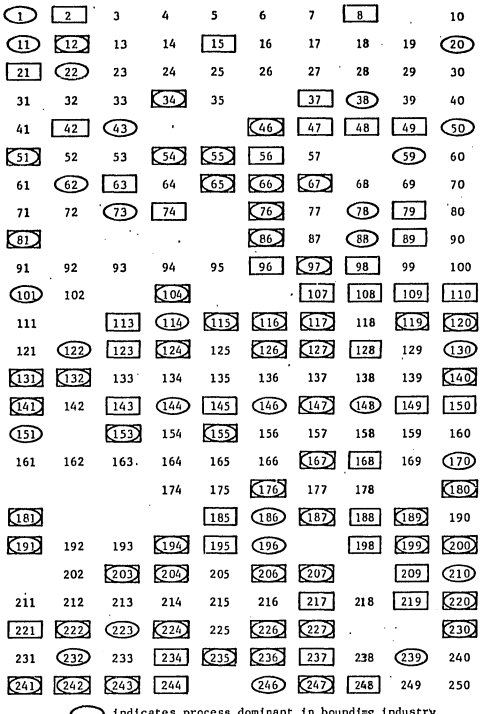

Figure 5. A comparison of the processes dominant in the actual industry in 1960 and those in the bounding industry for that year. Each number corresponds to a process listed in Table 2. Numbers not appearing represent processes not commercialized on a large scale as of 1960.

Table 5. Fraction of processes dominant in the actual industry that lose this position. Note that processes also in the bounding industry are less likely to lose the dominant position. Processes that represent the only route to a chemical are not counted.

Year	Status of processes: dominant in actual industry?	dominant in bounding industry?	Number of processes	Fraction of processes no longer dominant in actual industry as of: 1950	1960	1970
1940	yes	yes	17	0	0.18	0.35
	yes	no	17	0.18	0.41	0.59
1950	yes	yes	23		0.17	0.22
	yes	no	31		0.35	0.52
1960	yes	yes	28			0.07
	yes	no	40			0.25

In 13 cases the bounding industry for 1940 uses processes not dominant in the actual industry in 1940. Three of these processes were in a predominant position in the actual industry after one decade, four were in this position after two decades, and five after three decades. Another 22 processes do not appear in the bounding industry nor were they dominant in the actual industry. Two of these processes were in a predominant position in the actual industry after one decade, five were in this position after two decades, and four after three decades. These results are summarized in Table 6, along with the results of similar analyses for 1950 and 1960. It is evident that processes not dominant in the actual industry are more likely candidates for investment if they appear in the bounding industry.

It appears that the bounding industry found using the mimimum feedstock consumption criterion is useful in evaluating investment alternatives. Unfortunately, only conclusions concerning the relative probability of investment can be drawn from the bounding industry. The absolute probability that a process in the bounding industry will later expand to a dominant position in the actual industry is not particularly impressive. At this point it should be noted that the structure of the bounding industry is quite sensitive to changes in some input-output coefficients. Thus, in using the minimum feedstock consumption criterion to rate investment alternatives it may be wise to consider a number of nearly optimal industrial structures. The results of sensitivity analyses for the bounding industries in 1940, 1950, 1960, and 1970 are given in

Table 6. Fraction of processes not dominant in the actual industry that gain this position. Note that processes in the bounding industry are more likely to gain a dominant position. Processes that represent the only route to a chemical are not counted.

Year	Status of processes: dominant in actual industry?	dominant in bounding industry?	Number of processes	Fraction of processes dominant in actual industry as of: 1950	1960	1970
1940	no	yes	13	0.23	0.31	0.38
	no	no	22	0.09	0.23	0.18
1950	no	yes	22		0.27	0.55
	no	no	45		0.13	0.09
1960	no	yes	28			0.39
	no	no	98			0.09

Appendix 2. It should also be noted here that an alternative criterion, the minimization of total feedstock cost, has been considered, but the results are less satisfactory than those obtained using the minimum feedstock consumption criterion.

The feedstock conservation indices for the processes in the bounding industry are measures of the importance of each process in maintaining minimum feedstock consumption. As discussed above, the relative values of the feedstock conservation indices may be useful in evaluating investment alternatives in a dynamic model of industrial development. The feedstock conservation indices for the bounding industries in 1940, 1950, and 1960 are listed in Table 4.

Consider again the 30 processes used in the bounding industry for 1940 to manufacture the chemicals to which two or more routes existed. If the 17 processes that appear in the bounding industry and were dominant in the actual industry are ranked according to their feedstock conservation indices, it can be seen that, of the processes with the eight highest feedstock conservation indices, only one became obsolete after three decades, and none were obsolete after two decades. On the other hand, of the processes with the nine lowest feedstock conservation indices, five became obsolete after three decades, and three were obsolete after two decades. This is shown schematically in Figure 6; the results of similar analyses for 1950 and 1960 are shown in Figure 7 and 8. It is evident that a process dominant in the actual industry and the bounding industry is less likely to become obsolete and more likely to attract continued investment if it has a relatively high

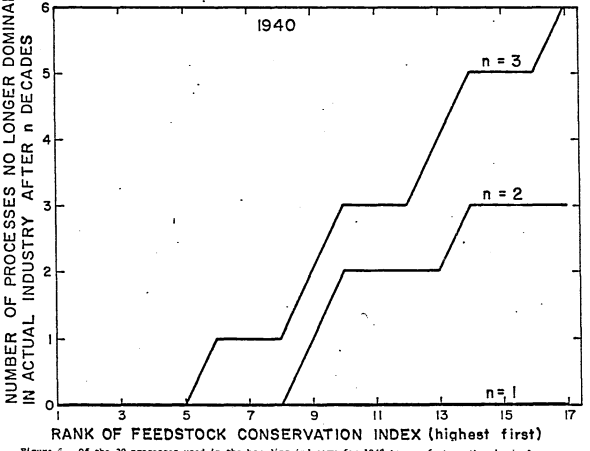

Figure 6. Of the 30 processes used in the bounding industry for 1940 to manufacture the chemicals to which two or more routes existed, 17 were also dominant in the actual industry. These 17 are ranked according to their feedstock conservation indices. The ordinate shows the number of processes with rank greater than or equal to the abscissa that were no longer dominant in the actual industry after n decades. Note that most of the upward slope occurs at low ranking feedstock conservation indices.

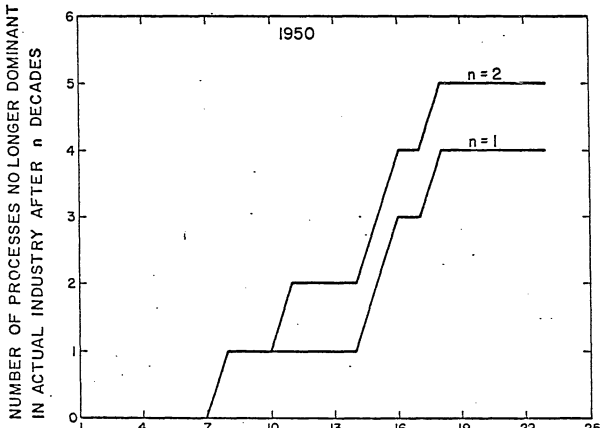

Figure 7. Of the 45 processes used in the bounding industry for 1950 to manufacture the chemicals to which two or more routes existed, 23 were also dominant in the actual industry. These 23 are ranked according to their feedstock conservation indices. The ordinate shows the number of processes with rank greater than or equal to the abscissa that were no longer dominant in the actual industry after n decades. Note that most of the upward slope occurs at low ranking feedstock conservation indices.

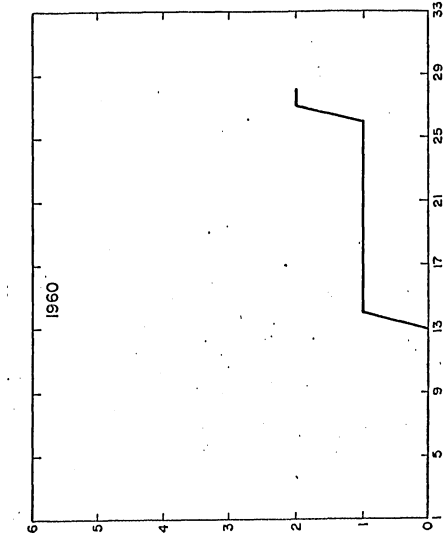

Figure 8. Of the 56 processes used in the bounding industry for 1960 to manufacture the chemicals considered, two processes existed that were also dominant in the actual industry. These 28 are ranked according to their feedstock conservation indices. The ordinate shows the number of these processes with rank greater than or equal to the abscissa that were no longer dominant in the actual industry after one decade. Note that most of the upward slope occurs at low ranking feedstock conservation indices.

feedstock conservation index.

If the 13 processes that appear in the bounding industry for 1940 but were not dominant in the actual industry are ranked according to their feedstock conservation indices, it can be seen that, of the processes with the six highest feedstock conservation indices, two reached a dominant position in the actual industry after three decades. However, three of the processes with the seven lowest feedstock conservation indices also reached this position after three decades. This is shown graphically in Figure 9; the results of similar analyses for 1950 and 1960 are shown in Figures 10 and 11. There appears to be little correlation between the relative values of the feedstock conservation indices and the relative probability that a process in the bounding industry will expand to a position of dominance in the actual industry.

It appears that the feedstock conservation indices are useful in assessing the relative probability that a process dominant in both the bounding industry and the actual industry will remain an attractive investment alternative. However, for processes in the bounding industry not dominant in the actual industry no conclusions concerning the relative probability of expansion can be drawn from the feedstock conservation indices.

Also needed in a model of industrial development are indicators that point to the need for new technology or to a change in patterns of supply and demand. The feedstock efficiency indices are measures of the relative strengths and weaknesses of the parts of the industry with respect to feedstock consumption, and thus may provide some of

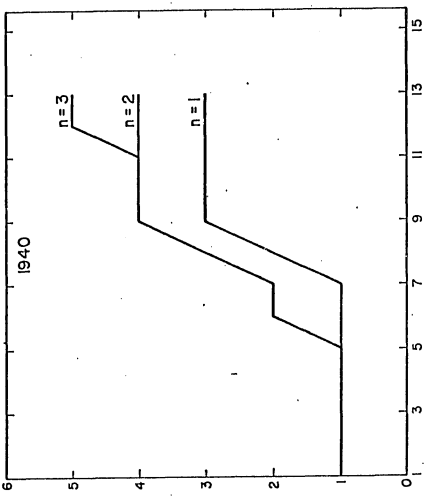

Figure 9. Of the 30 processes used in the bounding industry for 1940 to manufacture the chemicals to which two or more routes existed, 13 were not dominant in the actual industry. These 13 are ranked according to their feedstock conservation indices. The ordinate shows the number of processes with rank greater than or equal to the abscissa that became dominant in the actual industry after n decades. Note that most of the upward slope does not occur at high ranking feedstock conservation indices.

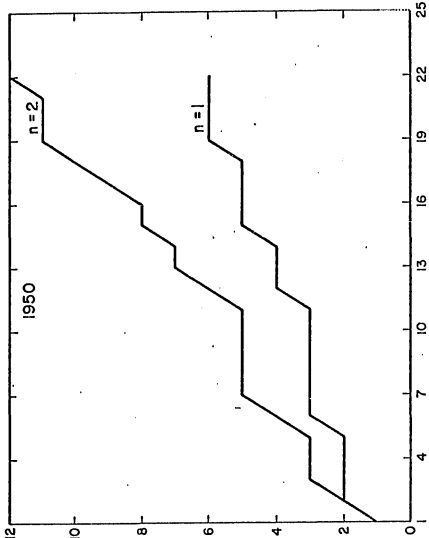

Figure 10. Of the 45 processes used in the boundion industry for 1950 to manufacture the chemicals to which two or more routes existed, 22 were not dominant in the actual industry. These 22 are ranked according to their feedstock conservation indices. The ordinate shows the number of processes with rank greater than or equal to the abscissa that became dominant in the actual industry after n decades. Note that most of the upward slope does not occur at high ranking feedstock conservation indices.

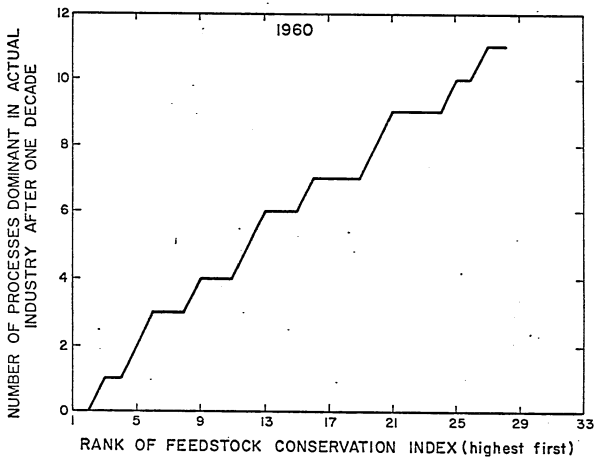

Figure 11. Of the 56 processes used in the bounding industry for 1960 to manufacture the chemicals to which two or more routes existed, 28 were not dominant in the actual industry. These 28 are ranked according to their feedstock conservation indices. The ordinate shows the number of processes with rank greater than or equal to the abscissa that became dominant in the actual industry after one decade. Note that most of the upward slope does not occur at high ranking feedstock conservation indices.

the necessary indicators. For instance, several very low feedstock efficiency indices may indicate the presence of a bottleneck in the bounding industry, which would then have to be resolved by the development of new technology, the expansion of old technology, or the alteration of supply and demand patterns. The feedstock efficiency indices for the bounding industries in 1940, 1950, and 1960 are listed in Table 3.

The feedstock efficiency indices for most chemicals do not differ considerably from 1950 to 1970. However, in the bounding industry for 1940, the feedstock efficiency indices for ethylene, acetylene, and their derivatives are substantially lower than the corresponding indices for later decades. Since the technology used to manufacture ethylene and acetylene in the bounding industries for 1950, 1960, and 1970 was available in 1940, the increase in their feedstock efficiency indices from 1940 to 1950 is not due to new technological developments. This suggests that a bottleneck in the 1940 bounding industry prevents the most efficient network of processes from being used. Because capacity constraints are not used (except to fix the x_j for yet to be commercialized processes at zero), the bottleneck must be in the supply of feedstocks to the industry. By perturbing the supply constraints it can be shown that the bottleneck is in the supply of ethane, propane, and butane. If the supply of any of these three feedstocks is increased sufficiently, the feedstock efficiency indices for ethylene, acetylene, and their derivatives increase to roughly the levels observed in the bounding industries for later decades. Since the structure of the actual

industry tends to approach the structure of the bounding industry, a bottleneck in the bounding industry implies that such a bottleneck may later develop in the actual industry, and points to the need for a new technological development or a change in the pattern of feedstock supply. In fact, relative to other feedstocks, the use of ethane, propane, and butane has increased substantially since 1940. In this case at least, the feedstock efficiency indices seem to be a useful indicator of an impending shift in the pattern of feedstock supply.

In summary, the static model constructed above can be used as part of a recursive programming model of industrial development in the petrochemical industry. Moreover, when used with the minimum feedstock consumption criterion the model is useful in evaluating investment alternatives, and may be useful in pointing to new technological developments or changes in patterns of supply and demand.

7. PERTURBATIONS IN SUPPLY AND DEMAND

In this section we use the model to study the effects of perturbations in present patterns of supply and demand. As shown above, the actual structure of the industry tends to approach the structure of the bounding industry that minimizes feedstock consumption. Thus, by using the model to determine the effect of perturbations on the bounding industry, it is possible to gain some insight into what may occur within the actual industry when so perturbed. Such insight provides a point of departure for long-range planning by the industry.

Essentially all of the industry's primary feedstocks are now derived from petroleum and natural gas. However, the possibility of natural gas shortages may cause the industry to turn away from natural gas as a feedstock supplier. For instance, it has been predicted for several years that liquid petroleum fractions such as naphtha or gas oil would replace feedstocks derived from natural gas in the production of ethylene and other chemicals. Another more recent suggestion is that synthesis gas and methane produced from coal would replace natural-gas-derived feedstocks in some applications. A third possibility is that ethanol produced by fermentation could become an important feedstock. We use the model to consider these three scenarios.

Consider a scenario in which natural gas is completely eliminated as a feedstock source and an unlimited supply of naphtha and gas oil is available as a replacement. When the supply constraints are perturbed accordingly, changes are observed in the

structure of the bounding industry, as shown in Figure 12. The resultant changes in the feedstock efficiency indices are indicated in Table 7 for 25 selected chemicals.

The most important structural change shown in Figure 12 is the switch to naphtha as the feedstock for ethylene manufacture. Other structural changes can be interpreted in terms of the increased production of byproducts (such as propylene, n-butylenes, butadiene, isobutylene, isoprene, benzene, and toluene) that results when ethylene is produced from naphtha. For example, processes using isobutylene to produce methyl methacrylate, butadiene to produce adiponitrile, n-butylenes to produce maleic anhydride, and propylene and toluene to produce cresylic acid and acetone enter the perturbed industry. All the isobutylene, acetylene, and isoprene, nearly 60 percent of the butadiene, over 40 percent of the benzene, and essentially all of the methane are produced as byproducts of ethylene manufacture; in fact isoprene is produced in surplus. The feedstock efficiency indices listed in Table 7 indicate that for ethylene and its derivatives the naphtha-based industry is somewhat less efficient in terms of carbon consumption than the natural-gas-based industry. On the other hand, some chemicals produced from ethylene byproducts can be manufactured with less feedstock consumption in the naphtha-based industry.

Consider next a scenario in which natural gas is completely eliminated as a feedstock source and an unlimited supply of coal-derived methane, hydrogen, and carbon monoxide is available as a replacement. The structural changes observed when the industry is

1	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48	49	50
51	52	53	54	55	56	57	58	59	60
61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80
81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100
101	102	103	104	105	106	107	108	109	110
111	112	113	114	115	116	117	118	119	120
121	122	123	124	125	126	127	128	129	130
131	132	133	134	135	136	137	138	139	140
141	142	143	144	145	146	147	148	149	150
151	152	153	154	155	156	157	158	159	160
161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180
181	182	183	184	185	186	187	188	189	190
191	192	193	194	195	196	197	198	199	200
201	202	203	204	205	206	207	208	209	210
211	212	213	214	215	216	217	218	219	220
221	222	223	224	225	226	227	228	229	230
231	232	233	234	235	236	237	238	239	240
241	242	243	244	245	246	247	248	249	250

indicates process dominant in bounding industry

indicates process dominant in perturbed industry

Figure 12. A comparison of the bounding industry for 1970 and the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and naphtha and gas oil are made available as a replacement. Each number corresponds to a process listed in Table 2.

Table 7. Feedstock efficiency indices for five cases: (a) the bounding industry that minimizes the consumption of feedstock carbon, (b) the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and naphtha and gas oil are available as a replacement, (c) the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and coal-derived methane, hydrogen, and carbon monoxide are available as a replacement, (d) the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and fermentation-derived ethanol is available as a replacement, (e) the perturbation of the bounding industry in which an unlimited supply of hydrogen derived from water is available.

Chemical	Feedstock Efficiency Indices for Case: (a)	(b)	(c)	(d)	(e)
Acetaldehyde	.86	.82	.55	1.00	.82
Acetic Acid	1.67	1.21	1.21	1.21	.87
Acetone	1.22	.97	1.09	.94	.94
Acetylene	.65	.67	.58	.45	.81
Acrylic Acid	1.11	.81	.93	.79	.75
Acrylonitrile	.64	.62	.72	.61	.73
Adiponitrile	.58	.59	.66	.55	.68
Aniline	.79	.84	.92	.80	.93
Butadiene	.67	.90	.57	.75	.62
n-Butyraldehyde	.88	.83	.82	.85	.75
Caprolactam	.57	.62	.75	.65	.90
Carbon Tetrachloride	.94	.85	.99	.82	.95
Chloroprene	.51	.70	.45	.58	.64
Ethanol	.84	.80	.45	1.00	.80
Ethylene	.90	.86	.49	.96	.87
Ethylene Oxide	.75	.71	.40	.79	.71
Isoprene	.86	∞	.88	.80	.81
Maleic Anhydride	.37	.45	.46	.39	.51
Methyl Ethyl Ketone	.67	.87	.59	.73	.65
Methyl Methacrylate	.87	.68	.81	.67	.67
Phenol	.77	.86	.78	.82	.79
Phthalic Anhydride	.71	.71	.75	.71	.71
Propylene Oxide	.79	.79	.79	.78	.79
Vinyl Acetate	1.12	.97	.73	1.02	.84
Vinyl Chloride	.81	.78	.54	.86	.78

so perturbed are shown in Figure 13. The feedstock efficiency indices for the perturbed industry are shown in Table 7 for 25 selected chemicals.

The most significant change indicated in Figure 13 is the increased use of acetylene, which is used to produce all of the vinyl chloride, vinyl acetate, acetaldehyde, chloroprene, and trichloroethylene, nearly a third of the ethylene, and nearly a quarter of the butadiene. Although the supply of carbon monoxide to the perturbed industry is unbounded, all of the carbon monoxide used is produced as a byproduct of the manufacture of acetylene from methane using the partial oxidation process. The feedstock efficiency indices listed in Table 7 show that ethylene and its derivatives are manufactured quite inefficiently. This suggests the need for developing new process technology, in particular technology which would permit the conversion of synthesis gas directly to ethylene or ethanol. This has been accomplished in the laboratory, but there have been no commercial developments other than a small plant operated briefly in 1956 that converted synthesis gas to ethanol and acetaldehyde[36]. A technological perturbation in which ethylene is derived from synthesis gas is considered in the next section.

Now consider a scenario in which natural gas is completely eliminated as a feedstock source and an unlimited supply of fermentation-derived ethanol is available as a replacement. The structural changes observed when the industry is so perturbed are shown in Figure 14. Table 7 shows the feedstock efficiency indices

(1)	2	3	4	5	[6]	7	8	[9]	10
11	[12]	13	14	15	16	17	18	19	[20]
21	[22]	[23]	24	25	26	27	28	29	30
31	32	33	[34]	35	36	37	[38]	39	40
[41]	42	43	44	45	(46)	[47]	[48]	49	(50)
[51]	52	(53)	(54)	[55]	56	57	58	(59)	[60]
61	[62]	63	64	[65]	[66]	(67)	68	69	[70]
71	72	73	74	[75]	[76]	77	[78]	79	80
81	(82)	[83]	84	85	[86]	87	(88)	89	90
91	[92]	93	94	95	96	[97]	98	99	100
[101]	102	(103)	[104]	(105)	[106]	107	108	[109]	110
111	[112]	(113)	114	[115]	[116]	[117]	118	[119]	[120]
121	[122]	123	[124]	125	[126]	[127]	128	[129]	130
(131)	(132)	133	134	[135]	136	137	[138]	139	[140]
[141]	142	143	[144]	145	[146]	[147]	[148]	149	150
[151]	152	[153]	154	(155)	156	157	158	159	160
161	162	163	164	165	166	(167)	168	169	[170]
171	172	173	174	175	[176]	177	178	[179]	[180]
181	182	[183]	184	185	[186]	[187]	188	[189]	190
[191]	192	193	[194]	195	[196]	197	198	[199]	200
[201]	202	[203]	[204]	205	[206]	[207]	(208)	209	(210)
211	212	213	214	215	[216]	217	218	219	[220]
221	[222]	[223]	[224]	225	[226]	[227]	228	229	[230]
231	[232]	233	234	[235]	[236]	[237]	238	(239)	240
[241]	[242]	[243]	[244]	(245)	246	(247)	[248]	249	250

( ) indicates process dominant in bounding industry

[ ] indicates process dominant in perturbed industry

Figure 13. A comparison of the bounding industry for 1970 and the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and coal-derived methane, hydrogen, and carbon monoxide are made available as a replacement. Each number corresponds to a process listed in Table 2.

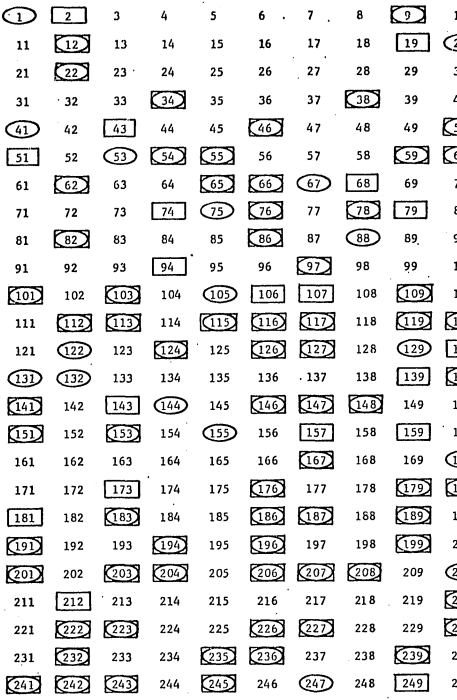

Figure 14. A comparison of the bounding industry for 1970 and the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and fermentation-derived ethanol is made available as a replacement. Each number corresponds to a process listed in Table 2.

for 25 chemicals in the perturbed industry.

The major change shown in Figure 14 is that in the perturbed industry ethylene is derived from ethanol rather than vice versa. Ethanol is also used to produce all the acetaldehyde, acetone, and ethyl chloride and 60 percent of the butadiene. The feedstock efficiency indices for the ethanol-based industry reveal no major weaknesses compared to the natural-gas-based industry. Thus, ethanol could be an attractive feedstock should the large-scale production of inexpensive ethanol from fermentation become a reality. Although this scenario and the two considered above are extreme cases, they serve to demonstrate the applicability of the model to problems of long-range industrial development.

Today nearly all hydrogen used in the petrochemical industry is derived from methane or other hydrocarbons. However, there is considerable interest in the development of processes for cheaply and efficiently producing hydrogen from water. As a final example of a perturbation in supply, consider the case in which there is available an unlimited supply of hydrogen derived from water. Figure 15 shows the structural changes occurring in the industry when so perturbed. The feedstock efficiency indices for 25 chemicals in the perturbed industry are listed in Table 7.

As shown in Figure 15, a variety of changes occur in the perturbed industry. Most can be explained by considering the production of carbon monoxide. Hydrogen and carbon monoxide are usually coproduced in the reforming of methane; however the coproduced hydrogen has no value in the perturbed industry. Thus processes

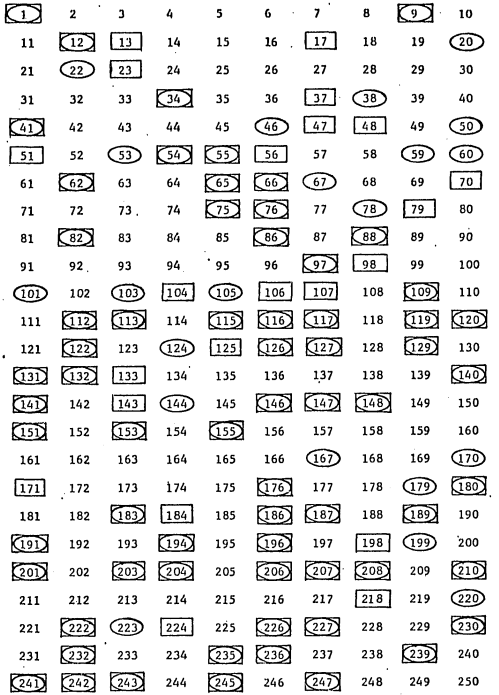

Figure 15. A comparison of the bounding industry for 1970 and the perturbation of the bounding industry in which an unlimited supply of hydrogen derived from water is made available. Each number corresponds to a process listed in Table 2.

used in the bounding industry to make acetone, acrylic acid, n-butyraldehyde, chloroform, cresylic acid, ethyl acetate, ethylene glycol, and methylene dichloride from carbon monoxide or its derivatives do not appear in the perturbed industry, as there would be no market for the hydrogen coproduced with the carbon monoxide required. This is borne out by the fact that relative to the bounding industry the feedstock efficiency indices for carbon monoxide derivatives in the perturbed industry are considerably lower. Also note that because carbon monoxide is a byproduct when acetylene is produced from methane by partial oxidation, acetylene becomes a more attractive feedstock and is used in the perturbed industry to produce all the acrylic acid and chloroprene, 70 percent of the isoprene, and 20 percent of the butadiene.

We now use the model to consider two perturbations in the present pattern of demand for petrochemicals: the reduction in demand for vinyl chloride due to restrictions on the use of polyvinyl chloride in food-related applications, and the reduction in demand for chlorofluoromethanes due to restrictions on its use as an aerosol propellant.

The discovery that vinyl chloride is a carcinogen has prompted the proposal of regulations that would ban the use of polyvinyl chloride (PVC) in food packages such as bottles and blister packages. It is not likely that PVC will be replaced in these applications by a single plastic; instead a variety of plastics, including polyethylene terephthalate, oriented polypropylene, polycarbonate, and acrylonitrile copolymers, will compete to replace PVC. A number of

scenarios were considered in which PVC was replaced by another plastic or combination of plastics. In each case no structural changes in the bounding industry were observed. This is not surprising since the use of PVC in the food packages affected by the proposed ban accounts for less than one percent of the total demand for vinyl chloride[37]. Even if PVC were banned from all food-related use, including water pipes, the demand for vinyl chloride would be reduced by only about 15 percent. Perturbations of this magnitude still produce no structural changes in the bounding industry.

There is evidence suggesting that the release of chlorofluorocarbons into the atmosphere could be reducing the concentration of ozone in the stratosphere, thereby increasing the amount of ultraviolet radiation reaching the earth's surface. Since this would result in an increased incidence of skin cancer, there are proposals that would ban the use of chlorofluorocarbons in aerosol propellants. This application accounts for about half the demand for chlorofluoromethanes. Possible replacements in aerosol formulations are n-butane, isobutane, and carbon dioxide. However, n-butane and isobutane are flammable and thus not suitable for household use, and carbon dioxide aerosols are subject to clogging. Thus, at least for the near future, it seems likely that if chlorofluoromethanes were banned, new propellants would be avoided entirely, and finger-powered spray pumps would be used. Imposing this perturbation on the bounding industry reveals no structural changes, but does show that nearly all the carbon tetrachloride required by the perturbed

industry is produced as a byproduct of perchloroethylene manufacture.

8. PERTURBATIONS IN TECHNOLOGY

As shown above, processes not dominant in the actual industry are more likely candidates for investment if they appear in the bounding industry that minimizes feedstock consumption. Thus, by perturbing the industry with the introduction of a new process and observing whether the new process enters the bounding industry, the relative probability that the new process will be important in the actual industry can be estimated. Also, by parametrically varying the yield of the new process and observing the yield at which the new process enters the bounding industry, an estimate of the yield required to make this process attractive can be obtained. The information so obtained could be useful in models of industrial development that account for the introduction of new technology.

Consider the addition to the model of four processes recently developed but not yet commercialized. These processes produce vinyl chloride from ethane, acetic acid from n-butylenes, ethylene glycol from ethylene, and ethylene glycol from synthesis gas. Table 8 compares the reported yields for these processes with the yields required to make the processes appear in the bounding industry. These results suggest that the vinyl chloride and acetic acid processes are less likely to become important in the industry than either of the ethylene glycol processes. In fact, there has apparently been little commercial development of the vinyl chloride or acetic acid processes, but a large plant using the ethylene acetoxylation process is due on stream in 1977[38] and the ethylene glycol from synthesis gas process is well into the pilot plant

Table 8. Comparison of reported yields for four new processes and the yields required to make these processes appear in the bounding industry.

Process	Required Molar Yield	Reported Molar Yield	Reference for Reported Molar Yield
Vinyl chloride via chlorination of ethane	95%	80%	[18]
Acetic acid via oxidation of n-butylenes	>100%	60%	[29]
Ethylene glycol via acetoxylation of ethylene	95%	95%	[38]
Ethylene glycol via reaction of hydrogen and carbon monoxide	45%[1]	50%	[38]

[1]assuming yields on both reactants are the same, and assuming byproduct credits per pound of ethylene glycol as 0.1 lb propylene glycol, 0.1 lb glycerin, and 0.1 lb methanol (this is probably a conservative estimate of byproduct credits)

stage[39].

It was shown above that, in the perturbation of the bounding industry for which natural gas is eliminated as a source of feedstocks and coal-derived methane, hydrogen, and carbon monoxide are made available as replacements, the feedstock efficiency indices for ethylene and its derivatives are markedly lower than in the unperturbed industry. This suggests the need for developing the technology to derive ethylene or ethanol from synthesis gas. The model can be used to estimate the yields required to make these processes attractive. Adding these processes to the model shows that, even without byproduct credits (which probably would be considerable), a 40 percent molar yield of ethylene from carbon monoxide and a 35 percent molar yield of ethanol from carbon monoxide is sufficient to make these processes appear in the optimal industry for the supply perturbation considered. This type of information might be used together with estimates of the yield potential of the yet to be developed processes, in forecasting new technological developments under various scenarios of supply and demand, and may provide the industry points of departure for the planning of long-range research goals.

9. TECHNOLOGY TRANSFER

The basic problem of technology transfer is how to best match existing technology to social and economic problems needing solutions. We consider here the transfer of petrochemical technology from developed to developing economies. In this case, the problem is how to identify the network of processes best suited to the needs of the developing economy. Given a suitable objective function, as well as the appropriate supply and demand data, the model constructed above can be used for this purpose.

As an example, consider the rapidly developing Mexican petrochemical industry. Estimated demand data, based on observed levels of production and importation for Mexico in 1970[40,41,42], is listed in Appendix 3. If the minimum feedstock consumption criterion is used, and no capacity or supply constraints are imposed, the bounding industry for Mexico is that indicated in Figure 16. By not using supply constraints one can determine the optimal supply pattern, and, if possible, resources can be developed accordingly. In most cases the processes used in the bounding industry for Mexico also appear in the bounding industry for the United States. The most interesting difference is that the Mexican bounding industry uses ethylene-based processes to manufacture acrylonitrile, perchloroethylene, and 2-ethylhexanol, chemicals produced from propylene or propane in the bounding industry for the United States. This occurs because in finding the bounding industry for Mexico no constraint was placed on the supply of ethane, and thus all ethylene could be derived via the most efficient route, the pyrolysis of ethane (in

(1)	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	(20)
21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40
41	42	(43)	44	45	46	47	48	49	50
51	52	53	54	(55)	56	57	58	(59)	60
61	62	63	64	65	(66)	67	68	69	70
71	72	73	74	75	76	77	78	79	80
81	(82)	83	84	85	86	87	88	89	90
91	92	93	94	95	96	(97)	98	99	100
(101)	102	103	104	105	106	(107)	108	(109)	110
111	(112)	(113)	114	115	116	(117)	118	(119)	120
121	(122)	123	124	125	126	(127)	128	129	(130)
(131)	132	133	134	135	136	137	138	139	(140)
(141)	142	143	(144)	145	(146)	(147)	(148)	149	150
151	152	153	154	(155)	156	157	158	159	160
161	162	163	164	165	166	(167)	168	169	(170)
171	172	173	174	175	176	177	178	179	180
181	182	183	184	185	186	187	(188)	189	(190)
(191)	192	193	(194)	195	(196)	197	198	(199)	200
201	202	203	(204)	205	(206)	(207)	(208)	209	210
211	(212)	213	214	215	216	217	218	219	(220)
221	(222)	(223)	224	225	(226)	(227)	228	229	(230)
231	(232)	233	234	(235)	(236)	237	238	(239)	240
241	242	(243)	244	(245)	(246)	247	248	(249)	250

( ) indicates process dominant in bounding industry for Mexico (1970)

Figure 16. The bounding industry for Mexico (1970). Each number corresponds to a process listed in Table 2.

fact, nearly all ethylene produced in Mexico is produced from ethane). In the bounding industry for the United States, propane must also be pyrolyzed to ethylene. Because this process is less efficient in producing ethylene and produces substantial quantities of propylene, ethylene is less attractive and propylene more attractive as a feedstock in the bounding industry for the United States.

The optimal structure shown in Figure 16 provides planners a blueprint for the long-range development of the industry, presuming efficient resource use is the desired objective. Other objectives such as the minimization of imports or the minimization of capital costs may also be appropriate. A complete discussion of the applications of these concepts in planning the Mexican industry will be reported soon[43].

10. CONCLUDING REMARKS

The ultimate goal of the study of which this is a part is the construction of a dynamic model of the industry able to reproduce observed industrial behavior. Such a model could then be used to project future industrial development for a variety of economic and technological scenarios. This information may be helpful to policymakers charged with insuring the health of the petrochemical industry in this and other well-developed economies. It may also be useful in planning for the transfer of technology from developed to developing economies. The static model constructed here is the first step toward this ultimate goal.

APPENDIX 1

In this appendix the uses and manufacturing methods for each chemical in the model are discussed briefly, the values of the input-output coefficients for each process in the model are tabulated, and supply and demand data are given, as are the references used in estimating these parameters. When appropriate, the reactions involved in each process are listed, as are the theoretical values of the input-output coefficients (the values that would be observed at 100 percent molar yield). In many cases typical reaction conditions are also given. Since the exogeneous demand values reflect only the demand for a chemical as a final output, they are the d_i values used in the model. Total production data, which also reflects the demand for a chemical as an intermediate, is also given in most cases.

The model used here is a slightly revised and expanded version of the model used earlier[33]. The expanded model better reflects the flexibility of the industry with respect to feedstocks. For instance, in the original model, only methane and naphtha were considered as raw materials for hydrogen manufacture; in the expanded model, however, methane, ethane, propane, butane, naphtha, gas oil, and fuel oil are all available for hydrogen production. The expanded model also offers a more complete accounting of the oldest and the newest chemical technology. In three cases, involving processes for manufacturing acetic anhydride, ethyl acetate, and vinyl acetate, errors in the input-output coefficients (that in

effect raised the yields for these three processes by a factor of two) were corrected. Despite the revision, the conclusions reached in [33] are unchanged.

Acetaldehyde

Acetaldehyde is used almost entirely for the synthesis of other chemicals, primarily acetic acid, acetic anhydride, n-butanol, and 2-ethylhexanol. However, other routes to these chemicals are beginning to predominate; thus the future of acetaldehyde as a large-volume chemical intermediate is somewhat clouded.

Today most acetaldehyde is produced by the catalytic liquid-phase oxidation of ethylene, the so-called Wacker process. This process began commercial operation in 1960 and rapidly assumed a dominant position. As of 1970 a substantial fraction of the acetaldehyde produced was still derived from ethanol, which has been an important feedstock for acetaldehyde manufacture since before 1930. Ethanol can be converted to acetaldehyde by either dehydrogenation or oxidation, though the former is the usual procedure. When oxidation is used, operating conditions may be so adjusted that dehydrogenation occurs simultaneously and the exothermic heat of oxidation is balanced by the endothermic heat of dehydrogenation. Since 1945 some acetaldehyde has been manufactured by the oxidation of propane or butane. Substantial quantities of other chemicals are produced in this process; of these, formaldehyde, methanol, and acetone are the most important. The hydration of acetylene was once a major route to acetaldehyde, but by the early-1960s was no longer used in the United States.

Manufacturing Processes

1. Acetaldehyde via oxidation of ethylene

Reaction: $CH_2{=}CH_2 + \frac{1}{2} O_2 \rightarrow CH_3CHO$

Comments: Reaction occurs in liquid phase at about 100 C and 10 atm. with a palladium chloride catalyst promoted by cuprous chloride.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.64	-.67	[5],[17],[18],[20]
Acetaldehyde	1.00	1.00	

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2. Acetaldehyde via dehydrogenation of ethanol

Reaction: $CH_3CH_2OH \rightarrow CH_3CHO + H_2$

Comments: Reaction occurs in vapor phase at about 270-300 C over catalyst of chromium oxide and activated copper.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-1.05	-1.2	[17],[20]
Acetaldehyde	1.00	1.00	
Hydrogen	.05	.04	[5]

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3. Acetaldehdye via oxidation of ethanol

Reaction: $CH_3CH_2OH + \frac{1}{2} O_2 \rightarrow CH_3CHO + H_2O$

Comments: Reaction occurs in vapor phase at about 450 C and 3 atm. over a silver catalyst. The process may be operated so that dehydrogenation occurs simultaneously and the exothermic heat of oxidation balances the endothermic heat of dehydrogenation.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-1.05	-1.15	[17],[20]
Acetaldehyde	1.00	1.00	

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4. Acetaldehyde via oxidation of propane

Reaction (not balanced): $C_3H_8 + O_2 \rightarrow CH_3CHO + HCHO + CH_3OH + CH_3COCH_3 +$ other byproducts

Comments: Product distribution is variable.

Input-Output Coefficients:	Model	References
Propane	-3.5	estimate of yields based on
Acetaldehyde	1.00	yields for acetaldehyde from
Formaldehyde	1.06	n-butane oxidation
Methanol	.65	
Acetone	.13	

5. Acetaldehyde via oxidation of n-butane

Reaction (not balanced): $C_4H_{10} + O_2 \rightarrow CH_3CHO + HCHO + CH_3OH + CH_3COCH_3$ + other byproducts

Comments: Product distribution is variable.

Input-Output Coefficients:	Model	References
n-Butane	-3.23	[20]
Acetaldehyde	1.00	
Formaldehyde	1.06	
Methanol	.65	
Acetone	.13	

6. Acetaldehyde via hydration of acetylene

Reaction: $CH{\equiv}CH + H_2O \rightarrow CH_3CHO$

Comments: Reaction occurs at about 70-100 C and 1 atm. in a solution of mercurous sulfate in sulfuric acid.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.59	-.62	[19],[20]
Acetaldehyde	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	210	600	930	1610	[20],[24], [30],[31]
Exogeneous Demand	10	25	100	300	[18-20], [27-31]

Acetic Acid

Acetic acid is used primarily for the manufacture of acetic anhydride, vinyl acetate, and various acetate esters.

Most acetic acid plants built today employ Monsanto's low pressure process, first commercialized in 1970, for the carbonylation of methanol. Another process for the carbonylation of methanol is operated, but at lower yields and much higher pressure. The oldest commercial route to acetic acid, the oxidation of acetaldehyde, is still important, accounting for about one-third of acetic acid production of 1973. Another important route to acetic acid is the oxidation of butane. First commercialized in the mid-1950s, this process began to rival the acetaldehyde route by the early-1960s. Naphtha can also be oxidized to acetic acid; though this process is practiced on a large scale in Europe, it is not used in the United States. Recently there has been interest in the oxidation of butylenes to acetic acid, but this has yet to reach commercialization. Two traditional sources of acetic acid, the fermentation of ethanol and the destructive distillation of wood, lost their significance many years ago, though the former is still used.

Manufacturing Processes

7. Acetic acid via oxidation of n-butane

Reaction (not balanced): $C_4H_{10} + O_2 \rightarrow CH_3COOH +$ various byproducts

Comments: Reaction occurs in liquid phase at about 150-225 C and 800 psi with cobalt acetate catalyst.

Input-Output Coefficients:	Model	References
n-Butane	-.85	[44]
Acetic Acid	1.00	

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8. Acetic acid via oxidation of acetaldehyde

Reaction: $CH_3CHO + \frac{1}{2} O_2 \rightarrow CH_3COOH$

Comments: Reaction occurs in liquid phase at about 40-65 C and 5 atm. with manganous or cobalt acetate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-.73	-.77	[17],[19],[44]
Acetic Acid	1.00	1.00	

---

9. Acetic acid via carbonylation of methanol (low pressure)

Reaction: $CH_3OH + CO \rightarrow CH_3COOH$

Comments: Reaction occurs at about 175-245 C and 15 atm. or less with iodide-promoted rhodium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methanol	-.53	-.54	[44]
Carbon Monoxide	-.47	-.52	[44]
Acetic Acid	1.00	1.00	

---

10. Acetic acid via oxidation of naphtha

Reaction (not balanced): naphtha + $O_2 \rightarrow CH_3COOH$ + various byproducts

Comments: Reaction occurs in liquid phase at about 200 C and 750 psi with manganous acetate catalyst.

Input-Output Coefficients:	Model	References
Naphtha	-1.2	[44]
Acetic Acid	1.00	

---

11. Acetic acid via carbonylation of methanol (high pressure)

Reaction: $CH_3OH + CO \rightarrow CH_3COOH$

Comments: Reaction occurs at about 210-250 C and 7000-10000 psi with cobaltous iodide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methanol	-.53	-.61	[5],[44-46]
Carbon Monoxide	-.47	-.80	[44-46]
Acetic Acid	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production (synthetic)	185	440	740	1930	[24],[26]
Exogeneous Demand	50	150	200	400	[5],[20], [29-31]

Acetic Anhydride

Most acetic anhydride is used to manufacture cellulose acetate. Other uses include the production of aspirin and vinyl acetate.

The usual feedstocks for acetic anhydride production are ketene and acetic acid. The ketene may be obtained from either acetone or acetic acid, the latter being the usual source today. Acetic anhydride can also be produced by the oxidation of acetaldehyde and by the reaction of acetylene and acetic acid. Of these, the former retains some importance, but the latter is definitely obsolete.

Manufacturing Processes

12. Acetic anhydride via reaction of ketene and acetic acid

Reaction: $CH_2{=}CO + CH_3COOH \rightarrow (CH_3CO)_2O$

Comments: Reaction can occur in vapor phase or in aqueous solution.

Input-Output Coefficients:	Theoretical	Model	References
Acetic Acid	-.59	-.62	[5],[17]
Ketene	-.41	-.43	
Acetic Anhydride	1.00	1.00	

---

13. Acetic anhydride via oxidation of acetaldehyde

Reaction: $2\ CH_3CHO + O_2 \rightarrow (CH_3CO)_2O + H_2O$

Comments: Reaction occurs in liquid phase at about 50-70 C and 60 psi with a catalyst of copper and cobalt acetates.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-.86	-1.20	[17],[20]
Acetic Anhydride	1.00	1.00	
Acetic Acid		.43	[17]

---

14. Acetic anhydride via reaction of acetylene and acetic acid

Reactions: $2\ CH_3COOH + CH{\equiv}CH \rightarrow CH_3CH(OCOCH_3)_2$

$CH_3CH(OCOCH_3)_2 \rightarrow (CH_3CO)_2O + CH_3CHO$

Comments: First reaction occurs at about 60-85 C in liquid phase with catalyst of mercury sulfate and mercury acetate. Second reaction occurs in presence of acid catalyst such as zinc chloride or sodium pyrophosphate.

Input-Output Coefficients:	Theoretical	Model	References
Acetic Acid	-1.18	-1.38	[31]
Acetylene	-.25	-.37	[31]
Acetic Anhydride	1.00	1.00	
Acetaldehyde	.43	.43	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	260	910	1095	1590	[24],[26]
Exogeneous Demand	260	910	1000	1510	[5],[20], [28-31]

Acetone

Acetone is used mainly as a solvent and as a feedstock for the manufacture of methyl methacrylate, methyl isobutyl ketone, and bisphenol-A. A variety of other chemicals, including hexylene glycol, mesityl oxide, and isophorone, are also derived from acetone.

Today about half the acetone produced is derived from isopropanol, usually by dehydrogenation. Most of the remainder occurs as a coproduct of phenol manufacture from cumene. If isopropanol is oxidized to acetone, the process may be so operated that dehydrogenation occurs simultaneously, the endothermic heat of dehydrogenation balancing the exothermic heat of oxidation. In some countries acetone is now produced by the direct oxidation of propylene in a process similar to the Wacker process for acetaldehyde production from ethylene. Ethanol, acetic acid, and acetlyene have been used as feedstocks for acetone manufacture at various times, though not in the United States. A fermentation process coproducing acetone and butanol was once important, but beginning in the 1920s gave way to isopropanol-based processes, which by 1940 represented over 80 percent of acetone production.

Manufacturing Processes

15. Acetone via dehydrogenation of isopropanol

Reaction: $CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + H_2$

Comments: Reaction occurs in vapor phase at about 380-500 C and 40-50 psi over brass, copper, or zinc oxide catalyst. Alternatively, the reaction may occur in the liquid phase at about 150 C and 1 atm. with a Raney nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Isopropanol	-1.03	-1.14	[5],[17],[20]
Acetone	1.00	1.00	
Hydrogen	.03	.03	

16. Acetone via oxidation of isopropanol

Reaction: $CH_3CHOHCH_3 + \frac{1}{2} O_2 \rightarrow CH_3COCH_3 + H_2O$

Comments: Reaction occurs in vapor phase at about 400-600 C and 40-50 psi over silver or copper catalyst. The process may be so operated that dehydrogenation occurs simultaneously, the exothermic heat of oxidation balancing the endothermic heat of dehydrogenation.

Input-Output Coefficients:	Theoretical	Model	References
Isopropanol	-1.03	-1.20	[19],[20]
Acetone	1.00	1.00	

17. Acetone via oxidation of propylene

Reaction: $CH_3CH{=}CH_2 + \frac{1}{2} O_2 \rightarrow CH_3COCH_3$

Comments: Reaction occurs in liquid phase at about 90-120 C and 9-12 atm. with palladium catalyst promoted by cuprous chloride.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.72	-.77	[29]
Acetone	1.00	1.00	

18. Acetone via hydration of acetylene

Reaction: $2\ CH{\equiv}CH + 3\ H_2O \rightarrow CH_3COCH_3 + CO_2 + 2\ H_2$

Comments: Reaction occurs at about 470 C with a catalyst of iron and zinc oxides.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.90	-1.12	[19],[30]
Acetone	1.00	1.00	
Carbon Dioxide	.76	.76	
Hydrogen	.07	.07	

19. Acetone via hydration of ethanol

Reaction: $2\ CH_3CH_2OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4\ H_2$

Comments: Reaction occurs at about 470 C over iron oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-1.59	-1.85	[19]
Acetone	1.00	1.00	
Carbon Dioxide	.76	.76	
Hydrogen	.14	.14	

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20. Acetone via decarboxylation of acetic acid

Reaction: $2\ CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O$

Comments: Reaction occurs in vapor phase at about 400-450 C and 1 atm. over cerium oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetic Acid	-2.07	-2.18	[19]
Acetone	1.00	1.00	
Carbon Dioxide	.76	.76	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	200	480	760	1615	[24],[26]
Exogeneous Demand	100	250	375	800	[5],[18-20], [26],[27-31]

Acetylene

Acetylene was once important as a feedstock for the production of acetaldehyde, acrylic acid and its esters, acrylonitrile, chloroprene, perchloroethylene, trichloroethylene, vinyl chloride, and vinyl acetate. Some of these markets have vanished and all will vanish eventually if the current trend toward other feedstocks continues. The one growing market for acetylene is the production of 1,4-butyne diol, from which a range of increasingly important chemicals is derived; these include butyrolactone, vinyl pyrrolidone, 1,4-butane diol, and tetrahydrofuran. Appreciable amounts of acetylene are also consumed in non-chemical uses such as metal cutting and welding.

The traditional route to acetylene is the hydration of coal-derived calcium carbide. As of the early-1970s this process still accounted for somewhat over half the acetylene capacity. Since 1940 a number of processes producing acetylene by the pyrolysis of hydrocarbons have been commercialized. Essentially these processes differ in the way in which they supply the energy necessary for the pyrolysis. Energy may be supplied by electric discharge (arc process), by contact with a hot solid (regenerative process), by partial combustion of the feedstock (one-stage partial combustion process), or by injection of the feedstock into hot combustion gases (two-stage partial combustion process). Of these, the only process used to a significant extent in the United States has been one-stage partial combustion. There are many versions of this process, but the most widely used in the BASF or Sachsse process,

which was first commercialized in Germany during World War II. Methane is the usual feedstock, but the process has also been adapted to use naphtha. The arc process was the first to be used for the large-scale production of acetylene from hydrocarbons; it was commercialized in Germany in 1940. Hydrocarbons from methane to naphtha can serve as feedstock, but in practice a methane-rich gas seems to be preferred. Butane or naphtha may be used to quench the hot pyrolysis gases; in this case substantial amounts of ethylene are also produced. The only regenerative process to achieve commercial significance is the Wulff process. This was operated on a demonstration plant scale in the United States in 1951. It was not until the 1960s however that further commercial development occurred. Methane can serve as feedstock, but hydrocarbons from ethane to naphtha are preferred. Operating conditions can be so adjusted that substantial quantities of ethylene are coproduced. The Hoechst HTP process is the most widely used two-stage partial combustion process. It has been operated in Germany since 1960. As feedstock any hydrocarbon from methane to naphtha can be used. Ethylene is coproduced when hydrocarbons heavier than methane are used.

Manufacturing Processes

21. Acetylene via hydration of calcium carbide

Reactions: $3\ C\ (coke) + CaO \rightarrow CaC_2 + CO$

$CaC_2 + H_2O \rightarrow CH{\equiv}CH + CaO$

Comments: First reaction occurs at about 2000-2100 C in an electric furnace.

Input-Output Coefficients:	Theoretical	Model	References
Carbon	-1.38	-2.90	[20],[47]
Acetylene	1.00	1.00	
Carbon Monoxide	1.08	1.10	[48]

(Note: Input-output coefficients account for the fact that the production of one pound of coke requires about 1.25 lb of carbon in the form of coal.)

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22. Acetylene via pyrolysis of methane (arc process)

Reaction (not balanced): $CH_4 \rightarrow CH{\equiv}CH + CH_2{=}CH_2 + H_2$

Comments: Heat necessary for pyrolysis is supplied by electric discharge.

Input-Output Coefficients:	Model	References
Methane	-2.2	[19],[20],[49-51]
n-Butane	-.7	[19],[20],[50]
Acetylene	1.00	
Ethylene	.48	[19],[20],[50]
Hydrogen	.24	[19],[50]

(Note: Input-output coefficients are for the case in which butane is used to quench the pyrolysis gases.)

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23. Acetylene via pyrolysis of methane (one-stage partial combustion)

Reaction (not balanced): $CH_4 + O_2 \rightarrow CH{\equiv}CH + CO + CO_2 + H_2$

Comments: Heat necessary for pyrolysis is supplied by partial combustion of the feedstock.

Input-Output Coefficients:	Model	References
Methane	-3.7	[17-19],[50],[52]
Acetylene	1.00	
Carbon Monoxide	3.3	[18],[19],[50],[52]
Carbon Dioxide	.7	[19],[50],[52]
Hydrogen	.55	[18],[19],[50],[52]

(Note: Input-output coefficients are for the BASF process assuming recovery of the methane in the off-gas.)

---

24. Acetylene via pyrolysis of naphtha (one-stage partial combustion)

Reaction (not balanced): $\text{naphtha} + O_2 \rightarrow CH{\equiv}CH + CO + CO_2 + H_2 + CH_4$

Comments: Heat necessary for pyrolysis is supplied by partial combustion of the feedstock.

Input-Output Coefficients:	Model	References
Naphtha	-4.2	[17],[19]
Acetylene	1.00	
Carbon Monoxide	2.1	[52]
Carbon Dioxide	1.8	[52]
Hydrogen	.35	[19],[52]
Methane	.3	[19]

(Note: Input-output coefficients are for the BASF process.)

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25. Acetylene via pyrolysis of ethane (regenerative process)

Reaction (not balanced): $CH_3CH_3 \rightarrow CH{\equiv}CH + CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by contact with hot refractory tile. By adjusting operating conditions the ratio of acetylene to ethylene can be varied.

Input-Output Coefficients:	Model	References
Ethane	-2.6	[20],[47],[48]
Acetylene	1.00	
Ethylene	.15	[51]

(Note: Input-output coefficients assume that off-gases are consumed as fuel in the process.)

---

26. Acetylene via pyrolysis of propane (regenerative process)

Reaction (not balanced): $CH_3CH_2CH_3 \rightarrow CH{\equiv}CH + CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by contact with hot refractory tile. By adjusting operating conditions the ratio of acetylene to ethylene can be varied.

Input-Output Coefficients:	Model	References
Propane	-2.9	[20],[48],[51]
Acetylene	1.00	
Ethylene	.35	[48],[51]

(Note: Input-output coefficients assume that off-gases are consumed as fuel in the process.)

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27. Acetylene via pyrolysis of n-butane (regenerative process)

Reaction (not balanced): $CH_3CH_2CH_2CH_3 \rightarrow CH{\equiv}CH + CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by contact with hot refractory tile. By adjusting operating conditions the ratio of acetylene to ethylene can be varied.

Input-Output Coefficients:	Model	References
n-Butane	-3.0	[48]
Acetylene	1.00	
Ethylene	.4	[48]

(Note: Input-output coefficients assume that off-gases are consumed as fuel in the process.)

---

28. Acetylene via pyrolysis of naphtha (regenerative process)

Reaction (not balanced): naphtha → $CH{\equiv}CH$ + $CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by contact with hot refractory tile. By adjusting operating conditions the ratio of acetylene to ethylene can be varied.

Input-Output Coefficients:	Model	References
Naphtha	-4.7	[48]
Acetylene	1.00	
Ethylene	.9	[48]

(Note: Input- utput coeffcients assume that off-gases are consumed as fuel in the process.)

---

29. Acetylene via pyrolysis of methane (two-stage partial combustion)

Reaction (not balanced): CH_4 → $CH{\equiv}CH$

Comments: Heat necessary for pyrolysis is supplied by burning some fuel (usually the process off-gas) and then injecting the feedstock into the hot combustion gases.

Input-Output Coefficients:	Model	References
Methane	-2.5	[19],[48],[50]
Acetylene	1.00	

(Note: Input-output coefficients are for the Hoechst HTP process assuming off-gas is used as fuel in the process.)

---

30. Acetylene via pyrolysis of ethane (two-stage partial combustion)

Reaction (not balanced): CH_3CH_3 → $CH{\equiv}CH$ + $CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by burning some fuel (usually the process off-gas) and then injecting the feedstock into the hot combustion gases. The ratio of acetylene to ethylene is variable.

Input-Output Coefficients:	Model	References
Ethane	-3.0	estimate of yields based on
Acetylene	1.00	yields for two-stage partial
Ethylene	.33	combustion of other hydro-carbons

(Note: Input-output coefficients are for the Hoechst HTP process assuming off-gas is used as fuel in the process.)

---

31. Acetylene via pyrolysis of propane (two-stage partial combustion)

Reaction (not balanced): $CH_3CH_2CH_3 \rightarrow CH{\equiv}CH + CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by burning some fuel (usually the process off-gas) and then injecting the feedstock into the hot combustion gases. The ratio of acetylene to ethylene is variable.

Input-Output Coefficients:	Model	References
Propane	-3.3	estimate of yields based on
Acetylene	1.00	yields for two-stage partial
Ethylene	.7	combustion of other hydro-carbons

(Note: Input-output coefficients are for the Hoechst HTP process assuming off-gas is used as fuel in the process.)

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32. Acetylene via pyrolysis of n-butane (two-stage partial combustion)

Reaction (not balanced): $CH_3CH_2CH_2CH_3 \rightarrow CH{\equiv}CH + CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by burning some fuel (usually the process off-gas) and then injecting the feedstock into the hot combustion gases. The ratio of acetylene to ethylene is variable.

Input-Output Coefficients:	Model	References
n-Butane	-3.65	[48],[50]
Acetylene	1.00	
Ethylene	1.00	[48],[50]

(Note: Input-output coefficients are for the Hoechst HTP process assuming off-gas is used as fuel in the process.)

---

33. Acetylene via pyrolysis of naphtha (two-stage partial combustion)

Reaction (not balanced): naphtha → $CH{\equiv}CH$ + $CH_2{=}CH_2$

Comments: Heat necessary for pyrolysis is supplied by burning some fuel (usually the process off-gas) and then injecting the feedstock into the hot combustion gases. The ratio of acetylene to ethylene is variable.

Input-Output Coefficients:	Model	References
Naphtha	-4.8	[18],[19],[48],[50]
Acetylene	1.00	
Ethylene	1.50	[18]

(Note: Input-output coefficients are for the Hoechst HTP process assuming off-gas is used as fuel in the process.)

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	125	370	835	985	[18],[26]
Exogeneous Demand	90	100	150	130	[18],[26], [30]

(Note: Production figures exclude acetylene produced from calcium carbide in portable generators for welding.)

Acrolein

Acrolein is used primarily for the manufacture of glycerin via allyl alcohol and for the production of acrylic acid and its esters. Of the various other chemicals derived from acrolein, methionine, a poultry feed additive, is the most important.

The first large-scale, commercial manufacture of acrolein began in the early-1950s and was based on the aldol condensation of acetaldehyde with formaldehyde. However, since the late-1950s most acrolein has been produced by oxidizing propylene.

Manufacturing Processes

34. Acrolein via oxidation of propylene

Reaction: $CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO + H_2O$

Comments: Reaction occurs in vapor phase at about 350 C and 2 atm. with copper oxide or molybdenum oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.75	-.89	[19],[20],[53]
Acrolein	1.00	1.00	

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35. Acrolein via reaction of formaldehyde and acetaldehyde

Reaction: $HCHO + CH_3CHO \rightarrow CH_2{=}CHCHO + H_2O$

Comments: Reaction occurs in vapor phase at about 300 C and 1 atm. with sodium silicate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Formaldehdye	-.53	-.82	[51]
Acetaldehyde	-.79	-1.05	[51]
Acrolein	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	--	--	5	15	[5],[53]

Acrylic Acid

Most acrylic acid is consumed as ethyl acrylate or some other acrylate ester. The esterification may occur in situ if the appropriate alcohol replaces water in one of the processes described below. The acrylate esters are used to produce acrylic polymers and copolymers; these are used primarily as coatings and in textiles.

As of 1970, five different routes to acrylic acid were in commercial production: the oxidation of acrolein, the carbonylation of acetylene, the hydrolysis of acrylonitrile, the reaction of ketene and formaldehyde to form β-propiolactone for subsequent hydration, and the cyanation of ethylene oxide to form ethylene cyanohydrin for later hydrolysis. The acrolein route, commercialized here in the late-1960s, and the acetylene route, which dates back to the 1940s, are the most important, though the former is preferred today. If the acrolein route is used, a separate esterification reactor is used when acrylate esters are desired. The ethylene oxide process, the original commercial route to acrylic acid, is today considered obsolete. The acrylonitrile and β-propiolactone processes continue to be used; however, the former is no longer operated in the United States.

Manufacturing Processes

36. Acrylic acid via oxidation of acrolein

Reaction: $CH_2{=}CHCHO + \frac{1}{2} O_2 \rightarrow CH_2{=}CHCOOH$

Comments: Reaction occurs in vapor phase at about 300-400 C over metal oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acrolein	-.78	-1.00	[17],[18]
Acrylic Acid	1.00	1.00	

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37. Acrylic acid via carbonylation of acetylene

Reaction: $CH{\equiv}CH + CO + H_2O \rightarrow CH_2{=}CHCOOH$

Comments: Reaction occurs in tetrahydrofuran at 60-200 atm. with nickel halide catalyst. Alternatively, reaction may occur in methyl ethyl ketone at 1-2 atm. in the presence of hydrogen chloride and nickel carbonyl.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.36	-.42	[17],[18],[32]
Carbon Monoxide	-.39	-.45	
Acrylic Acid	1.00	1.00	

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38. Acrylic acid via reaction of ketene and formaldehyde

Reactions: $CH_2{=}CO + HCHO \rightarrow CH_2CH_2CO$ (O bridge)

CH_2CH_2CO (O bridge) $+ ROH \rightarrow CH_2{=}CHCOOR$

Comments: First reaction occurs in liquid phase at about 10-20 C and 1-2 psia with zinc chloride catalyst. Second reaction occurs in liquid phase at about 140-150 C and 3 psia with phosphoric acid catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ketene	-.58	-.68	[23]
Formaldehyde	-.42	-.50	[23]
Acrylic Acid	1.00	1.00	

---

39. Acrylonitrile via sulfonation of acrylonitrile

Reaction: $CH_2{=}CHCN + H_2SO_4 + 2\,H_2O \rightarrow CH_2{=}CHCOOH + NH_4HSO_4$

Comments: Reaction occurs at about 100 C.

Input-Output Coefficients:	Theoretical	Model	References
Acrylonitrile	-.74	-.92	[23]
Sulfuric Acid	-1.36	-1.5	
Acrylic Acid	1.00	1.00	
Ammonium Bisulfate	1.60	1.60	

40. Acrylic Acid via cyanation of ethylene oxide

Reactions: $CH_2CH_2O + HCN \rightarrow CH_2OHCH_2CN$

$CH_2OHCH_2CN + H_2SO_4 + H_2O \rightarrow CH_2{=}CHCOOH + NH_4HSO_4$

Comments: First reaction occurs in liquid phase at about 90-150 C and 100-500 psi with alkaline catalyst. Second reaction occurs in liquid phase at about 150 C and 1 atm.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Oxide	-.61	-.81	[23]
Hydrogen Cyanide	-.37	-.50	
Sulfuric Acid	-1.36	-1.50	
Acrylic Acid	1.00	1.00	
Ammonium Bisulfate	1.60	1.60	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	2	12	55	250	
Exogeneous Demand	1	5	20	100	[18],[24]

Acrylonitrile

The production of acrylic and modacrylic fibers accounts for about half the demand for acrylonitrile. Most of the remainder is consumed in the production of various copolymers, the most important of which are acrylonitrile-butadiene-styrene, styrene-acrylonitrile, and butadiene-acrylonitrile. There is also a substantial export market. Acrylonitrile has a potentially large-volume use as an intermediate for producing adiponitrile, from which adipic acid and hexamethylenediamine, the monomers for nylon 66, can be derived.

Acrylonitrile was first produced commercially in the United States in 1940. In the original manufacturing process, ethylene oxide and hydrogen cyanide reacted to form ethylene cyanohydrin, which was then dehydrated to acrylonitrile. Though this process was operated until the mid-1960s, since the early-1950s most acrylonitrile has been manufactured from acetylene by cyanation, or, more recently, from propylene by ammoxidation. The acetylene route was developed during World War II but did not become important in the United States until a decade later. The propylene route was developed in the late-1950s, commercialized in 1960, and, because propylene was cheap and plentiful, assumed a dominant position within a few years. Today the propylene route accounts for all the acrylonitrile produced in the United States.

Manufacturing Processes

41. Acrylonitrile via ammoxidation of propylene

Reaction: $CH_3CH{=}CH_2 + NH_3 + \frac{3}{2} O_2 \rightarrow CH_2{=}CHCN + 3\ H_2O$

Comments: Reaction occurs in vapor phase at about 425-500 C and 1-3 atm. over a catalyst of bismuth phosphomolybdate or antimony-uranium oxide. In a variation of this process, ammonia and air are first reacted to form nitric oxide, which is then reacted with propylene at about 700 C over a silver catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.79	-1.15	[5],[18],[20]
Ammonia	-.32	-.37	[18]
Acrylonitrile	1.00	1.00	
Hydrogen Cyanide		.10	[5],[18],[20]

---

42. Acrylonitrile via cyanation of acetylene

Reaction: $CH{\equiv}CH + HCN \rightarrow CH_2{=}CHCN$

Comments: Reaction occurs in liquid phase at about 70 C and 1 atm. with cuprous chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.49	-.60	[5],[17-20]
Hydrogen Cyanide	-.51	-.60	[5],[18-20]
Acrylonitrile	1.00	1.00	

---

43. Acrylonitrile via cyanation of ethylene oxide

Reactions: $\underset{\underset{O}{\diagdown\!\diagup}}{CH_2CH_2} + HCN \rightarrow CH_2OHCH_2CN$

$CH_2OHCH_2CN \rightarrow CH_2{=}CHCN + H_2O$

Comments: First reaction occurs in liquid phase with basic catalyst such as diethylamine. Second reaction occurs in vapor phase over dehydration catalyst such as activated alumina at about 250-350 C. A liquid-phase process for the second reaction has also been used.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Oxide	-.83	-1.16	[54]
Hydrogen Cyanide	-.51	-.70	[54]
Acrylonitrile	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	1	17	230	1040	[24],[26]
Exogeneous Demand	1	17	230	1000	[29]

Adipic Acid

Adipic acid is one of the monomers for nylon 66. The other monomer, hexamethylenediamine, can be derived from adipic acid. Most adipic acid is thus consumed directly or indirectly in nylon 66 production. Significant quantities of adipic acid are also used to produce adipate plasticizers and in the manufacture of urethane and polyester resins.

Cyclohexanol or cyclohexanone can be oxidized to adipic acid. In practice a mixture of cyclohexanol and cyclohexanone is the usual feedstock. Originally the oxidation was carried out using nitric acid, but today an air oxidation process is gaining favor. Since the 1940s there have been attempts to prepare adipic acid directly from cyclohexane by oxidation. These processes have met with little commercial success.

Manufacturing Processes

44. Adipic acid via oxidation of cyclohexanone

Reaction: $C_6H_{10}O + \frac{3}{2} O_2 \rightarrow COOH(CH_2)_4COOH$

Comments: Reaction occurs in liquid phase at about 80-85 C and 6-7 atm. with catalyst of copper acetate and manganese acetate.

Input-Output Coefficients:	Theoretical	Model	Reference
Cyclohexanone	-.67	-.96	[55]
Adipic Acid	1.00	1.00	

---

45. Adipic acid via oxidation of cyclohexanol

Reaction: $C_6H_{11}OH + 2 O_2 \rightarrow COOH(CH_2)_4COOH + H_2O$

Comments: Reaction occurs in liquid phase at about 80-85 C and 6-7 atm. with catalyst of copper acetate and manganese acetate.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexanol	-.69	-.99	[55]
Adipic Acid	1.00	1.00	

---

46. Adipic acid via oxidation of cyclohexanone with nitric acid

Reactions: $C_6H_{10}O + 2\ HNO_3 \rightarrow COOH(CH_2)_4COOH + 2\ NO + H_2O$

$3\ NO + \frac{3}{2}\ O_2 \rightarrow 3\ NO_2$

$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

Comments: First reaction occurs in liquid phase at about 50-150 C and 50-250 psi with catalyst of ammonium metavanadate and copper.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexanone	-.67	-.71	[5],[55]
Nitric Acid		-1.1	[5]
Adipic Acid	1.00	1.00	

---

47. Adipic acid via oxidation of cyclohexanol with nitric acid

Reactions: $C_6H_{11}OH + \frac{8}{3}\ HNO_3 \rightarrow COOH(CH_2)_4COOH + \frac{8}{3}\ NO + \frac{7}{3}\ H_2O$

$4\ NO + 2\ O_2 \rightarrow 4\ NO_2$

$4\ NO_2 + \frac{4}{3}\ H_2O \rightarrow \frac{8}{3}\ HNO_3 + \frac{4}{3}\ NO$

Comments: First reaction occurs in liquid phase at about 50-150 C and 50-250 psi with catalyst of ammonium metavanadate and copper.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexanol	-.69	-.73	[5],[55]
Nitric Acid		-1.1	[5]
Adipic Acid	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	5	50	325	1080	[24],[30],[56]
Exogeneous Demand	3	30	125	380	[20],[30],[31]

Adiponitrile

Essentially all adiponitrile is hydrogenated to hexamethylenediamine, one of the monomers for nylon 66.

The original process for adiponitrile manufacture used the reaction of adipic acid and ammonia. This process is still used, but has been overshadowed somewhat by a process converting butadiene to adiponitrile via dichlorobutylene and dicyanobutylene. A variation of this route starts with the chlorination of tetrahydrofuran derived from furfural, which is obtained by processing agricultural residues. In a more recently commercialized process, adiponitrile is produced by the electrolytic hydrodimerization of acrylonitrile. This development has led some to suggest the large-scale conversion of adiponitrile to adipic acid, a reversal of current practice.

Manufacturing Processes

48. Adiponitrile via reaction of adipic acid and ammonia

Reaction: $COOH(CH_2)_4COOH + 2\ NH_3 \rightarrow CN(CH_2)_4CN + 4\ H_2O$

Comments: Reaction occurs at about 300 C in the presence of phosphoric acid.

Input-Output Coefficients:	Theoretical	Model	References
Adipic Acid	-1.35	-1.67	[5],[17]
Ammonia	-.32	-.43	[5]
Adiponitrile	1.00	1.00	

---

49. Adiponitrile via chlorination of butadiene

Reactions: $CH_2{=}CHCH{=}CH_2 + C\ell_2 \rightarrow CH_2C\ell CH{=}CHCH_2C\ell$

$CH_2C\ell CH{=}CHCH_2C\ell + 2\ HCN \rightarrow CNCH_2CH{=}CHCH_2CN + 2\ HC\ell$

$CNCH_2CH{=}CHCH_2CN + H_2 \rightarrow CN(CH_2)_4CN$

Comments: First reaction occurs in vapor phase at about 65-75 C. Second reaction occurs at about 85-95 C and may be catalyzed by cuprous salts. Sodium cyanide may replace hydrogen cyanide in this process. Third reaction occurs in vapor phase at about 250-300 C over palladium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Butadiene	-.50	-.82	[17]
Chlorine	-.66	-.75	
Hydrogen Cyanide	-.50	-.57	[5]
Hydrogen	-.02	-.03	
Adiponitrile	1.00	1.00	
Hydrogen Chloride	.68	.68	

---

50. Adiponitrile via hydrodimerization of acrylonitrile

Reaction: $2\ CH_2{=}CHCN + H_2O \rightarrow CN(CH_2)_4CN + \frac{1}{2}\ O_2$

Comments: Reaction occurs at the lead cathode of an electrolytic cell.

Input-Output Coefficients:	Theoretical	Model	References
Acrylonitrile	-.98	-1.09	[17]
Adiponitrile	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Allyl Alcohol

Since the late 1950s the major use of allyl alcohol has been as a feedstock for synthetic glycerin production, and the major process for its manufacture has been the reaction of acrolein and isopropanol. Before this process was introduced allyl alcohol was derived from the hydrolysis of allyl chloride, and, to a lesser extent, from the isomerization of propylene oxide. Though these processes were still used in the 1960s, neither is important today.

Manufacturing Processes

51. Allyl alcohol via reaction of acrolein and isopropanol

Reaction: $CH_2{=}CHCHO + CH_3CHOHCH_3 \rightarrow CH_2{=}CHCH_2OH + CH_3COCH_3$

Comments: Reaction occurs in vapor phase at about 400 C with catalyst of zinc oxide and magnesia.

Input-Output Coefficients:	Theoretical	Model	References
Acrolein	-.97	-1.02	[17]
Isopropanol	-1.03	-1.10	
Allyl Alcohol	1.00	1.00	
Acetone	1.00	1.00	

---

52. Allyl alcohol via isomerization of propylene oxide

Reaction: $\underset{\underset{\text{O}}{\diagup\diagdown}}{CH_2CHCH_3} \rightarrow CH_2{=}CHCH_2OH$

Comments: Reaction occurs over lithium phosphate catalyst in vapor phase at about 230-270 C or in liquid phase at about 275-280 C.

Input-Output Coefficients:	Theoretical	Model	References
Propylene Oxide	-1.00	-1.33	[30]
Allyl Alcohol	1.00	1.00	

---

53. Allyl alcohol via hydrolysis of allyl chloride

Reaction: $CH_2{=}CHCH_2Cl + NaOH \rightarrow CH_2{=}CHCH_2OH + NaCl$

Comments: Reaction occurs in aqueous phase at about 145-155 C and 200 psi.

Input-Output Coefficients:	Theoretical	Model	References
Allyl Chloride	-1.32	-1.50	[19],[30]
Sodium Hydroxide	-.69	-.78	
Allyl Alcohol	1.00	1.00	
Sodium Chloride	1.01	1.01	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	--	2	5	10	[5],[30]

Allyl Chloride

Most allyl chloride is converted to epichlorohydrin, which is then used to manufacture epoxy resins and synthetic glycerin. The chlorination of propylene is the only large-scale commercial process for allyl chloride production; it has been in use since the late-1940s.

Manufacturing Process

54. Allyl chloride via chlorination of propylene

Reaction: $CH_2{=}CHCH_3 + C\ell_2 \rightarrow CH_2{=}CHCH_2C\ell + HC\ell$

Comments: Reaction occurs in vapor phase at 400-500 C and 2 atm. using an excess of propylene.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.55	-.70	[5],[17],[20]
Chlorine	-.93	-1.15	[5],[20]
Allyl Chloride	1.00	1.00	
Hydrogen Chloride	.48	.48	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	40	200	285	[26]
Exogeneous Demand	--	5	10	15	[5]

Ammonia

Directly or indirectly, most ammonia is consumed as fertilizer. Though ammonia is primarily an agricultural chemical, large quantities are consumed by the petrochemical industry in the production of acrylonitrile, caprolactam, hexamethylenediamine, and other chemicals. Since nitric acid is manufactured from ammonia, important chemicals such as aniline and toluene diisocyanate are also ammonia derivatives.

Synthetic ammonia has long been manufactured directly from nitrogen and hydrogen. Coal-derived water-gas was once the primary source of the hydrogen required, but today this is obtained mainly from the steam reforming of hydrocarbons.

Manufacturing Process

55. Ammonia via reaction of hydrogen and nitrogen

Reaction: $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$

Comments: Reaction occurs in vapor phase at about 400-600 C and 130-650 atm. using an iron oxide catalyst promoted by aluminum, potassium, calcium, or magnesium oxides.

Input-Output Coefficients:	Theoretical	Model	References
Hydrogen	-.18	-.20	[19],[20]
Ammonia	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	800	3200	9600	28000	[20],[31], [32]
Exogeneous Demand	550	2250	7600	19700	[18],[26]

Ammonium Bisulfate

Ammonium bisulfate is produced in processes for making acrylic acid and methyl methacrylate. It has little use itself but can be converted to ammonium sulfate for fertilizer use.

Demand Data

There is no exogeneous demand, though ammonium bisulfate may be an output of the industry.

Ammonium Chloride

Ammonium chloride is produced as a byproduct in a little used route to aniline. Usually ammonium chloride is produced by the reaction of sodium chloride and ammonium sulfate or is recovered as a byproduct of the ammonia-soda (Solvay) process for sodium carbonate. Its major use is in the manufacture of dry cell batteries. It is also used as a mordant for dyes and inks and as a soldering and galvanizing flux.

Demand Data

There is no exogeneous demand, though ammonium chloride may be an output of the industry.

Ammonium Sulfate

Ammonium sulfate is produced in the manufacture of caprolactam. It is used as a fertilizer, but is considered a low-grade one compared to ammonia or ammonium nitrate. Thus, ammonium sulfate may be a waste disposal problem for caprolactam producers. Currently, however, the worldwide demand for fertilizer seems to be sufficient to absorb the coproduced ammonium sulfate.

Demand Data

There is no exogeneous demand, though ammonium sulfate may be an output of the petrochemical industry.

Aniline

Aniline is used primarily to produce anti-oxidants and vulcanization accelerators for rubber. Dyestuffs, once the major aniline derivatives, now represent only 10 to 15 percent of total demand. A growing market for aniline is the production of isocyanates, in particular methylenephenylene diisocyanate.

Once manufactured largely by the reduction of nitrobenzene with iron and hydrochloric acid, aniline is now derived from nitrobenzene by catalytic hydrogenation. Some aniline has also been derived from the ammonolysis of chlorobenzene. In Japan a process producing aniline from phenol has been commercialized.

Manufacturing Processes

56. Aniline via hydrogenation of nitrobenzene

Reaction: $C_6H_5NO_2 + 3\ H_2 \rightarrow C_6H_5NH_2 + 2\ H_2O$

Comments: Reaction occurs in vapor phase at about 270 C and 5 psi over copper catalyst. Alternatively, the reaction may occur in the liquid phase using a Raney nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Nitrobenzene	-1.32	-1.35	[5],[17],[18],[20]
Hydrogen	-.06	-.07	[20]
Aniline	1.00	1.00	

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57. Aniline via reaction of chlorobenzene and ammonia

Reaction: $C_6H_5C\ell + 2\ NH_3 \rightarrow C_6H_5NH_2 + NH_4C\ell$

Comments: Reaction occurs in aqueous phase at about 210-220 C and 750-850 psi with cuprous chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Chlorobenzene	-1.21	-1.37	[17]
Ammonia	-.37	-.44	
Aniline	1.00	1.00	
Ammonium Chloride	.57	.57	

---

58. Aniline via reaction of phenol and ammonia

Reaction: $C_6H_5OH + NH_3 \rightarrow C_6H_5NH_2 + H_2O$

Comments: Reaction occurs in vapor phase over catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Phenol	-1.01	-1.10	[57]
Ammonia	-.18	-.20	[57]
Aniline	1.00	1.00	

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59 Aniline via reduction of nitrobenzene with iron

Reaction: $C_6H_5NO_2 + \frac{9}{4} Fe + H_2O \rightarrow C_6H_5NH_2 + \frac{3}{4} Fe_3O_4$

Comments: Reaction occurs at about 200 C in the presence of hydrochloric acid.

Input-Output Coefficients:	Theoretical	Model	References
Nitrobenzene	-1.32	-1.39	[17],[20]
Iron	-1.35	-1.60	[20]
Aniline	1.00	1.00	
Iron Oxide	1.87	1.87	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	55	100	120	400	[24],[26]
Exogeneous Demand	55	100	120	400	[24],[26]

Benzene

Though it has some solvent use, most benzene is converted to other chemicals, primarily ethylbenzene, cumene, cyclohexane, nitrobenzene, and maleic anhydride. In turn these may be converted to still other chemicals, including styrene, phenol, adipic acid, caprolactam, and aniline. Thus benzene is the starting point for a wide variety of products.

Benzene is produced in catalytic reforming operations in petroleum refineries; such operations supply most of the benzene consumed by the petrochemical industry. Coal carbonization processes, once the primary source of benzene, still account for some of the benzene supply. These supplies are augmented by production from toluene by hydrodealkylation, a process introduced in the late-1950s and now used widely. Benzene also occurs as a byproduct of ethylene manufacture, particularly when naphtha or gas oil is the feedstock. In addition there are recently developed commercial processes for disproportionating toluene to benzene and xylenes.

Manufacturing Processes

60. Benzene via hydrodealkylation of toluene

Reaction: $C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$

Comments: Reaction occurs at about 600-900 psi and 200-300 F over a catalyst, or at 1400 F without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Toluene	-1.18	-1.23	[5],[17],[18],[20]
Hydrogen	-.03	-.03	[20]
Benzene	1.00	1.00	
Methane	.21	.21	

---

61. Benzene via disproportionation of toluene

Reaction: $2\ C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_4(CH_3)_2$

Comments: Reaction occurs in vapor phase over catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Toluene	-2.36	-2.70	[18]
Benzene	1.00	1.00	
m-Xylene	1.36	.74	[18],[32]
o-Xylene		.37	[18],[32]
p-Xylene		.37	[18],[32]

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply					
from coal	300	1400	1100	800	[18],[24],
from refineries	--	75	2200	5500	[26]
Production (from toluene and as ethylene byproduct)	--	--	100	2500	[18],[26], [29]
Exogeneous Demand	140	400	500	1300	[18],[26], [29]

Benzoic Acid

Though first prepared commercially in the 19th century, benzoic acid did not assume importance as a large-scale petrochemical until fairly recently. Since the early-1960s, substantial quantities of benzoic acid have been consumed in one route to phenol. Other important outlets for benzoic acid are the production of sodium benzoate, a food preservative, and the production of plasticizers for vinyl resins. Benzoic acid also has potentially large-scale markets as an intermediate for the manufacture of caprolactam and terephthalic acid.

Since its emergence as a large-scale petrochemical, most benzoic acid has been manufactured from toluene by oxidation. In other older processes, benzoic acid was derived from phthalic anhydride and from toluene via benzotrichloride.

Manufacturing Processes

62. Benzoic acid via oxidation of toluene

Reaction: $C_6H_5CH_3 + \frac{3}{2} O_2 \rightarrow C_6H_5COOH + H_2O$

Comments: Reaction occurs in liquid phase at about 300 F and 40-70 psi with cobalt naphthenate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Toluene	-.75	-.84	[17]
Benzoic Acid	1.00	1.00	

---

63. Benzoic acid via decarboxylation of phthalic anhydride

Reaction: $C_6H_4(CO)_2O + H_2O \rightarrow C_6H_5COOH + CO_2$

Comments: Reaction occurs in liquid phase at about 200 C with catalyst of chromium and disodium phthalate, or in vapor phase at about 380-420 C with catalyst of copper carbonate and $Ca(OH)_2$.

Input-Output Coefficients:	Theoretical	Model	References
Phthalic Anhydride	-1.21	-1.43	[17],[20]
Benzoic Acid	1.00	1.00	
Carbon Dioxide	.36	.36	

---

64. Benzoic acid via chlorination of toluene

Reactions: $C_6H_5CH_3 + 3\ C\ell_2 \rightarrow C_6H_5CC\ell_3 + 3\ HC\ell$

$C_6H_5CC\ell_3 + 2\ H_2O \rightarrow C_6H_5COOH + 3\ HC\ell$

Comments: First reaction occurs at about 100-150 C in the presence of light. Second reaction occurs at about 100-115 C with zinc chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Toluene	-.75	-.98	[17],[20]
Chlorine	-1.74	-1.90	
Benzoic Acid	1.00	1.00	
Hydrogen Chloride	1.79	1.79	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	10	125	[5],[24]
Exogeneous Demand	--	--	10	60	[5]

Bisphenol-A

Most bisphenol-A is consumed in the manufacture of epoxy resins. Its only other large scale use is as a monomer for polycarbonate resins. The reaction of phenol and acetone is the only commercial route to bisphenol-A.

Manufacturing Process

65. Bisphenol-A via reaction of phenol and acetone

Reaction: $2\ C_6H_5OH + CH_3COCH_3 \rightarrow (CH_3)_2C(C_6H_4OH)_2 + H_2O$

Comments: Reaction occurs in liquid phase at about 50 C using a hydrogen chloride catalyst with methyl mercaptan promoter.

Input-Output Coefficients:	Theoretical	Model	References
Phenol	-.82	-.88	[17],[20]
Acetone	-.25	-.28	[17],[20]
Bisphenol-A	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	50	200	[20],[24]
Exogeneous Demand	--	--	50	200	[20],[24]

Bromine

Ethylene dibromide is the only large-scale petrochemical derived from bromine, and represents by far the largest market for bromine. Bromine is recovered from sea water or other natural brines.

Supply Data

The supply of bromine to the petrochemical industry is not constrained in the model.

Butadiene

Butadiene was not produced commercially in the United States on a large scale until the early-1940s. By 1943 huge quantities were being manufactured and then copolymerized with styrene to meet the wartime demand for the synthetic rubber GR-S (now known as SBR). This elastomer still accounts for about half the demand for butadiene. Other important derivatives are polybutadiene rubber, nitrile nubber (butadiene-acrylonitrile), and acrylonitrile-butadiene-styrene (ABS) plastic. In addition, butadiene is finding increasing use as a chemical intermediate for producing chloroprene, the monomer for neoprene rubber, and adiponitrile, an intermediate in nylon 66 manufacture.

The routes to butadiene all date back to World War II. In the United States, butadiene was produced by the dehydrogenation of n-butylenes, by the reaction of ethanol and acetaldehyde, and, to a lesser extent, by the dehydrogenation of n-butane. Some was also produced, along with ethylene and other olefins, from the thermal cracking of naphtha or gas oil. A small plant chlorinated n-butylenes and then dehydrochlorinated the chlorobutanes to butadiene. Other routes were developed in Europe. Butadiene was manufactured in Germany from acetaldehyde and from acetylene and formaldehyde. In Russia butadiene was manufactured from ethanol. In the United States today, most butadiene is derived from n-butane or n-butylenes, though increasing amounts are being made in ethylene plants using naphtha or gas oil feedstock. In Europe and Japan, ethylene plants already supply most of the butadiene.

Manufacturing Processes

66. Butadiene via dehydrogenation of n-butylenes

Reaction: $CH_3CH=CHCH_3$ or $CH_2=CHCH_2CH_3$ → $CH_2=CHCH=CH_2 + H_2$

Comments: Reaction occurs at about 620-675 C using an iron-oxide-based catalyst or a calcium-nickel phosphate catalyst stabilized with chromium oxide. Yields are somewhat higher with the latter catalyst but it requires more frequent regeneration. Oxidative dehydrogenation is also practiced.

Input-Output Coefficients:	Theoretical	Model	References
n-Butylenes	-1.04	-1.25	[17],[20],[50]
Butadiene	1.00	1.00	
Hydrogen	.04	.04	

67. Butadiene via dehydrogenation of n-butane

Reaction: $CH_3CH_2CH_2CH_3 \rightarrow CH_2=CHCH=CH_2 + 2\ H_2$

Comments: Reaction occurs at about 600-620 C and 150 mm Hg over a chromia-alumina catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butane	-1.07	-1.75	[17],[50]
Butadiene	1.00	1.00	
Hydrogen	.07	.08	

68. Butadiene via reaction of ethanol and acetaldehyde

Reaction: $CH_3CH_2OH + CH_3CHO \rightarrow CH_2=CHCH=CH_2 + 2\ H_2O$

Comments: Reaction occurs in vapor phase at about 325-350 C and 1 atm. over a tantalum oxide and silica gel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-.85	-1.15	[31]
Acetaldehyde	-.82	-1.10	[31]
Butadiene	1.00	1.00	

69. Butadiene via dimerization of acetaldehyde

Reactions: $2\ CH_3CHO \rightarrow CH_3CHOHCH_2CHO$

$CH_3CHOHCH_2CHO + H_2 \rightarrow CH_3CHOHCH_2CH_2OH$

$CH_3CHOHCH_2CH_2OH \rightarrow CH_2{=}CHCH{=}CH_2 + 2\ H_2O$

Comments: First reaction occurs in the presence of an alkaline catalyst. Second reaction occurs in liquid phase at about 50-150 C and 300 atm. using a copper catalyst promoted by chromic oxide. Third reaction occurs in vapor phase at about 280 C and 1 atm over a sodium phosphate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-1.63	-2.58	[19]
Hydrogen	-.04	-.05	
Butadiene	1.00	1.00	

---

70. Butadiene via reaction of acetylene and formaldehyde

Reactions: $CH{\equiv}CH + 2\ HCHO \rightarrow CH_2OHC{\equiv}CCH_2OH$

$CH_2OHC{\equiv}CCH_2OH + 2\ H_2 \rightarrow CH_2OHCH_2CH_2CH_2OH$

$CH_2OHCH_2CH_2CH_2OH \rightarrow CH_2{=}CHCH{=}CH_2 + 2\ H_2O$

Comments: First reaction occurs in liquid phase at about 90-110 C and 5 atm. with copper-bismuth catalyst. Second reaction occurs at about 40-130 C and 200-300 atm. with nickel-copper-manganese-silica catalyst. Third reaction occurs in vapor phase at about 280 C and 1 atm. over a sodium phosphate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.48	-.67	[19]
Formaldehyde	-1.11	-1.37	[19]
Hydrogen	-.07	-.08	
Butadiene	1.00	1.00	

---

71. Butadiene via dehydration/dehydrogenation of ethanol

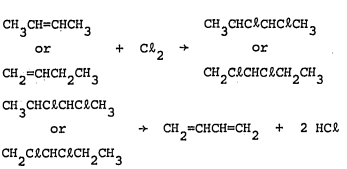
Reaction: $2\ CH_3CH_2OH \rightarrow CH_2{=}CHCH{=}CH_2 + 2\ H_2O + H_2$

Comments: Reaction occurs in vapor phase at about 400 C and 0.25 atm. over a catalyst of zinc oxide and alumina.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-1.70	-3.00	[19],[49]
Butadiene	1.00	1.00	
Hydrogen	.04	.04	

72. Butadiene via chlorination of n-butylenes

Reactions:



Comments: First reaction occurs in vapor phase at about 85 C. Second reaction occurs in vapor phase at about 500 C.

Input-Output Coefficients:	Theoretical	Model	References
n-Butylenes	-1.04	-1.70	[58]
Chlorine	-1.31	-1.50	[58]
Butadiene	1.00	1.00	
Hydrogen Chloride	1.35	1.35	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	610	1885	3050	[26]
Exogeneous Demand	--	610	1800	2625	[26],[29]

n-Butane

Aside from its use as fuel, n-butane is important primarily as a feedstock for butadiene manufacture. It can also be used to produce ethylene, acetylene, synthesis gas, acetic acid and other chemicals. Natural gas is the source of most of the n-butane consumed by the petrochemical industry; refinery gas streams account for the remainder.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply					
from natural gas	} 100	} 2000	} 6000	9200	} [24],[25]
from petroleum				2300	

n-Butanol

n-Butanol is consumed largely in the production of butyl esters, primarily the acetate, acrylate, methacrylate, phthalate, and glycol esters. Substantial quantities are also used as a solvent and in the production of amine resins.

Today most n-butanol is manufactured from n-butyraldehyde derived from the oxonation of propylene. The oxo process was commercialized in Germany during World War II and in the United States in 1948. Here it has only recently overtaken the process in which n-butanol is produced by hydrogenating crotonaldehyde derived from acetaldehyde. A process operated commercially in Japan converts propylene and carbon monoxide directly to n-butanol. In the past the fermentation of carbohydrates was used to produce most n-butanol, but today only a small fraction is so derived.

Manufacturing Processes

73. n-Butanol via hydrogenation of n-butyraldehyde

Reaction: $CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$

Comments: Reaction occurs in liquid phase at about 100 atm. with a metal oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butyraldehyde	-.97	-1.03	[17],[20]
Hydrogen	-.03	-.03	[20]
n-Butanol	1.00	1.00	

---

74. n-Butanol via hydrogenation of crotonaldehyde

Reaction: $CH_3CH{=}CHCHO + 2\ H_2 \rightarrow CH_3CH_2CH_2CH_2OH$

Comments: Reaction occurs at about 180 C and 30 atm. with nickel-chromium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Crotonaldehyde	-.95	-1.00	[17]
Hydrogen	-.05	-.05	
n-Butanol	1.00	1.00	

---

75. n-Butanol via carbonylation of propylene

Reaction: $CH_3CH{=}CH_2 + 3\ CO + 2\ H_2O \rightarrow CH_3CH_2CH_2CH_2OH + 2\ CO_2$

Comments: Reaction occurs in liquid phase at about 100 C and 16 atm. with metal carbonyl catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.57	-.75	[57]
Carbon Monoxide	-1.13	-1.50	[57]
n-Butanol	1.00	1.00	
Carbon Dioxide	1.19	1.41	
Isobutanol		.19	[57]

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from fermentation)	90	50	30	30	[20],[26], [30],[31]
Total Production (synthetic)	10	95	260	435	[24],[26]
Exogeneous Demand	100	145	290	465	[24],[26], [30],[31]

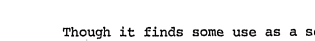
s-Butanol

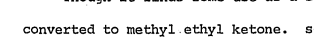
Though it finds some use as a solvent, most s-butanol is converted to methyl ethyl ketone. s-Butanol is manufactured from n-butylenes by hydration with sulfuric acid.

Manufacturing Process

76. s-Butanol via sulfonation of n-butylenes

Reactions:





Comments: Reaction occurs at about 20-35 C using 80-85% sulfuric acid.

Input-Output Coefficients:	Theoretical	Model	References
n-Butylenes	-.76	-.90	[17],[19]
s-Butanol	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	55	155	245	375	[24],[26]
Exogeneous Demand	2	8	12	35	[20],[29-31]

n-Butylenes

Aside from its fuel use (n-butylenes are fed to refinery alkylation units), most n-butylenes are dehydrogenated to butadiene. Substantial quantities are also converted to s-butanol.

Refinery cracking units are the major supplier of n-butylenes in the United States. It is also a byproduct of ethylene manufacture, and can be produced form n-butane by catalytic dehydrogenation.

Manufacturing Process

77. n-Butylenes via dehydrogenation of n-butane

Reaction:

$$CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_2{=}CHCH_2CH_3 \\ \text{or} \\ CH_3CH{=}CHCH_3 \end{matrix} + H_2$$

Comments: Reaction occurs at about 600-650 C over a chromia-alumina catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butane	-1.04	-1.50	yield estimate
n-Butylenes	1.00	1.00	based on yield
Hydrogen	.04	.05	of butadiene from n-butane

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	100	1000	1500	2300	[19],[24], [26]
Exogeneous Demand	10	75	175	400	[27-29]

n-Butyraldehyde

n-Butyraldehyde is used entirely as a chemical intermediate, primarily for n-butanol and 2-ethylhexanol. Other derivatives include butyric acid, polyvinylbutyral, and trimethylolpropane. The most important of these, butyric acid, is used primarily to produce cellulose acetate butyrate, once an important plastic in automobile manufacture.

Today most n-butyraldehyde is derived from propylene by oxonation with synthesis gas. Though this process was commercialized in Germany during World War II and in the United States in 1948, it is only within the last decade that it overtook the acetaldehyde-based process in which crotonaldehyde is hydrogenated to n-butyraldehyde. Isobutyraldehyde is produced as a byproduct when the oxonation route is employed. In the past some n-butyraldehyde was manufactured by dehydrogenating n-butanol derived from the fermentation of carbohydrates.

Manufacturing Processes

78. n-Butyraldehyde via oxonation of propylene

Reaction: $CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO$

Comments: Reaction occurs in liquid phase at about 120-150 C and 200-300 atm. using a cobalt-based catalyst. The ratio of n-butyraldehyde to isobutyraldehyde is variable from about 10:1 to 2:1.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.58	-.74	[17],[32]
Carbon Monoxide	-.39	-.60	[32]
Hydrogen	-.03	-.04	[32]
n-Butyraldehyde	1.00	1.00	
Isobutyraldehyde		.25	[32]

79. n-Butyraldehyde via hydrogenation of crotonaldehyde

Reaction: $CH_3CH{=}CHCHO + H_2 \rightarrow CH_3CH_2CH_2CHO$

Comments: Reaction occurs in vapor phase over nickel or palladium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Crotonaldehyde	-.97	-1.00	[17],[50]
Hydrogen	-.03	-.03	
n-Butyraldehyde	1.00	1.00	

---

80. n-Butyraldehyde via dehydrogenation of n-butanol

Reaction: $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHO + H_2$

Comments: Reaction occurs in vapor phase at about 280-320 C over cupric oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butanol	-1.03	-1.08	[50]
n-Butyraldehyde	1.00	1.00	
Hydrogen	.03	.03	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	10	40	60	30	[5],[26]

Calcium Acetate

Calcium acetate is produced in an obsolete process for making chloroform. It can be pyrolyzed to acetone, but this has not been practiced commercially for several decades.

Demand Data

There is no exogeneous demand, though calcium acetate may be an output of the petrochemical industry.

Calcium Chloride

Calcium chloride is produced in the chlorohydrin routes to ethylene and propylene oxide and in processes for manufacturing epichlorohydrin, perchloroethylene, and trichloroethylene. It is usually recovered from natural brines or as a byproduct of the ammonia-soda (Solvay) process for sodium carbonate. Its main use is in deicing and dust control on roads or sidewalks. It is also used in cement mixes to hasten setting.

Demand Data

There is no exogeneous demand, though calcium chloride may be an output of the industry.

Calcium Formate

Calcium formate is produced in an obsolete process for making chloroform. It can be pyrolyzed with other organic calcium salts to produce aldehydes, but this has not been practiced commercially for several decades.

Demand Data

There is no exogeneous demand, though calcium formate may be an output of the petrochemical industry.

Calcium Hydroxide

Calcium hydroxide (hydrated lime) is consumed in the chlorohydrin routes to ethylene oxide and propylene oxide and in processes for producing epichlorohydrin, perchloroethylene, and trichloroethylene. The amounts so consumed are very small compared to other demands for this chemical. The calcination of limestone is the major source of calcium hydroxide.

Supply Data

The supply of calcium hydroxide to the petrochemical industry is not constrained in the model.

Calcium Hypochlorite

Bleaching powder, a form of calcium hypochlorite, is consumed in an obsolete process for making chloroform. The reaction of lime and chlorine is the usual source of calcium hypochlorite.

Supply Data

The supply of calcium hypochlorite to the petrochemical industry is not constrained in the model.

Caprolactam

Caprolactam is the monomer for nylon 6; this is its only outlet. Most nylon 6 is used as fiber for carpets, textiles, or tires. Nylon 6 was first produced in Europe in the 1940s but did not come to the United States until the mid-1950s.

In the usual route to caprolactam, cyclohexanone reacts with hydroxylamine sulfate to form cyclohexanone oxime, which then undergoes rearrangement. Large quantities of ammonium sulfate, a low-grade fertilizer, are coproduced in the process, and can be a disposal problem, though this is apparently not the case today. Much research has been devoted to developing processes which reduce or eliminate the coproduction of ammonium sulfate. Three such processes were commercialized in the 1960s. In the United States, processes involving the nitration of cyclohexane with nitric acid and the reaction of cyclohexanone with peracetic acid were used but have since been shut down. In Japan a process in which cyclohexane is reacted with nitrosyl chloride is used. Another route to caprolactam uses toluene-derived benzoic acid as the feedstock; this is operated in Italy. This process offers no significant reduction in ammonium sulfate production.

Manufacturing Processes

81. Caprolactam via reaction of cyclohexanone and hydroxylamine

Reactions: $C_6H_{10}O + NH_2OH \rightarrow C_6H_{10}NOH + H_2O$

$C_6H_{10}NOH \rightarrow CO(CH_2)_5NH$

Comments: The sulfate salt of hydroxylamine is usually used in the first reaction; thus ammonium sulfate is coproduced with the oxime. The hydroxylamine sulfate is usually produced from ammonia, sulfur, carbon dioxide, and air in a multistep process. Other schemes produce hydroxylamine from ammonia, hydrogen, and air. The second reaction occurs at about 120 C in the presence of sulfuric acid (oleum). The reactor effluent is neutralized with ammonia, so ammonium sulfate is coproduced.

Input-Output Coefficients:	Model	References
Cyclohexanone	-.89	[32]
Ammonia	-1.46	[32]
Sulfur	-.68	[32]
Carbon Dioxide	-.52	[32]
Sulfuric Acid	-1.35	[32]
Caprolactam	1.00	
Ammonium Sulfate	4.50	[5],[29],[32]

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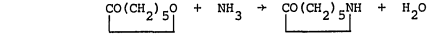
82. Caprolactam via reaction of cyclohexanone and peracetic acid

Reactions:



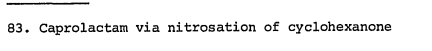
Comments: First reaction occurs in liquid phase at about 25-50 C and 1 atm. Second reaction occurs in liquid phase at about 300-450 C and 300-400 atm.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexanone	-.87	-.95	[17]
Peracetic Acid	-.67	-.96	[17]
Ammonia	-.15	-.18	
Caprolactam	1.00	1.00	
Acetic Acid	.53	1.10	[17]

---

83. Caprolactam via nitrosation of cyclohexanone

Reactions:



Comments: First reaction occurs at about 20 C under influence of actinic light. The nitrosyl chloride is formed in a multistep process using ammonia, oxygen, and hydrogen chloride. Second reaction occurs in the presence of sulfuric acid (oleum). The reactor effluent is neutralized with ammonia so ammonium sulfate is coproduced.

Input-Output Coefficients:	Model	References
Cyclohexane	-.95	[17],[18]
Ammonia	-1.00	[18]
Sulfuric Acid	-1.70	[18]
Caprolactam	1.00	
Ammonium Sulfate	2.20	[29]

---

84. Caprolactam via hydrogenation of benzoic acid

Reactions: $C_6H_5COOH + 3\ H_2 \rightarrow C_6H_{11}COOH$

$C_6H_{11}COOH + SO_2(OH)ONO \rightarrow \underbrace{CO(CH_2)_5NH} + H_2SO_4 + CO_2$

Comments: First reaction occurs at about 150 C and 10 atm. using a palladium catalyst. Second occurs at about 80 C. The nitrosyl sulfuric acid is produced from ammonia, air, and sulfuric acid. The reactor effluent is neutralized with ammonia so the sulfuric acid is converted to ammonium sulfate.

Input-Output Coefficients:	Model	References
Benzoic Acid	-1.32	[17],[45]
Hydrogen	-.07	[45]
Ammonia	-1.30	[45]
Sulfuric Acid	-3.00	[45]
Caprolactam	1.00	
Ammonium Sulfate	4.20	[45]
Carbon Dioxide	.39	

---

85. Caprolactam via nitration of cyclohexane

Reactions: $C_6H_{12} + HNO_3 \rightarrow C_6H_{11}NO_2 + H_2O$

$C_6H_{11}NO_2 + H_2 \rightarrow C_6H_{10}NOH + H_2O$

$C_6H_{10}NOH \rightarrow \underbrace{CO(CH_2)_5NH}$

Comments: First reaction occurs at about 120 C and 4 atm. using 30% nitric acid. Second reaction occurs at about 100-150 C and 3 atm. over a zinc-chromium catalyst. Third reaction occurs in the presence of sulfuric acid (oleum). The reactor effluent is neutralized with ammonia so ammonium sulfate is coproduced.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexane	-.74	-1.30	[17]
Nitric Acid	-.56	-.70	
Hydrogen	-.02	-.03	
Ammonia		-.65	
Sulfuric Acid		-1.90	
Caprolactam		1.00	
Ammonium Sulfate		2.50	[29]
Adipic Acid		.30	[17]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	50	500	[32]
Exogeneous Demand	--	--	50	500	[32]

Carbon

Substantial quantities of elemental carbon (as coke) are still consumed in producing acetylene via calcium carbide. In other applications, such as the production of carbon disulfide, hydrogen cyanide, and synthesis gas, methane or other hydrocarbons have replaced carbon as the feedstock.

Supply Data

The supply of carbon to the petrochemical industry is not constrained in the model.

Carbon Dioxide

Carbon dioxide is produced from carbon monoxide when the water-gas shift reaction is used to remove the carbon monoxide from the synthesis gas for ammonia production. Frequently the ammonia manufacturer uses this carbon dioxide to produce urea. The off-gases from various other petrochemical processes also contain carbon dioxide. The production of dry ice and carbonated beverages accounts for most of the demand for carbon dioxide. The amounts so consumed are produced primarily by the combustion of fuels. Carbon dioxide is also produced from limestone, recovered from fermentation processes, and drawn from natural wells.

Demand Data

Carbon dioxide is not considered a petrochemical product in the model; thus there is no exogeneous demand, though carbon dioxide may be an output of the industry.

Carbon Disulfide

Most carbon disulfide is used in the production of viscose rayon and cellophane. Substantial quantities are also converted to carbon tetrachloride. Among various other derivatives are fungicides, rubber accelerators, and ore flotation reagents.

For many years carbon disulfide was derived from charcoal and sulfur. This process has now been almost entirely replaced by one which combines methane and sulfur.

Manufacturing Processes

86. Carbon disulfide via reaction of methane and sulfur

Reactions:

$$CH_4 + 4\,S \rightarrow CS_2 + 2\,H_2S$$

$$\tfrac{2}{3}\,H_2S + O_2 \rightarrow \tfrac{2}{3}\,SO_2 + \tfrac{2}{3}\,H_2O$$

$$\tfrac{4}{3}\,H_2S + \tfrac{2}{3}\,SO_2 \rightarrow 2\,S + \tfrac{4}{3}\,H_2O$$

Comments: First reaction occurs in vapor phase at about 1250 F and 30-40 psia over an activated alumina or clay catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.21	-.23	[17],[20]
Sulfur	-.84	-.93	[20]
Carbon Disulfide	1.00	1.00	

---

87. Carbon disulfide via reaction of charcoal and sulfur

Reaction: $C\ (charcoal) + 2\,S \rightarrow CS_2$

Comments: Reaction occurs at about 800-1000 C in a retort or electric furnace.

Input-Output Coefficients:	Theoretical	Model	References
Carbon	-.16	-.32	[17],[20]
Sulfur	-.84	-.92	[20]
Carbon Disulfide	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	200	425	525	720	[24],[26], [30]
Exogeneous Demand	150	360	450	520	[5],[20], [26],[28-31]

Carbon Monoxide

Carbon monoxide is produced along with hydrogen in the steam reforming or partial oxidation of hydrocarbons. It is used almost entirely as a feedstock for producing methanol, acetic acid, n-butyraldehyde, and other chemicals.

Supply and Demand Data

It is assumed that all carbon monoxide is produced within the petrochemical industry; thus there is no exogeneous supply. Exogeneous demand is negligible.

Carbon Tetrachloride

Most carbon tetrachloride is converted to dichlorofluoromethane and trichlorofluoromethane for use as a refrigerant or as a propellant in aerosol formulations. Carbon tetrachloride is also used as a grain fumigant and has various uses as a solvent.

The two most important routes to carbon tetrachloride are the chlorination of methane and the chlorination of carbon disulfide. Both have been practiced for many years, but until fairly recently the carbon disulfide process was dominant. Substantial quantities are also produced by the chlorinolysis of hydrocarbons or chlorohydrocarbons, usually ethane, propane, propylene, or propylene dichloride. The chlorinolysis is usually directed toward perchloroethylene manufacture; in this case carbon tetrachloride occurs as a byproduct and may be converted to more perchloroethylene. However, chlorinolysis processes have also been used to produce carbon tetrachloride as the main product with perchloroethylene as a byproduct. Methyl chloride derived from methanol can also be chlorinated to carbon tetrachloride.

Manufacturing Processes

88. Carbon tetrachloride via chlorination of methane

Reaction: $CH_4 + 4\ C\ell_2 \rightarrow CC\ell_4 + 4\ HC\ell$

Comments: This is a flexible process which can be used to produce any chloromethane or mixture thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.10	-.11	[17]
Chlorine	-1.85	-1.95	
Carbon Tetrachloride	1.00	1.00	
Hydrogen Chloride	.95	.95	

---

89. Carbon tetrachloride via chlorination of carbon disulfide

Reactions: $CS_2 + 3\ C\ell_2 \rightarrow CC\ell_4 + S_2C\ell_2$

$\frac{1}{2}\ CS_2 + S_2C\ell_2 \rightarrow \frac{1}{2}\ CC\ell_4 + 3\ S$

Comments: First reaction occurs in liquid phase at about 30 C with an iron catalyst. Second reaction occurs in liquid phase at about 60 C.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Disulfide	-.49	-.55	[5],[17],[20]
Chlorine	-.92	-1.15	[20]
Carbon Tetrachloride	1.00	1.00	
Sulfur	.42	.42	

---

90. Carbon tetrachloride via chlorinolysis of propane

Reaction (not balanced): $CH_3CH_2CH_3 + C\ell_2 \rightarrow CC\ell_4 + CC\ell_2{=}CC\ell_2 + HC\ell$

Comments: This is a flexible process that can also be operated to produce a predominance of perchloroethylene.

Input-Output Coefficients:	Model	References
Propane	-.19	[46]
Chlorine	-2.56	[46]
Carbon Tetrachloride	1.00	
Perchloroethylene	.43	[46]
Hydrogen Chloride	1.20	[46]

---

91. Carbon tetrachloride via chlorinolysis of propylene dichloride

Reaction (not balanced): $CH_3CHC\ell CH_2C\ell + C\ell_2 \rightarrow CC\ell_4 + CC\ell_2{=}CC\ell_2 + HC\ell$

Comments: This is a flexible process that can also be operated to produce a predominance of perchloroethylene.

Input-Output Coefficients:	Model	References
Propylene Dichloride	-.50	estimate of yields based on
Chlorine	-1.97	yields for chlorinolysis of
Carbon Tetrachloride	1.00	propylene
Perchloroethylene	.43	
Hydrogen Chloride	.90	

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92. Carbon tetrachloride via chlorination of methyl chloride

Reaction: $CH_3C\ell + 3\ C\ell_2 \rightarrow CC\ell_4 + 3\ HC\ell$

Comments: This is a flexible process that can be operated to produce methylene dichloride, chloroform, carbon tetrachloride, or mixtures thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methyl Chloride	-.33	-.36	estimate of yield
Chlorine	-1.38	-1.45	based on yield for
Carbon Tetrachloride	1.00	1.00	chlorination of
Hydrogen Chloride	.71	.71	methane

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93. Carbon tetrachloride via chlorinolysis of ethane

Reaction (not balanced): $CH_3CH_3 + C\ell_2 \rightarrow CC\ell_4 + CC\ell_2{=}CC\ell_2 + HC\ell$

Comments: This is a flexible process that can also be operated to produce a predominance of perchloroethylene.

Input-Output Coefficients:	Model	References
Ethane	-.19	estimate of yields based on
Chlorine	-2.57	yields for chlorinolysis of
Carbon Tetrachloride	1.00	propane
Perchloroethylene	.43	
Hydrogen Chloride	1.20	

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94. Carbon Tetrachloride via chlorinolysis of propylene

Reaction (not balanced): $CH_3CH{=}CH_2 + C\ell_2 \rightarrow CC\ell_4 + CC\ell_2{=}CC\ell_2 + HC\ell$

Comments: This is a flexible process that can also be operated to produce a predominance of perchloroethylene.

Input-Output Coefficients:	Model	References
Propylene	-.19	[46]
Chlorine	-2.27	[46]
Carbon Tetrachloride	1.00	
Perchloroethylene	.43	[46]
Hydrogen Chloride	.90	[46]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	100	215	370	1010	[24],[26]
Exogeneous Demand	90	110	90	50	[5],[20], [28-31]

(Note: Published production statistics apparently do not include carbon tetrachloride produced by chlorinolysis and converted immediately to perchloroethylene.)

Chlorine

Chlorine is consumed in the production of several large-volume petrochemicals, including vinyl chloride, trichloroethylene, perchloroethylene, and carbon tetrachloride. In addition there are chemicals such as propylene oxide, ethylene oxide, and adiponitrile, which contain no chlorine, but which are or have been manufactured using processes requiring chlorine. The petrochemical industry is the largest single outlet for chlorine.

Most chlorine is derived from the electrolysis of sodium chloride. Sodium chloride generated as a coproduct in the petrochemical industry can be recycled to produce additional chlorine.

Manufacturing Process

95. Chlorine via electrolysis of sodium chloride

Reaction: $2\ NaCl + 2\ H_2O \rightarrow Cl_2 + 2\ NaOH + H_2$

Input-Output Coefficients	Theoretical	Model	References
Sodium Chloride	-1.65	-1.83	[20]
Chlorine	1.00	1.00	
Sodium Hydroxide	1.13	1.14	[20]
Hydrogen	.03	.03	[20]

Supply Data

The supply of chlorine to the petrochemical industry is not constrained in the model.

Chlorobenzene

Historically the major use for chlorobenzene has been in the manufacture of phenol. However, the processes producing phenol from chlorobenzene have now largely been replaced; thus the production of chlorobenzene has declined in recent years. Restrictions on the use of DDT, another major chlorobenzene derivative, have contributed to this decline. Other outlets for chlorobenzene include the synthesis of intermediates for the production of dyes and pesticides.

Chlorobenzene can be produced by the chlorination or oxychlorination of benzene. Both processes have been used on a very large scale, though the oxychlorination process was used only in connection with phenol production and has now been abandoned.

Manufacturing Processes

96. Chlorobenzene via chlorination of benzene

Reaction: $C_6H_6 + C\ell_2 \rightarrow C_6H_5C\ell + HC\ell$

Comments: Reaction occurs in liquid phase at about 25-60 C using an iron or iron chloride catalyst. Some dichlorobenzene is also produced.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.69	-.95	[20]
Chlorine	-.63	-.87	[20]
Chlorobenzene	1.00	1.00	
Hydrogen Chloride	.32	.32	

---

97. Chlorobenzene via oxychlorination of benzene

Reaction: $C_6H_6 + HC\ell + \frac{1}{2} O_2 \rightarrow C_6H_5C\ell + H_2O$

Comments: Reaction occurs in vapor phase at about 200-230 C over a copper-iron catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.69	-.82	[20]
Hydrogen Chloride	-.32	-.36	
Chlorobenzene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	100	385	605	485	[24],[26]
Exogeneous Demand	10	90	210	200	[20],[30], [31]

Chloroform

Most chloroform is used to produce fluorocarbons, primarily chlorodifluoromethane (fluorocarbon 22), a refrigerant and aerosol propellant, and tetrafluoroethylene, a monomer for fluorocarbon resins such as Teflon. Chloroform is also used as a solvent, especially in the pharmaceutical industry.

Today most chloroform is produced by chlorinating methane. The chlorination of methyl chloride derived from methanol is also practiced. The first commercially important process was the treatment of ethanol with bleaching powder. Later acetone replaced ethanol as the preferred feedstock in this type of process. The bleaching powder route was important until the early-1950s. Some chloroform has also been made commercially by the reduction of carbon tetrachloride with iron.

Manufacturing Processes

98. Chloroform via chlorination of methane

Reaction: $CH_4 + 3\ Cl_2 \rightarrow CHCl_3 + 3\ HCl$

Comments: This is a flexible process that can be used to produce any chloromethane or mixture thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.13	-.14	[17]
Chlorine	-1.79	-1.90	
Chloroform	1.00	1.00	
Hydrogen Chloride	.92	.92	

---

99. Chloroform via reaction of acetone and bleaching powder

Reaction: $CH_3COCH_3 + 3\ CaOCl_2 \rightarrow CHCl_3 + \frac{1}{2}\ Ca(CH_3COO)_2 + Ca(OH)_2 + \frac{3}{2}\ CaCl_2$

Comments: Reaction occurs in liquid phase at about 130-150 C.

Input-Output Coefficients:	Theoretical	Model	References
Acetone	-.49	-.55	[20]
Calcium Hypochlorite	-3.19	-5.36	[20]
Chloroform	1.00	1.00	
Calcium Hydroxide	.62	.62	
Calcium Chloride	1.40	2.80	
Calcium Acetate	.66	.66	

---

100. Chloroform via reaction of ethanol and bleaching powder

Reaction: $\frac{2}{3}\ CH_3CH_2OH + \frac{8}{3}\ CaOCl_2 \rightarrow CHCl_3 + \frac{1}{6}\ Ca(CHOO)_2 + \frac{4}{3}\ Ca(OH)_2 + \frac{7}{6}\ CaCl_2$

Comments: The process is similar to the process producing chloroform from acetone and bleaching powder.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-.26	-.73	[20]
Calcium Hypochlorite	-2.84	-8.32	[20]
Chloroform	1.00	1.00	
Calcium Formate	.18	.18	
Calcium Hydroxide	.83	.83	
Calcium Chloride	1.09	5.10	

---

101. Chloroform via chlorination of methyl chloride

Reaction: $CH_3Cl + 2\ Cl_2 \rightarrow CHCl_3 + 2\ HCl$

Comments: This is a flexible process that can be used to produce methylene dichloride, chloroform, carbon tetrachloride, or mixtures thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methyl Chloride	-.42	-.44	estimate of yield
Chlorine	-1.19	-1.25	based on yield for
Chloroform	1.00	1.00	chlorination of
Hydrogen Chloride	.61	.61	methane

---

102. Chloroform via reduction of carbon tetrachloride

Reaction: $CCl_4 + \frac{7}{8}\ Fe + \frac{1}{2}\ H_2O \rightarrow CHCl_3 + \frac{1}{8}\ Fe_3O_4 + \frac{1}{2}\ FeCl_2$

Comments: Reaction occurs at about 15 C in the presence of hydrogen chloride.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Tetrachloride	-1.29	-1.73	[31]
Iron	-.41	-1.38	[31]
Chloroform	1.00	1.00	
Iron Oxide	.24	1.10	
Iron (II) Chloride	.53	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	3	20	75	240	[24],[26]
Exogeneous Demand	3	20	75	240	[24],[26]

Chloroprene

Essentially all chloroprene is converted to polychloroprene (neoprene), the first commercially successful synthetic rubber. From 1932, when production began, until 1970, nearly all chloroprene produced in the United States was derived from acetylene. Today, however, this route is virtually obsolete, chloroprene now being derived from butadiene. The butadiene route was commercialized in France in the early-1960s; once it was adopted in the United States the swing away from the acetylene route was rapid.

Manufacturing Processes

103. Chloroprene via chlorination of butadiene

Reactions:

$$CH_2{=}CHCH{=}CH_2 + Cl_2 \rightarrow CH_2{=}CHCHCl{-}CH_2Cl$$

$$CH_2{=}CHCHCl{-}CH_2Cl + NaOH \rightarrow CH_2{=}CCl{-}CH{=}CH_2 + NaCl + H_2O$$

Comments: First reaction occurs in vapor phase at about 300-420 C and 1 atm. 1,4-dichloro-2-butene occurs as a byproduct; this is isomerized to the isomer desired for the second reaction using a catalyst of copper and cuprous chloride. Second reaction occurs at about 85 C.

Input-Output Coefficients:	Theoretical	Model	References
Butadiene	-.61	-.80	[17]
Chlorine	-.80	-.90	
Sodium Hydroxide	-.45	-.50	
Chloroprene	1.00	1.00	
Sodium Chloride	.66	.66	

---

104. Chloroprene via dimerization of acetylene

Reactions:

$$2\ CH{\equiv}CH \rightarrow CH_2{=}CH{-}C{\equiv}CH$$

$$CH_2{=}CH{-}C{\equiv}CH + HCl \rightarrow CH_2{=}CCl{-}CH{=}CH_2$$

Comments: First reaction occurs in liquid phase at about 50-75 C with a catalyst of cuprous chloride and ammonium chloride. Second reaction occurs in liquid phase at about 30-60 C using the same catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.59	-.75	[5],[17]
Hydrogen Chloride	-.41	-.45	
Chloroprene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	10	130	300	370	[5],[27],[28]
Exogeneous Demand	10	130	300	370	[5],[27],[28]

Cresylic Acid

The term cresylic acid refers to mixtures of cresols and xylenols. Cresylic acid and cresols are used primarily for the production of phenolic resins and phosphate esters such as tricresyl phosphate. They are also used as solvents and for miscellaneous chemical synthesis.

Synthetic production of cresylic acid and cresols did not become important until the 1960s, when demand began to exceed the amounts being recovered from coal tar and refinery streams. In the United States the methylation of phenol is the major synthetic process. In a process important in Japan, toluene and propylene react to form cymene, which can then be oxidized to cresylic acid. This is analogous to the cumene process for phenol. Small quantities of cresylic acid have been derived from toluene via sulfonation in a process similar to the benzene sulfonation process for phenol.

Manufacturing Processes

105. Cresylic acid via methylation of phenol

Reaction (not balanced): $C_6H_5OH + CH_3OH \rightarrow$ mixture of cresols and xylenols

Comments: Reaction occurs at about 250 C over an alumina catalyst.

Input-Output Coefficients:	Model	References
Phenol	-.87	[18]
Methanol	-.36	[18]
Cresylic Acid	1.00	

---

106. Cresylic acid via reaction of toluene and propylene

Reactions (not balanced): $C_6H_5CH_3 + CH_3CH{=}CH_2 \rightarrow CH_3C_6H_4CH(CH_3)_2$

$CH_3C_6H_4CH(CH_3)_2 + O_2 \rightarrow$ mixture of cresols and xylenols

Comments: First reaction occurs over phosphoric acid-clay catalyst. Cresols are the main product of the second reaction.

Input-Output Coefficients:	Model	References
Toluene	-.95	[18]
Propylene	-.48	[18]
Cresylic Acid	1.00	
Acetone	.54	[18]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand (synthetic)	--	--	--	100	[18]

Crotonaldehyde

Essentially all crotonaldehyde is converted to n-butanol or n-butyraldehyde. Crotonaldehyde is manufactured commercially from acetaldehyde via the aldol condensation reaction.

Manufacturing Process

107. Crotonaldehyde via dimerization of acetaldehyde

Reactions: $2\ CH_3CHO \rightarrow CH_3CHOHCH_2CHO$

$CH_3CHOHCH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$

Comments: First reaction occurs at about 5-25 C in the presence of an alkaline catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-1.26	-1.35	[17],[19]
Crotonaldehyde	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Cumene

Today cumene is used almost entirely for phenol production. During World War II large quantities of cumene were manufactured for use in aviation gasoline. All cumene is produced by alkylating benzene with propylene.

Manufacturing Process

108. Cumene via reaction of benzene and propylene

Reaction: $C_6H_6 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH(CH_3)_2$

Comments: Reaction occurs in vapor phase at about 250 C and 100 psi with a phosphoric acid catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.65	-.79	[17]
Propylene	-.35	-.41	[17]
Cumene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	250	1980	[24],[26]
Exogeneous Demand	--	--	--	--	

Cyclohexane

Most cyclohexane is oxidized to cyclohexanol and cyclohexanone, which are subsequently converted to adipic acid for nylon 66 manufacture and caprolactam for nylon 6 manufacture. Substantial quantities of cyclohexane are exported. Cyclohexane is manufactured by the hydrogenation of benzene. In addition there is a supply of cyclohexane obtained directly from petroleum by fractionation.

Manufacturing Process

109. Cyclohexane via hydrogenation of benzene

Reaction: $C_6H_6 + 3\,H_2 \rightarrow C_6H_{12}$

Comments: Reaction occurs in liquid phase at about 170-230 C and 20-40 atm. using a nickel catalyst. Alternatively, the reaction may occur in the vapor phase at about 35 atm. over a noble metal catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.93	-.93	[5],[17]
Hydrogen	-.07	-.08	[5]
Cyclohexane	1.00	1.00	

Supply and Demand Data (in million of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from petroleum)	--	80	240	400	[18],[24], [26],[59]
Production (from benzene)	--	120	320	1420	[18],[24], [26],[59]
Exogeneous Demand	--	150	200	600	[5],[29], [59]

Cyclohexanol

Cyclohexanol is used almost entirely for the production of adipic acid and caprolactam for eventual consumption as nylon. A mixture of cyclohexanol and cyclohexanone is suitable for adipic acid manufacture. If used for caprolactam production, cyclohexanol must first be dehydrogenated to cyclohexanone.

Most cyclohexanol is derived from cyclohexane by oxidation. Cyclohexanone is coproduced in this process. In a fairly recent development, this oxidation is carried out in the presence of boric acid, thereby increasing the overall yield of cyclohexanol and cyclohexanone. Cyclohexanol was originally derived from phenol. Although this process gave way to the cyclohexane route in the 1940s, it is still used and cannot be regarded as obsolete.

Manufacturing Processes

110. Cyclohexanol via oxidation of cyclohexane

Reaction: $C_6H_{12} + \frac{1}{2} O_2 \rightarrow C_6H_{11}OH$

Comments: Reaction occurs in liquid phase at about 140-165 C and 8-12 atm. using a catalyst of manganese and cobalt acetates or cobalt naphthenate

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexane	-.84	-2.00	[5],[17]
Cyclohexanol	1.00	1.00	
Cyclohexanone		.67	[60]

---

111. Cyclohexanol via hydrogenation of phenol

Reaction: $C_6H_5OH + 3 H_2 \rightarrow C_6H_{11}OH$

Comments: Reaction occurs in liquid phase at about 150 C and 15 atm. using a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Phenol	-.94	-.98	[17]
Hydrogen	-.06	-.06	
Cyclohexanol	1.00	1.00	

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112. Cyclohexanol via oxidation of cyclohexane (boron-assisted)

Reaction: $C_6H_{12} + \frac{1}{2} O_2 \rightarrow C_6H_{11}OH$

Comments: Reaction occurs in liquid phase at about 155-170 C and 8-10 atm. in the presence of boric acid.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexane	-.84	-1.03	[5],[19],[29],[45]
Cyclohexanol	1.00	1.00	
Cyclohexanone		.11	[19],[29]

Demand Data

There is essentially no exogeneous demand.

Cyclohexanone

Virtually all cyclohexanone is used to produce adipic acid and caprolactam, both of which are monomers for nylon manufacture. A mixture of cyclohexanone and cyclohexanol is suitable for adipic acid production.

Most cyclohexanone is obtained as a coproduct with cyclohexanol from the oxidation of cyclohexane. Significant quantities are also produced from cyclohexanol by dehydrogenation and from phenol by hydrogenation. These two routes account for much of the cyclohexanone converted to caprolactam.

Manufacturing Processes

113. Cyclohexanone via dehydrogenation of cyclohexanol

Reaction: $C_6H_{11}OH \rightarrow C_6H_{10}O + H_2$

Comments: Reaction occurs in vapor phase at about 400-450 C over a zinc-iron catalyst. Alternatively, reaction may oocur in liquid phase at about 200 C with a cupric chromite catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Cyclohexanol	-1.02	-1.05	[17]
Cyclohexanone	1.00	1.00	
Hydrogen	.02	.02	

---

114. Cyclohexanone via hydrogenation of phenol

Reaction: $C_6H_5OH + 2\ H_2 \rightarrow C_6H_{10}O$

Comments: Reaction occurs over a palladium catalyst.

Input-Ouput Coefficients:	Theoretical	Model	References
Phenol	-.96	-.98	[17]
Hydrogen	-.04	-.04	
Cyclohexanone	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Dichlorodifluoromethane

Most dichlorodifluoromethane (fluorocarbon 12) is used either as a refrigerant or as a propellant in aerosol formulations. Its use as a propellant is currently the subject of some controversy (see p. 62). Fluorocarbon 12 is produced by the reaction of carbon tetrachloride and hydrogen fluoride. There has been some interest recently in processes that simultaneously chlorinate and fluorinate methane to mixtures of chlorofluoromethanes.

Manufacturing Process

115. Dichlorodifluoromethane via reaction of carbon tetrachloride and hydrogen fluoride

Reaction: $CC\ell_4 + 2\ HF \rightarrow CC\ell_2F_2 + 2\ HC\ell$

Comments: Reaction occurs in liquid phase at about 80 C and 115 psi with antimony pentachloride catalyst. Trichlorofluoromethane can be coproduced.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Tetrachloride	-1.27	-1.60	[20]
Hydrogen Fluoride	-.33	-.41	[20]
Dichlorodifluoromethane	1.00	1.00	
Hydrogen Chloride	.60	.60	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	15	80	165	375	[24],[26], [31]
Exogeneous Demand	15	80	165	375	[24],[26], [31]

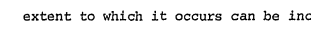
Diethylene Glycol

The major use for diethylene glycol is the production of polyurethane and unsaturated polyester resins. Other important outlets are triethylene glycol production, natural gas dehydration, textile dyeing, solvent extraction, and plasticizer and surfactant manufacture.

Diethylene glycol is produced as a byproduct when ethylene oxide is hydrated to ethylene glycol. The quantities so produced have been sufficient to satisfy the demand. Should additional diethylene glycol be required it can be produced by reacting ethylene oxide and ethylene glycol. It is this reaction that is responsible for the formation of byproduct diethylene glycol; the extent to which it occurs can be increased by decreasing the water to ethylene oxide ratio in the feed to the hydration process.

Manufacturing Process

116. Diethylene glycol via reaction of ethylene glycol and ethylene oxide

Reaction: 

Comments: This reaction is responsible for the formation of byproduct diethylene glycol when ethylene oxide is hydrated to ethylene glycol; the extent to which it occurs can be increased by decreasing the water to ethylene oxide ratio in the feed to the hydration process. Alternatively, ethylene glycol can first be searated and then reacted with ethylene oxide.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Oxide	-.42	-.50	estimate of yield
Ethylene Glycol	-.58	-.70	based on yield for
Diethylene Glycol	1.00	1.00	hydration of ethylene oxide to ethylene glycol

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	10	40	100	340	[24],[26]
Exogeneous Demand	10	40	100	340	[24],[26]

Dimethyl Terephthalate

Dimethyl terephthalate (DMT) is used almost entirely for the production of polyethylene terephthalate, a polyester first prepared commercially in the United States in the early-1950s. Until the mid-1960s all polyethylene terephthalate was manufactured from DMT and ethylene. Today terephthalic acid is gradually displacing DMT as the preferred monomer for polyethylene terephthalate production.

DMT was first prepared commercially by esterifying terephthalic acid. Later a stepwise oxidation and esterification starting with p-xylene was developed. As of the early 1970s more DMT was manufactured via the direct esterification route, though the alternative was also operated on a very large scale.

Manufacturing Processes

117. Dimethyl terephthalate via esterification of terephthalic acid

Reaction: $C_6H_4(COOH)_2 + 2\ CH_3OH \rightarrow C_6H_4(COOCH_3)_2 + 2\ H_2O$

Comments: Reaction is acid-catalyzed.

Input-Output Coefficients:	Theoretical	Model	References
Terephthalic Acid	-.86	-.87	[45]
Methanol	-.33	-.34	[45]
Dimethyl Terephthalate	1.00	1.00	

---

118. Dimethyl terephthalate via reaction of methanol and p-xylene

Reactions:

$$C_6H_4(CH_3)_2 + \frac{3}{2}\ O_2 \rightarrow CH_3C_6H_4COOH + H_2O$$

$$CH_3C_6H_4COOH + CH_3OH \rightarrow CH_3C_6H_4COOCH_3 + H_2O$$

$$CH_3C_6H_4COOCH_3 + \frac{3}{2}\ O_2 \rightarrow COOHC_6H_4COOCH_3 + H_2O$$

$$COOHC_6H_4COOCH_3 + CH_3OH \rightarrow C_6H_4(COOCH_3)_2 + H_2O$$

Comments: First reaction occurs in liquid phase at about 165 C and 65 psig using a catalyst of cobalt acetate or naphthenate. Second and fourth reactions are acid-catalyzed. Third reaction occurs in liquid phase at about 200 C and 400 psig with a cobalt acetate or naphthenate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
p-Xylene	-.55	-.68	[5],[17-19]
Methanol	-.33	-.44	[5],[18]
Dimethyl Terephthalate	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	150	1450	[24],[26]
Exogeneous Demand	--	--	150	1450	[24],[26]

Dinitrotoluene

The only major market for dinitrotoluene is the production of toluene diamine for conversion to toluene diisocyanate. The latter is used to produce polyurethane plastics. Dinitrotoluene is manufactured by nitrating toluene with nitric acid. An 80:20 mixture of the 2,4 and 2,6 isomers is the usual commercial product.

Manufacturing Process

119. Dinitrotoluene via nitration of toluene

Reactions: $CH_3C_6H_5 + HNO_3 \rightarrow CH_3C_6H_4NO_2 + H_2O$

$CH_3C_6H_4NO_2 + HNO_3 \rightarrow CH_3C_6H_3(NO_2)_2 + H_2O$

Comments: First reaction occurs at about 40 C in the presence of sulfuric acid. The second reaction requires stronger acid and occurs at about 50-55 C. The usual product is an 80:20 mixture of the 2,4 and 2,6 isomers.

Input-Output Coefficients:	Theoretical	Model	References
Toluene	-.51	-.54	[17]
Nitric Acid	-.69	-1.30	[5]
Dinitrotoluene	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Epichlorohydrin

Once important only as an intermediate for synthetic glycerin production, epichlorohydrin is now also important as a raw material for the manufacture of epoxy resins. These two uses account for nearly all epichlorohydrin produced.

Since 1948, when it was first produced on a large scale, most epichlorohydrin has been derived from allyl chloride. The conversion of allyl alcohol to epichlorohydrin has also been practiced commercially.

Manufacturing Processes

120. Epichlorohydrin via chlorohydration of allyl chloride

Reactions:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$CH_2{=}CHCH_2Cl + HOCl \rightarrow CH_2ClCHOHCH_2Cl$$

$$CH_2ClCHOHCH_2Cl + \tfrac{1}{2}\,Ca(OH)_2 \rightarrow \underset{\underset{O}{\lfloor\rfloor}}{CH_2CHCH_2Cl} + \tfrac{1}{2}\,CaCl_2 + H_2O$$

Comments: Second reaction occurs in aqueous phase at about 85-100 F. Third reaction occurs in dilute aqueous phase.

Input-Output Coefficients:	Theoretical	Model	References
Chlorine	-.77	-.96	[5]
Allyl Chloride	-.83	-1.04	[5]
Calcium Hydroxide	-.40	-.50	
Epichlorohydrin	1.00	1.00	
Calcium Chloride	.60	.60	
Hydrogen Chloride	.39	.39	

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121. Epichlorohydrin via chlorination of allyl alcohol

Reactions:

$$CH_2{=}CHCH_2OH + Cl_2 \rightarrow CH_2ClCHClCH_2OH$$

$$CH_2ClCHClCH_2OH + NaOH \rightarrow \underset{\underset{O}{\lfloor\rfloor}}{CH_2CHCH_2Cl} + NaCl + H_2O$$

Comments: First reaction occurs in liquid phase at about 15 C.

Input-Output Coefficients:	Theoretical	Model	References
Allyl Alcohol	-.63	-.80	[5]
Chlorine	-.77	-.96	[5]
Sodium Hydroxide	-.43	-.54	
Epichlorohydrin	1.00	1.00	
Sodium Chloride	.63	.63	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	40	150	300	[26]
Exogeneous Demand	--	--	50	130	[26],[5]

Ethane

Ethane is important primarily as a feedstock for ethylene manufacture, though it can also be used to produce acetylene, synthesis gas, and chlorinated solvents such as methyl chloroform and perchloroethylene. Natural gas is the source of most of the ethane consumed by the petrochemical industry; refinery gas streams account for the remainder.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply					
from natural gas	} 150	} 600	} 3200	10200	} [25]
from refineries				1300	

Ethanol

Ethanol is a versatile solvent and chemical intermediate. As a solvent it is used primarily in surface coatings, hair and scalp preparations, cosmetics, and pharmaceuticals. Ethanol was once used primarily as an intermediate for acetaldehyde, but this is no longer a major market as ethylene is now converted directly to acetaldehyde. Ethyl acetate, ethyl acrylate, ethylene glycol monoethyl ether, and other esters and ethers account for most of the demand for ethanol as a chemical intermediate.

Today most ethanol is produced by the direct catalytic hydration of ethylene, a process first commercialized in the late-1940s. Until the mid-1960s, however, most synthetic ethanol was produced from ethylene via ethyl sulfate. Before 1930 all industrial ethanol was manufactured by fermentation. Although some is still so produced, since the mid-1940s most has been derived synthetically from ethylene.

Manufacturing Processes

122. Ethanol via hydration of ethylene

Reaction: $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$

Comments: Reaction occurs in vapor phase at about 300 C and 68 atm. over a phosphoric acid catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.61	-.66	[5],[17],[19],
Ethanol	1.00	1.00	[20],[45]

123. Ethanol via sulfonation of ethylene

Reactions: $CH_2=CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_2OH$

$CH_3CH_2OSO_2OH + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$

Comments: First reaction occurs at about 55-75 C and 225-350 psi using 96% sulfuric acid. Second reaction occurs at about 70 C. Some ethyl ether is produced as a byproduct.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.61	-.68	[5],[19]
Ethanol	1.00	1.00	

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from fermentation)	600	380	160	100	[18],[26]
Production (from ethylene)	200	650	1550	1960	[18],[24], [26]
Exogeneous Demand	480	330	560	1060	[26],[29]

Ethyl Acetate

Ethyl acetate is used almost entirely as a solvent, primarily for coatings. It is produced commercially from acetic acid by esterification with ethanol. Another process used commercially employs the so-called Tischtschenko reaction to produce ethyl acetate from acetaldehyde.

Manufacturing Processes

124. Ethyl acetate via esterification of acetic acid

Reaction: $CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$

Comments: The reaction is acid-catalyzed.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-.52	-.59	[17],[20]
Acetic Acid	-.68	-.69	[17],[20]
Ethyl Acetate	1.00	1.00	

---

125. Ethyl acetate via dimerization of acetaldehyde

Reaction: $2\ CH_3CHO \rightarrow CH_3COOCH_2CH_3$

Comments: Reaction occurs at about 0 C using an aluminum ethoxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-1.00	-1.02	[19]
Ethyl Acetate	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	75	90	105	160	[24],[26]
Exogeneous Demand	75	90	105	160	[24],[26]

Ethyl Acrylate

Ethyl acrylate and other acrylate esters are used almost entirely to produce acrylic polymers and copolymers. These are used primarily as coatings and in the textile industry. Ethyl acrylate is produced from acrylic acid by esterification. This may be done in situ by using ethanol in place of water in one of the processes for acrylic acid manufacture.

Manufacturing Process

126. Ethyl acrylate via esterification of acrylic acid

Reaction: $CH_2{=}CHCOOH + CH_3CH_2OH \rightarrow CH_2{=}CHCOOCH_2CH_3 + H_2O$

Comments: This reaction occurs in situ if ethanol replaces water in the processes for acrylic acid manufacture.

Input-Output Coefficients:	Theoretical	Model	References
Acrylic Acid	-.72	-.77	[45]
Ethanol	-.46	-.50	[45]
Ethyl Acrylate	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	1	10	50	210	[18],[24], [32]
Exogeneous Demand	1	10	50	210	[18],[24], [32]

Ethylbenzene

Styrene production accounts for essentially all the demand for ethylbenzene, most of which is manufactured from benzene and ethylene. Since 1957 some ethylbenzene has been recovered from refinery reformate streams. Today this accouts for about ten percent of ethylbenzene production.

Manufacturing Process

127. Ethylbenzene via reaction of benzene and ethylene

Reaction: $C_6H_6 + CH_2{=}CH_2 \rightarrow C_6H_5CH_2CH_3$

Comments: Reaction occurs in liquid phase at about 85-95 C using an aluminum chloride or phosphoric acid catalyst. Alternatively, the reaction may occur at about 300 C and 40 atm. in the vapor phase over a catalyst of phosphoric acid or silica-alumina.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.74	-.76	[17],[19],[20]
Ethylene	-.26	-.28	[17],[19],[20]
Ethylbenzene	1.00	1.00	

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	--	--	100	480	[18],[60]

There is essentially no exogeneous demand.

Ethyl Chloride

Most ethyl chloride is converted to tetraethyl lead for gasoline antiknock fluid. Since most cars manufactured after 1974 require unleaded gasoline, the demand for ethyl chloride can be expected to decline. Ethyl chloride is also used to manufacture ethyl cellulose plastics, and various dyes and pharmaceuticals. In addition it has some use as a solvent and as a refrigerant. For many years ethyl chloride was manufactured from ethanol and hydrogen chloride. By the mid-1940s, however, most ethyl chloride was being derived from ethylene and hydrogen chloride; this remains the most important route. Some ethyl chloride is also produced by chlorinating ethane.

Manufacturing Processes

128. Ethyl chloride via hydrochlorination of ethylene

Reaction: $CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$

Comments: Reaction occurs in vapor phase at about 130-250 C or liquid phase at about 35-40 C using an aluminum chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.44	-.50	[5],[17],[20]
Hydrogen Chloride	-.56	-.63	[20]
Ethyl Chloride	1.00	1.00	

---

129. Ethyl chloride via chlorination of ethane

Reaction: $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

Comments: Reaction occurs in the vapor phase at about 300 C over an iron chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethane	-.47	-.49	[17]
Chlorine	-1.10	-1.20	
Ethyl Chloride	1.00	1.00	
Hydrogen Chloride	.57	.57	

---

130. Ethyl chloride via hydrochlorination of ethanol

Reaction: $CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$

Comments: Reaction occurs in liquid phase at about 145 C and 30 psi with a zinc chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-.71	-.75	[17],[20]
Hydrogen Chloride	-.57	-.60	[20]
Ethyl Chloride	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	125	355	545	680	[24],[26]
Exogeneous Demand	125	355	545	680	[24],[26]

Ethylene

Next to ammonia, ethylene is the petrochemical produced in the largest tonnage. Over half the ethylene produced in the United States is converted to other chemicals, primarily acetaldehyde, ethanol, ethylene oxide, ethyl chloride, ethylene dichloride, ethylbenzene, and vinyl acetate. From these chemicals is produced a wide range of other chemicals, including acetic acid, ethylene glycol, styrene, and vinyl chloride. The largest single market for ethylene is the manufacture of polyethylene. Ethylene is also polymerized with propylene to yield elastomers.

Ethylene is manufactured by pyrolysis from ethane, propane, n-butane, naphtha, or gas oil. In the United States the usual feedstocks are ethane and propane obtained from refinery gas streams or natural gas. Ethylene itself is present in refinery gases but not at a concentration sufficient to make large-scale recovery attractive. In Europe and Japan, where natural gas is not rich in ethane or propane, the usual feedstocks are naphtha and gas oil. The use of heavier feedstocks is increasing gradually in the United States. The pyrolysis is carried out in the presence of steam in tubular furnace coils in an operation known as 'coil cracking' or 'steam cracking.' Various other means of pyrolysis, some of which can accept crude oil as the feedstock, have been developed but have not been used to a significant extent. Many of the pyrolysis operations for producing acetylene also yield ethylene.

Alternatives to hydrocarbon pyrolysis for producing ethylene

are ethanol dehydration and acetylene hydrogenation. Neither process has been important in the United States, but both have been used extensively abroad.

Manufacturing Processes

131. Ethylene via pyrolysis of ethane

Reaction (not balanced): $CH_3CH_3 \rightarrow CH_2=CH_2 + \text{byproducts}$

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	Reference
Ethane	-1.25	[5],[18],[17],[61]
Ethylene	1.00	
Methane	.10	[18],[61]
Hydrogen	.07	[18],[61]
Propylene	.03	[18],[61]
Butadiene	.02	[17],[18]
Benzene	.01	[17],[18],[61]
Pyrolysis Gasoline	.01	[18],[61]

132. Ethylene via pyrolysis of propane.

Reaction (not balanced): $C_3H_8 \rightarrow CH_2=CH_2 + \text{byproducts}$

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Propane	-2.30	[5],[17],[18],[61]
Ethylene	1.00	
Methane	.60	[18],[61]
Hydrogen	.02	[18],[61]
Acetylene	.01	[61]
Propylene	.32	[5],[17],[18],[61]
Butylenes	.04	[17],[18]
Butadiene	.07	[5],[18]
Benzene	.06	[17],[18]
Toluene	.03	[18]
Pyrolysis Gasoline	.12	[18],[61]

133. Ethylene via pyrolysis of n-butane

Reaction (not balanced): $C_4H_{10} \rightarrow CH_2=CH_2 + \text{byproducts}$

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
n-Butane	-2.70	[17],[18],[61]
Ethylene	1.00	
Methane	.64	[18],[61]
Hydrogen	.02	[61]
Acetylene	.02	[61]
Propylene	.48	[17],[18],[61]
n-Butylenes	.06	[61]
Butadiene	.05	[17],[18],[61]
Benzene	.10	[18],[61]
Toluene	.05	[18],[61]
m-Xylene	.01	[18],[61]
o-Xylene	.01	[18],[61]
p-Xylene	.01	[18],[61]
Pyrolysis Gasoline	.18	[18],[61]

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134. Ethylene via pyrolysis of naphtha (low severity)

Reaction (not balanced): naphtha → $CH_2=CH_2$ + byproducts

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Naphtha	-4.20	[29],[61]
Ethylene	1.00	
Methane	.45	[61]
Hydrogen	.02	
Acetylene	.02	[18]
Propylene	.70	[29],[61]
n-Butylenes	.18	[17],[29],[61]
Isobutylene	.18	[17],[29],[61]
Butadiene	.20	[29],[61]
Benzene	.24	[18],[29],[61]
Toluene	.12	[18],[29],[61]
m-Xylene	.02	[18],[29],[61]
o-Xylene	.02	[18],[29],[61]
p-Xylene	.02	[18],[29],[61]
Styrene	.03	[17],[18],[29],[61]
Isoprene	.06	[18]
Pyrolysis Gasoline	.70	[29],[61]
Fuel Oil	.15	[29],[61]

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135. Ethylene via pyrolysis of naphtha (high severity)

Reaction (not balanced): naphtha → $CH_2=CH_2$ + byproducts

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Naphtha	-3.00	[5],[18],[29],[61]
Ethylene	1.00	
Methane	.45	[18],[61]
Hydrogen	.02	[18],[61]
Acetylene	.02	[18]
Propylene	.45	[5],[18],[29],[61]
n-Butylenes	.06	[5],[17],[18],[29],[61]
Isobutylene	.06	[5],[17],[18],[29],[61]
Butadiene	.12	[5],[18],[61]
Benzene	.20	[5],[18],[29],[61]
Toluene	.10	[5],[18],[29],[61]
m-Xylene	.02	[5],[18],[29],[61]
o-Xylene	.02	[5],[18],[29],[61]
p-Xylene	.02	[5],[18],[29],[61]
Styrene	.03	[5],[17],[18],[29],[61]
Isoprene	.06	[18]
Pyrolysis Gasoline	.20	[61]
Fuel Oil	.12	[18],[29],[61]

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136. Ethylene via pyrolysis of gas oil (low severity)

Reaction (not balanced): gas oil → $CH_2=CH_2$ + byproducts

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Gas Oil	-4.40	[61]
Ethylene	1.00	
Methane	.35	[61]
Hydrogen	.02	
Acetylene	.02	[18]
Propylene	.62	[61]
n-Butylenes	.14	[17],[61]
Isobutylene	.14	[17],[61]
Butadiene	.20	[61]
Benzene	.26	[18],[61]
Toluene	.12	[18],[61]
m-Xylene	.02	[18],[61]
o-Xylene	.02	[18],[61]
p-Xylene	.02	[18],[61]
Styrene	.03	[17],[61]
Isoprene	.06	[18]
Pyrolysis Gasoline	.35	[18],[61]
Fuel Oil	.95	[61]

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137. Ethylene via pyrolysis of gas oil (high severity)

Reaction (not balanced): gas oil → $CH_2=CH_2$ + byproducts

Comments: Pyrolysis occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Gas Oil	-3.50	[61]
Ethylene	1.00	
Methane	.48	[61]
Hydrogen	.02	
Acetylene	.02	[18]
Propylene	.35	[61]
n-Butylene	.04	[17],[61]
Isobutylene	.04	[17],[61]
Butadiene	.15	[61]
Benzene	.24	[18],[61]
Toluene	.11	[18],[61]
m-Xylene	.02	[18],[61]
o-Xylene	.02	[18],[61]
p-Xylene	.02	[18],[61]
Styrene	.03	[17],[61]
Isoprene	.06	[18]
Pyrolysis Gasoline	.22	[18],[61]
Fuel Oil	.65	[61]

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138. Ethylene via hydrogenation of acetylene

Reaction: $CH\equiv CH + H_2 \rightarrow CH_2=CH_2$

Comments: Reaction occurs at about 270 C and 1 atm. over a palladium on silica gel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.93	-1.09	[36]
Hydrogen	-.07	-.08	
Ethylene	1.00	1.00	

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139. Ethylene via dehydration of ethanol

Reaction: $CH_3CH_2OH \rightarrow CH_2=CH_2 + H_2O$

Comments: Reaction occurs over an activated alumina catalyst at about 340-350 C.

Input-Output Coefficients:	Theoretical	Model	References
Ethanol	-1.64	-1.71	[20]
Ethylene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	275	1410	5300	18100	[24],[26]
Exogeneous Demand	--	60	1400	8500	[18],[26], [29]

Ethylene Dibromide

Essentially all ethylene dibromide is used as a lead scavenger in leaded gasoline. Since cars manufactured after 1974 require non-leaded gasoline, the demand for ethylene dibromide is likely to decline. All ethylene dibromide is produced by the reaction of ethylene and bromine.

Manufacturing Process

140. Ethylene dibromide via bromination of ethylene

Reaction: $CH_2=CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$

Comments: Reaction occurs in liquid phase at about 35-85 C and 1 atm.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.15	-.16	[17],[32]
Bromine	-.85	-.86	[32]
Ethylene Dibromide	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	12	85	175	300	[24],[26]
Exogeneous Demand	12	85	175	300	[24],[26]

Ethylene Dichloride

Most ethylene dichloride is converted to vinyl chloride. The production of chlorinated solvents such as trichloroethylene, perchloroethylene, and methyl chloroform represents the next largest market. Other important derivatives are vinylidene chloride and ethylenediamine. Ethylene dichloride is also used with ethylene dibromide as a lead scavenger in leaded gasoline.

Ethylene can be chlorinated or oxychlorinated to ethylene dichloride. The oxychlorination route was developed in the 1950s as an outlet for the hydrogen chloride produced as a byproduct in the conversion of ethylene dichloride to vinyl chloride. Today most manufacturers operate both chlorination and oxychlorination processes.

Manufacturing Processes

141. Ethylene dichloride via chlorination of ethylene

Reaction: $CH_2{=}CH_2 + C\ell_2 \rightarrow CH_2C\ell CH_2C\ell$

Comments: Reaction usually occurs in the liquid phase at about 50 C and 1 atm with a ferric chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.28	-.30	[5],[17],[19],[20]
Chlorine	-.72	-.80	[20]
Ethylene Dichloride	1.00	1.00	

---

142. Ethylene dichloride via oxychlorination of ethylene

Reaction: $CH_2{=}CH_2 + 2\ HC\ell + \frac{1}{2}\ O_2 \rightarrow CH_2C\ell CH_2C\ell + H_2O$

Comments: Reaction occurs in vapor phase at about 250-315 C over a cupric chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.28	-.31	[17],[19]
Hydrogen Chloride	-.74	-.80	[19]
Ethylene Dichloride	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	60	305	1270	7460	[24],[26]
Exogeneous Demand	50	125	250	1200	[5],[18],[20], [28-31]

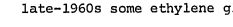
Ethylene Glycol

Ethylene glycol is used as an antifreeze in automotive cooling systems, and is the monomer for ethylene glycol terephthalate, a polyester. These are the two major markets for ethylene glycol. It is also used in deicing compounds, in latex paints and other emulsions, in brake and shock absorber fluid, as a solvent for certain dyes, for the production of explosives, and for various other purposes.

The hydration of ethylene oxide is the only commercial route to ethylene glycol used today. This may soon change, since promising new technologies producing ethylene glycol directly from ethylene or synthesis gas are nearing commercialization. Until the late-1960s some ethylene glycol was derived from formaldehyde and synthesis gas.

Manufacturing Processes

143. Ethylene glycol via hydration of ethylene oxide

Reaction: 

Comments: Reaction occurs in liquid phase at about 200 C and 20 atm. without a catalyst or at about 50-100 C and 1 atm. with an acid catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Oxide	-.71	-.88	[17],[36]
Ethylene Glycol	1.00	1.00	
Diethylene Glycol		.12	[17],[36]
Triethylene Glycol		.01	[36]

144. Ethylene glycol via carbonylation of formaldehyde

Reactions: $HCHO + CO + H_2O \rightarrow CH_2OHCOOH$

$CH_2OHCOOH + CH_3OH \rightarrow CH_2OHCOOCH_3 + H_2O$

$CH_2OHCOOCH_3 + 2\,H_2 \rightarrow CH_2OHCH_2OH + CH_3OH$

Comments: First reaction occurs at about 200 C and 700 atm. The second reaction is acid-catalyzed. The third reaction occurs in vapor phase at about 200 C and 30 atm. using a chromite catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Formaldehyde	-.48	-.65	[17],[20]
Carbon Monoxide	-.45	-.62	[20]
Hydrogen	-.07	-.08	[20]
Ethylene Glycol	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	135	520	1300	3040	[24],[26]
Exogeneous Demand	135	520	1300	3040	[24],[26]

Ethylene Oxide

Most ethylene oxide is converted to ethylene glycol. Other important derivatives are polyglycols, glycol ethers, ethanolamines, and phenoxyphenols. There are many other derivatives produced on a small scale.

Ethylene oxide was first manufactured from ethylene via ethylene chlorohydrin. In the 1930s a process in which ethylene was oxidized directly to ethylene oxide was introduced. Since then the direct oxidation route has gradually come to the forefront. By 1950 it accounted for nearly one-third the ethylene oxide produced; by 1960 two-thirds was so produced; and today all is derived from this process.

Manufacturing Processes

145. Ethylene oxide via oxidation of ethylene

Reaction: $CH_2{=}CH_2 + \frac{1}{2} O_2 \rightarrow \underset{\llcorner O \lrcorner}{CH_2CH_2} + H_2O$

Comments: Reaction occurs at about 230-290 C and 1-30 atm. over a silver oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.64	-1.01	[5],[17],[18],[20]
Ethylene Oxide	1.00	1.00	

---

146. Ethylene oxide via chlorohydration of ethylene

Reactions:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$CH_2{=}CH_2 + HOCl \rightarrow CH_2ClCH_2OH$$

$$CH_2ClCH_2OH + \frac{1}{2} Ca(OH)_2 \rightarrow \underset{\llcorner O \lrcorner}{CH_2CH_2} + \frac{1}{2} CaCl_2 + H_2O$$

$$HCl + \frac{1}{2} Ca(OH)_2 \rightarrow \frac{1}{2} CaCl_2 + H_2O$$

Comments: Third reaction occurs at about 95-105 C and 60-80 mm Hg using a 10% slurry of lime. The fourth reaction is used to remove the hydrogen chloride from the effluent of the first reactor ($NaOH$ may replace $Ca(OH)_2$).

Input-Output Coefficients:	Theoretical	Model	References
Chlorine	-1.61	-2.00	[5],[20]
Ethylene	-.64	-.80	[5],[17],[20]
Calcium Hydroxide	-1.68	-2.10	[20]
Ethylene Oxide	1.00	1.00	
Calcium Chloride	2.52	2.60	
Ethylene Dichloride		.10	[5],[17],[20]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	110	480	1470	3865	[24],[26]
Exogeneous Demand	15	80	380	1430	[26],[18], [29]

2-Ethylhexanol

2-Ethylhexanol is used mainly to produce plasticizers, the most important of which is di-2-ethylhexyl phthalate, which is used in vinyl chloride resins. Also, substantial quantities of the alcohol are converted to its acrylate ester for use in producing adhesives and surface coatings. It also has some use as a solvent, and has various other small-scale markets.

The aldol condensation of n-butyraldehyde is used commercially to produce 2-ethylhexanol. The n-butyraldehyde can be derived from acetaldehyde via crotonaldehyde or from propylene by oxonation, the latter being preferred today.

Manufacturing Process

147. 2-Ethylhexanol via dimerization of n-butyraldehyde

Reactions: $2\ CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CH{=}C(C_2H_5)CHO$

$CH_3CH_2CH_2CH{=}C(C_2H_5)CHO + 2\ H_2 \rightarrow CH_3(CH_2)_3CH(C_2H_5)CH_2OH$

Comments: First reaction occurs in the presence of an alkaline catalyst. Second reaction occurs in liquid phase at about 150 C and 150-180 atm. using a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butyraldehyde	-1.11	-1.23	[17]
Hydrogen	-.03	-.03	
2-Ethylhexanol	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	2	25	100	460	[24],[26], [50]
Exogeneous Demand	2	25	100	460	[24],[26], [50]

Formaldehyde

Most formaldehyde is polymerized to form resins such as polyacetal, urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde. Other important derivatives are hexamethylenetetramine, used chiefly as a cross-linking agent in phenolic resins, and pentaerythritol, used largely in producing alkyd resins. Substantial quantities of formaldehyde were once used to manufacture ethylene glycol, but this market no longer exists. There are various other formaldehyde derivatives including acrylic acid and tetrahydrofuran.

In the usual route to formaldehyde, methanol is simultaneously oxidized and dehydrogenated over a metal catalyst in such a way that the endothermic dehydrogenation thermally balances the exothermic oxidation. Another process, involving methanol oxidation over a metal oxide catalyst, has long been operated, and now seems to be gaining ground on the thermally balanced process. Some formaldehyde is also produced, along with acetaldehyde and methanol, by oxidizing propane or butane.

Manufacturing Processes

148. Formaldehyde via oxidation of methanol

Reaction: $CH_3OH + \frac{1}{2} O_2 \rightarrow HCHO + H_2O$

Comments: Reaction occurs at about 350-450 C over a metal oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methanol	-1.07	-1.15	[45],[62]
Formaldehyde	1.00	1.00	

149. Formaldehyde via oxidation/dehydrogenation of methanol

Reactions: $CH_3OH + \frac{1}{2} O_2 \rightarrow HCHO + H_2O$

$CH_3OH \rightarrow HCHO + H_2$

Comments: By using a slight deficiency of air, the endothermic dehydrogenation can be made to thermally balance the exothermic oxidation. The process occurs at about 450-600 C over a silver or copper catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methanol	-1.07	-1.18	[5],[17],[20],[62]
Formaldehyde	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	65	330	740	1640	[24],[26], [30]
Exogeneous Demand	65	310	640	1615	[18],[20], [26],[31]

Fuel Oil

As used here, the term fuel oil refers to heavy liquid hydrocarbon fractions (400°F+) that can be used to manufacture synthesis gas for the production of ammonia, methanol, and other chemicals. In addition to supplies from refineries, such a liquid fraction is produced as a byproduct when gas oil is pyrolyzed to ethylene and other olefins.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	--	--	2000	5000	

Gas Oil

Gas oil is a liquid petroleum fraction (400-600°F) that can serve as a feedstock for the manufacture of synthesis gas and ethylene and other olefins.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply	--	50	1000	5000	

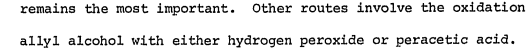
Glycerin

In its most significant applications glycerin is used as a raw material in the production of alkyd resins, explosives, and food additives, as a humectant and flavoring in tobacco processing, as a softener for cellophane, and as an emulsant for drugs and cosmetics.

Until 1948, when synthetic glycerin was first produced commercially from propylene via allyl chloride and epichlorohydrin, nearly all glycerin was obtained as a byproduct of soap manufacture. This is still a major source of glycerin today, accounting for nearly half the glycerin produced. The original synthetic route remains the most important. Other routes involve the oxidation of allyl alcohol with either hydrogen peroxide or peracetic acid. The hydrogen peroxide process has been operated since the late-1950s; the peracetic acid process is a relatively recent development.

Manufacturing Processes

150. Glycerin via hydrolysis of epichlorohydrin

Reaction: 

Comments: Reaction occurs at about 150 C using a 10% solution of sodium hydroxide.

Input-Output Coefficients:	Theoretical	Model	References
Epichlorohydrin	-1.00	-1.05	[5]
Sodium Hydroxide	-.43	-.45	
Glycerin	1.00	1.00	
Sodium Chloride	.63	.63	

---

151. Glycerin via reaction of allyl alcohol and hydrogen peroxide

Reaction: $CH_2{=}CHCH_2OH + H_2O_2 \rightarrow CH_2OHCHOHCH_2OH$

Comments: Reaction occurs in aqueous phase at about 60-70 C using a tungstic oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Allyl Alcohol	-.63	-.70	[17],[20]
Hydrogen Peroxide	-.37	-.49	[20]
Glycerin	1.00	1.00	

---

152. Glycerin via reaction of allyl alcohol and peracetic acid

Reactions: $CH_2{=}CHCH_2OH + CH_3COOOH \rightarrow CH_2\underset{O}{\underset{|}{\langle}}CHCH_2OH + CH_3COOH$

$CH_2\underset{O}{\underset{|}{\langle}}CHCH_2OH + H_2O \rightarrow CH_2OHCHOHCH_2OH$

Input-Output Coefficients:	Theoretical	Model	References
Allyl Alcohol	-.63	-.74	
Peracetic Acid	-.83	-.92	
Glycerine	1.00	1.00	
Acetic Acid	.65	.65	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production (synthetic)	--	35	150	190	[24],[26]
Exogeneous Demand (synthetic)	--	35	150	190	[24],[26]

Hexamethylenediamine

Hexamethylenediamine is used almost exclusively as a monomer for nylon 66 production. It is manufactured from adiponitrile by hydrogenation.

Manufacturing Process

153. Hexamethylenediamine via hydrogenation of adiponitrile

Reaction: $CN(CH_2)_4CH + 4\ H_2 \rightarrow NH_2(CH_2)_6NH_2$

Comments: Reaction occurs at about 125-200 C and 300-680 atm. using a cobalt catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Adiponitrile	-.93	-.93	[17]
Hydrogen	-.07	-.07	
Hexamethylenediamine	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	2	40	200	615	[24],[56], [59]
Exogeneous Demand	2	40	200	615	[24],[56], [59]

Hydrogen

Hydrogen is used in several petrochemical processes, but ammonia and methanol production are by far the largest consumers. For many years hydrogen for methanol and ammonia synthesis was derived from carbon and steam using the so-called water-gas reaction. Today most is produced from hydrocarbons by steam reforming, and, to a lesser extent, by partial oxidation. In either case, methane is the usual feedstock, but heavier hydrocarbons can be used. Carbon monoxide is coproduced in these processes; when the hydrogen is to be used for ammonia synthesis the carbon monoxide is converted to additional hydrogen via the water-gas shift reaction. Hydrogen is also produced in the various dehydrogenation processes used in the petrochemical industry; the quantities so produced may be sufficient to supply allied hydrogenation processes.

Manufacturing Processes

154. Hydrogen via water-gas reaction

Reaction: $C + H_2O \rightarrow H_2 + CO$

Comments: Reaction occurs at 1830 F or higher.

Input-Output Coefficients:	Theoretical	Model	References
Carbon	-6.00	-13.7	[20]
Hydrogen	1.00	1.00	
Carbon Monoxide	14.00	10.6	[20]

---

155. Hydrogen via steam reforming of methane

Reaction: $\frac{1}{3} CH_4 + \frac{1}{3} H_2O \rightarrow H_2 + \frac{1}{3} CO$

Comments: Reaction occurs in vapor phase over a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-2.67	-2.70	[20],[50]
Hydrogen	1.00	1.00	
Carbon Monoxide	4.67	4.67	

---

156. Hydrogen via steam reforming of ethane

Reaction: $\frac{1}{5}\ CH_3CH_3 + \frac{2}{5}\ H_2O \rightarrow H_2 + \frac{2}{5}\ CO$

Comments: Reaction occurs in vapor phase over a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethane	-3.01	-3.10	estimate of yield
Hydrogen	1.00	1.00	based on yield of
Carbon Monoxide	5.60	5.60	hydrogen from reforming of methane and naphtha

---

157. Hydrogen via steam reforming of propane

Reaction: $\frac{1}{7}\ CH_3CH_2CH_3 + \frac{3}{7}\ H_2O \rightarrow H_2 + \frac{3}{7}\ CO$

Comments: Reaction occurs in vapor phase over a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propane	-3.15	-3.27	estimate of yield
Hydrogen	1.00	1.00	based on yield of
Carbon Monoxide	6.00	6.00	hydrogen from reforming of methane and naphtha

---

158. Hydrogen via steam reforming of n-butane

Reaction: $\frac{1}{9}\ CH_3CH_2CH_2CH_3 + \frac{4}{9}\ H_2O \rightarrow H_2 + \frac{4}{9}\ CO$

Comments: Reaction occurs in vapor phase over a nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butane	-3.23	-3.35	estimate of yield
Hydrogen	1.00	1.00	based on yield of
Carbon Monoxide	6.22	6.22	hydrogen from reforming of methane and naphtha

---

159. Hydrogen via steam reforming of naphtha

Reaction (not balanced): naphtha + H_2O → H_2 + CO

Comments: Reaction occurs in vapor phase over a nickel catalyst.

Input-Output Coefficients:	Model	References
Naphtha	-3.65	[50]
Hydrogen	1.00	
Carbon Monoxide	7.00	

---

160. Hydrogen via partial oxidation of methane

Reaction: $\frac{1}{2}\ CH_4 + \frac{1}{4}\ O_2 \rightarrow H_2 + \frac{1}{2}\ CO$

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-4.00	-4.84	[50]
Hydrogen	1.00	1.00	
Carbon Monoxide	7.00	7.69	[50]

---

161. Hydrogen via partial oxidation of ethane

Reaction: $\frac{1}{3}\ CH_3CH_3 + \frac{1}{3}\ O_2 \rightarrow H_2 + \frac{2}{3}\ CO$

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethane	-5.02	-5.70	estimate of yield
Hydrogen	1.00	1.00	based on yield of
Carbon Monoxide	9.33	9.50	hydrogen from partial oxidation of methane and naphtha

---

162. Hydrogen via partial oxidation of propane

Reaction: $\frac{1}{4}\ CH_3CH_2CH_3 + \frac{3}{8}\ O_2 \rightarrow H_2 + \frac{3}{4}\ CO$

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propane	-5.51	-6.30	estimate of yield
Hydrogen	1.00	1.00	based on yield of
Carbon Monoxide	10.5	10.5	hydrogen from partial oxidation of methane and naphtha

---

163. Hydrogen via partial oxidation of n-butane

Reaction: $\frac{1}{5}\ CH_3CH_2CH_2CH_3 + \frac{2}{5}\ O_2 \rightarrow H_2 + \frac{4}{5}\ CO$

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butane	-5.81	-6.80	estimate of yield based on yield of hydrogen from partial oxidation of methane and naphtha
Hydrogen	1.00	1.00	
Carbon Monoxide	11.2	11.2	

---

164. Hydrogen via partial oxidation of naphtha

Reaction (not balanced): naphtha + $O_2 \rightarrow H_2$ + CO

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Model	References
Naphtha	-7.50	[50]
Hydrogen	1.00	
Carbon Monoxide	12.5	[50]

---

165. Hydrogen via partial oxidation of gas oil

Reaction (not balanced): gas oil + $O_2 \rightarrow H_2$ + CO

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Model	References
Gas Oil	-7.95	estimate of yield based on yield of hydrogen from partial oxidation of naphtha and fuel oil
Hydrogen	1.00	
Carbon Monoxide	13.4	

---

166. Hydrogen via partial oxidation of fuel oil

Reaction (not balanced): fuel oil + $O_2 \rightarrow H_2$ + CO

Comments: Reaction occurs in vapor phase without a catalyst.

Input-Output Coefficients:	Model	References
Fuel Oil	-8.30	[50]
Hydrogen	1.00	
Carbon Monoxide	14.3	[50]

---

167. Hydrogen via water-gas shift reaction

Reaction: $CO + H_2O \rightarrow H_2 + CO_2$

Comments: Reaction occurs in two stages: first at about 370-430 C over a catalyst of chromium and iron oxide, and then at 200-250 C over a copper-zinc-chromium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Monoxide	-14.0	-14.7	[20]
Hydrogen	1.00	1.00	
Carbon Dioxide	22.0	22.0	

Supply and Demand Data

It is assumed that all hydrogen is produced within the petrochemical industry; thus, there is no exogeneous supply. The exogeneous demand is negligible.

Hydrogen Chloride

Large quantities of hydrogen chloride are produced in petrochemical chlorination processes as a byproduct. The surfeit of hydrogen chloride led to the development of oxychlorination processes, which use hydrogen chloride instead of chlorine as the chlorinating agent. Other than chemical manufacture, the metals industry is the largest consumer of hydrogen chloride.

Supply and Demand Data

The supply of hydrogen chloride to the petrochemical industry is not constrained in the model. There is no exogeneous demand, though hydrogen chloride may be an output of the industry.

Hydrogen Cyanide

Hydrogen cyanide is consumed mainly in the production of methyl methacrylate and adiponitrile. In the past, large quantities were used to manufacture acrylonitrile, but this market no longer exists, as the cyanide-based processes have been replaced by propylene ammoxidation. Other important derivatives include sodium nitrilotriacetate, used in place of phosphates in some detergent formulations, sodium cyanide, used in electroplating and gold extraction, and cyanuric chloride, used in herbicide manufacture.

Most hydrogen cyanide is produced by the reaction of methane, ammonia, and air. This process was developed in Germany before World War II, but was not used to a significant extent until the early-1950s. Processes which react methane and ammonia but require no air have also been commercialized. One of these processes can be adapted to use propane or naphtha in place of methane. In the traditional route, sodium cyanide produced from ammonia, charcoal, and metallic sodium reacts with sulfuric acid to form hydrogen cyanide and sodium sulfate. Another process once widely used is based on the decomposition of formamide, which is produced from methanol, carbon monoxide, and ammonia. Hydrogen cyanide is produced as a byproduct in the manufacture of acrylonitrile from propylene; the amounts so produced are becoming increasingly significant.

Manufacturing Processes

168. Hydrogen cyanide via ammoxidation of methane

Reaction: $CH_4 + NH_3 + \frac{3}{2} O_2 \rightarrow HCN + 3 H_2O$

Comments: Reaction occurs at about 1000 C over a platinum-rhodium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.59	-.82	[20]
Ammonia	-.63	-.83	[19],[20]
Hydrogen Cyanide	1.00	1.00	

---

169. Hydrogen cyanide via reaction of sodium cyanide and sulfuric acid

Reactions: $NH_3 + Na \rightarrow NaNH_2 + \frac{1}{2} H_2$

$NaNH_2 + C \rightarrow NaCN + H_2$

$NaCN + \frac{1}{2} H_2SO_4 \rightarrow HCN + \frac{1}{2} Na_2SO_4$

Comments: Calcium cyanide may be used in place of sodium cyanide.

Input-Output Coefficients:	Theoretical	Model	References
Ammonia	-.63	-.70	[20],[50]
Carbon	-.44	-.56	[20],[50]
Sodium	-.85	-.93	
Sulfuric Acid	-1.82	-1.98	
Hydrogen Cyanide	1.00	1.00	
Sodium Sulfate	2.63	2.70	
Hydrogen	.11	.12	

---

170. Hydrogen cyanide via decomposition of formamide

Reactions: $CH_3OH + CO \rightarrow CHOOCH_3$

$CHOOCH_3 + NH_3 \rightarrow CHONH_2 + CH_3OH$

$CHONH_2 \rightarrow HCN + H_2O$

Comments: First reaction occurs at about 100 C and 150 psi with a sodium methylate catalyst. Second reaction occurs at about 40 C and 200 psi. Third reaction occurs at about 400-900 C under reduced pressure using a dehydration catalyst such as activated alumina.

Input-Output Coefficients:	Theoretical	Model	References
Ammonia	-.63	-.75	[19],[20]
Carbon Monoxide	-1.04	-1.40	[19],[20]
Hydrogen Cyanide	1.00	1.00	

---

171. Hydrogen cyanide via reaction of methane and ammonia

Reaction: $CH_4 + NH_3 \rightarrow HCN + 3\ H_2$

Comments: Reaction occurs at about 1200-1300 C over a platinum catalyst or at about 1500 C in a fluidized bed of heated coke.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.59	-.69	[19]
Ammonia	-.63	-.74	[5],[19]
Hydrogen Cyanide	1.00	1.00	
Hydrogen	.11	.12	

---

172. Hydrogen cyanide via reaction of propane and ammonia

Reaction: $\frac{1}{3}\ CH_3CH_2CH_3 + NH_3 \rightarrow HCN + \frac{7}{3}\ H_2$

Comments: Reaction occurs in fluidized bed of heated coke.

Input-Output Coefficients:	Theoretical	Model	References
Propane	-.54	-.64	[5],[20]
Ammonia	-.63	-.74	[5],[20]
Hydrogen Cyanide	1.00	1.00	
Hydrogen	.17	.20	[5]

---

173. Hydrogen cyanide via reaction of ammonia and naphtha

Reaction (not balanced): naphtha + $NH_3 \rightarrow HCN + H_2$

Comments: Reaction occurs in fluidized bed of heated coke.

Input-Output Coefficients:	Model	References
Naphtha	-.62	estimate of yield based on
Ammonia	-.74	yield of hydrogen cyanide
Hydrogen Cyanide	1.00	from propane
Hydrogen	.18	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	10	50	180	500	[20],[26]
Exogeneous Demand	7	15	30	100	[20],[29],[31]

Hydrogen Fluoride

Hydrogen fluoride is used in the petrochemical industry to produce fluorocarbons. Aside from this, the main market for hydrogen fluoride is the manufacture of synthetic cryolite for use in extracting aluminum from bauxite. Hydrogen fluoride is produced by the action of concentrated sulfuric acid on naturally occurring calcium fluoride (fluorospar).

Supply Data

The supply of hydrogen fluoride to the petrochemical industry is not constrained in the model.

Hydrogen Peroxide

Aside from its military applications (such as use in rocket fuel), hydrogen peroxide is used primarily for bleaching in the textile and paper industries. Its only large-scale petrochemical use is in one process for producing synthetic glycerin. There are, however, several small-scale chemical derivatives. Hydrogen peroxide can be produced petrochemically from isopropanol; however, it is not primarily a petrochemical derivative.

Manufacturing Process

174. Hydrogen peroxide via oxidation of isopropanol

Reaction: $CH_3CHOHCH_3 + O_2 \rightarrow H_2O_2 + CH_3COCH_3$

Comments: Reaction occurs in liquid phase at about 90-140 C and 200-300 psi.

Input-Output Coefficients:	Theoretical	Model	References
Isopropanol	-1.76	-2.00	[20]
Hydrogen Peroxide	1.00	1.00	
Acetone	1.71	1.82	[20]

Supply Data

The supply of hydrogen peroxide to the petrochemical industry is not constrained in the model.

Iron

Iron was used as a reducing agent in obsolete processes for producing aniline from nitrobenzene and chloroform from carbon tetrachloride. This is its only petrochemical application as a raw material.

Supply Data

The supply of iron to the petrochemical industry is not constrained in the model.

Iron(II) Chloride

Iron(II) chloride occurs as a byproduct when carbon tetrachloride is reduced with iron to chloroform, a process now obsolete. Usually iron(II) chloride is produced from iron and hydrogen chloride. It is used as a mordant in dyeing, as a reducing agent in small-scale chemical synthesis, and as a raw material for making iron(III) chloride.

Demand Data

There is no exogeneous demand, though iron(II) chloride may be an output of the petrochemical industry.

Iron Oxide

Iron oxide is a byproduct when iron is used to reduce nitrobenzene to aniline or carbon tetrachloride to chloroform in now obsolete processes. Iron oxide occurs naturally as magnetite and can be produced by the action of steam on heated iron or the partial oxidation of other iron compounds. It is used as a pigment in paints, glass, and textiles and as a polishing compound.

Demand Data

There is no exogeneous demand, though iron oxide may be an output of the petrochemical industry.

Isobutane

Isobutane is important primarily in fuel production (it is fed to refinery alkylation units). Significant use of isobutane as a petrochemical feedstock in the United States did not begin until fairly recently. It is cracked to produce isobutylene and propylene, and is converted to isobutylene in one process for making propylene oxide. Dehydrogenation to isobutylene is an old process but was never important in the United States.

Isobutane can be recovered from natural gas or from refinery streams. If these supplies are insufficient, n-butane can be isomerized to isobutane (this process is responsible for much of the isobutane produced in refineries).

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply					
from natural gas	--	--	--	500	[24], [25]
from refineries	--	--	--	300	

Manufacturing Process

175. Isobutane via isomerization of n-butane

Reaction: $CH_3CH_2CH_2CH_3 \rightarrow CH_3CH(CH_3)CH_3$

Comments: Reaction occurs at about 90-150 C and 250-350 psi over a catalyst of aluminum chloride and hydrogen chloride.

Input-Output Coefficients:	Theoretical	Model	References
n-Butane	-1.00	-1.05	
Isobutane	1.00	1.00	

Isobutanol

There is no single most important use for isobutanol. It and its acetate ester are used as solvents, and it is used to produce lubricating-oil additives, amine resins, plasticizers, and a variety of small-scale chemicals.

In the United States today, all isobutanol is derived from the isobutyraldehyde that occurs as a byproduct in the oxonation of propylene to n-butyraldehyde. The process for manufacturing methanol from synthesis gas can be operated to produce byproduct isobutanol; this was once the major source of isobutanol. It can also be produced as a byproduct in the direct carbonylation of propylene to n-butanol, but this process is not operated in the United States.

Manufacturing Processes

176. Isobutanol via hydrogenation of isobutyraldehyde

Reaction: $(CH_3)_2CHCHO + H_2 \rightarrow (CH_3)_2CHCH_2OH$

Comments: Reaction occurs in liquid phase at about 100 atm. using a catalyst of cobalt, nickel, or a metal oxide.

Input-Output Coefficients:	Theoretical	Model	References
Isobutyraldehyde	-.97	-1.03	estimate of yield
Hydrogen	-.03	-.03	based on yield of
Isobutanol	1.00	1.00	n-butanol from n-butyraldehyde

---

177. Isobutanol via reaction of hydrogen and carbon monoxide

Reaction (not balanced): $H_2 + CO \rightarrow CH_3OH + (CH_3)_2CHCH_2OH$ + other alcohols

Comments: Reaction occurs at about 450 C and 300 atm. using a zinc oxide-chromic oxide catalyst.

Input-Output Coefficients:	Model	References
Carbon Monoxide	-6.67	[19],[63]
Hydrogen	-1.00	[19],[63]
Isobutanol	1.00	
Methanol	4.53	[19],[63]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	5	15	50	90	[5],[24],[26]
Exogeneous Demand	5	15	50	90	[5],[24],[26]

Isobutylene

Currently there are no large-volume petrochemicals derived from isobutylene in the United States. However, methyl methacrylate and isoprene are potential derivatives. Aside from its fuel use (isobutylene is fed to refinery alkylation units), most isobutylene is polymerized to form butyl rubber. Other isobutylene polymers have applications in lubricating oil and in caulking and sealing compounds.

Refinery cracking units are the major suppliers of isobutylene. Some is produced as a byproduct in ethylene plants, and it can be derived from isobutane by pyrolysis or catalytic dehydrogenation. In addition isobutane is converted to isobutylene in one process for manufacturing propylene oxide.

Manufacturing Processes

178. Isobutylene via dehydrogenation of isobutane

Reaction: $CH_3CH(CH_3)CH_3 \rightarrow CH_2=C(CH_3)CH_3 + H_2$

Comments: Reaction occurs over a chromia-alumina catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Isobutane	-1.04	-1.50	estimate of yield
Isobutylene	1.00	1.00	based on yield of
Hydrogen	.04	.05	butadiene from butane

---

179. Isobutylene via pyrolysis of isobutane

Reaction (not balanced): $CH_3CH(CH_3)CH_3 \rightarrow CH_2=C(CH_3)CH_3 + CH_2=CHCH_3 +$ byproducts

Comments: Reaction occurs in tubular furnace coils with steam present.

Input-Output Coefficients:	Model	References
Isobutane	-2.36	[18],[45],[61]
Isobutylene	1.00	
Propylene	.73	[18],[45],[61]
Methane	.43	[18],[45],[61]
Ethylene	.10	[18],[45],[61]
Hydrogen	.04	[18],[45],[61]

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	50	150	350	650	[19],[24], [26]
Exogeneous Demand	10	125	275	550	[19],[27-29]

Isobutyraldehyde

Isobutyraldehyde is produced as a byproduct when propylene is oxonated to n-butyraldehyde. It is usually hydrogenated to isobutanol; this represents virtually the only use for isobutyraldehyde.

Demand Data

There is essentially no exogeneous demand.

Isopentenes

Isopentenes, obtained from refinery cracking units, are used in the petrochemical industry to produce isoprene. This is the only large-scale use for isopentenes as a chemical feedstock.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	--	--	50	200	

Isophthalic Acid

Isophthalic acid was first produced commercially in 1956. It is used primarily to form polyesters and alkyd resins. All isophthalic acid is derived from m-xylene by oxidation. The original oxidation process involved the intermediate formation of amides or ammonium salts, which were then hydrolyzed to the acid. This has now been supplanted by a direct catalytic oxidation process.

Manufacturing Process

180. Isophthalic acid via oxidation of m-xylene

Reaction: $C_6H_4(CH_3)_2 + 3\ O_2 \rightarrow C_6H_4(COOH)_2 + 2\ H_2O$

Comments: Reaction occurs in liquid phase at about 200 C and 200 psi using a catalyst of cobalt and manganese acetates promoted by bromine.

Input-Output Coefficients:	Theoretical	Model	References
m-Xylene	-.64	-.80	[17]
Isophthalic Acid	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	35	110	[26]
Exogeneous Demand	--	--	35	110	[26]

Isoprene

Isoprene was not manufactured on a large-scale until the late-1950s, when cis-polyisoprene, a synthetic elastomer, was first commercialized. Small quantities of isoprene had been produced previously for copolymerization with isobutylene to form butyl rubber. Today cis-polyisoprene is by far the largest market, with butyl rubber a distant second.

In the United States most isoprene is produced from isopentenes or propylene. Elsewhere processes have been operated which derive isoprene from isobutylene and formaldehyde and from acetylene and acetone. Isoprene is also produced as a byproduct when naphtha or gas oil is cracked to ethylene. This source is not now important in the United States as most ethylene is derived from ethane or propane. In Europe and Japan, however, where naphtha cracking is the usual route to ethylene, this is a major source of isoprene.

Manufacturing Processes

181. Isoprene via dehydrogenation of isopentenes

Reaction: $CH_2=C(CH_3)CH_2CH_3$ or $(CH_3)_2C=CHCH_3 \rightarrow CH_2=C(CH_3)CH=CH_2 + H_2$

Comments: Reaction occurs at about 550-620 C over an iron oxide-chromium oxide-potassium carbonate or chromia-alumina catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Isopentenes	-1.03	-1.30	[17]
Isoprene	1.00	1.00	
Hydrogen	.03	.03	

182. Isoprene via dimerization of propylene

Reactions: $2\ CH_3CH{=}CH_2 \rightarrow CH_2{=}C(CH_3)CH_2CH_2CH_3$

$CH_2{=}C(CH_3)CH_2CH_2CH_3 \rightarrow (CH_3)_2C{=}CHCH_2CH_3$

$(CH_3)_2C{=}CHCH_2CH_3 \rightarrow CH_2{=}C(CH_3)CH{=}CH_2 + CH_4$

Comments: First reaction occurs at about 200 C and 200 atm. using a tripropyl aluminum catalyst. Second reaction occurs at about 100 C with a silica-alumina catalyst. Third reaction occurs at about 660 C with a hydrogen bromide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-1.24	-2.30	[17]
Isoprene	1.00	1.00	
Methane	.24	.24	

183. Isoprene via reaction of formaldehyde and isobutylene

Reactions: $(CH_3)_2C{=}CH_2 + 2\ HCHO \rightarrow (CH_3)_2\underset{\displaystyle\llcorner\!\!-\!\!O\!\!-\!\!\lrcorner}{CCH_2CH_2OCH_2}$

$(CH_3)_2\underset{\displaystyle\llcorner\!\!-\!\!O\!\!-\!\!\lrcorner}{CCH_2CH_2OCH_2} \rightarrow CH_2{=}C(CH_3)CH{=}CH_2 + HCHO + H_2O$

Comments: First reaction occurs in liquid phase at about 70-95 C with an acid catalyst. Second reaction occurs at about 250-400 C using a calcium phosphate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Isobutylene	-.82	-.96	[18]
Formaldehyde	-.44	-.52	[18]
Isoprene	1.00	1.00	

184. Isoprene via reaction of acetylene and acetone

Reactions: $CH{\equiv}CH + CH_3COCH_3 \rightarrow (CH_3)_2COHC{\equiv}CH$

$(CH_3)_2COHC{\equiv}CH + H_2 \rightarrow (CH_3)_2COHCH{=}CH_2$

$(CH_3)_2COHCH{=}CH_2 \rightarrow CH_2{=}C(CH_3)CH{=}CH_2 + H_2O$

Comments: First reaction occurs at about 10-40 C and 20 atm. in the liquid phase with a potassium hydroxide catalyst. Third step occurs at about 250-300 C and 1 atm. over an alumina catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.38	-.42	[57]
Acetone	-.85	-.95	[57]
Hydrogen	-.03	-.03	[57]
Isoprene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	25	350	[24]
Exogeneous Demand	--	--	25	350	[24]

Isopropanol

The largest single use for isopropanol is as an intermediate for acetone production. Glycerin and hydrogen peroxide are other derivatives. It is also an important solvent and is used for the synthesis of a variety of small-volume chemicals.

Isopropanol was the first petrochemical--that is, the first chemical manufactured commercially from a petroleum-derived feedstock. The original process, a two step hydration of propylene using sulfuric acid, was dominant until fairly recently. Today the direct catalytic hydration of propylene is preferred. This process was first operated in the early-1950s, but its early versions suffered from low conversion per pass.

Manufacturing Processes

185. Isopropanol via sulfonation of propylene

Reactions: $CH_3CH{=}CH_2 + H_2SO_4 \rightarrow CH_3CHOSO_3HCH_3$

$CH_3CHOSO_3HCH_3 + H_2O \rightarrow CH_3CHOHCH_3 + H_2SO_4$

Comments: First reaction occurs at about 20-30 C and 20-30 atm. in 75-85% sulfuric acid.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.70	-.85	[17]
Isopropanol	1.00	1.00	

---

186. Isopropanol via hydration of propylene

Reaction: $CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3$

Comments: Reaction occurs in vapor phase at about 240-260 C and 25-65 atm. over a phosphoric acid catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.70	-.72	[18],[45]
Isopropanol	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	220	865	1180	1920	[24],[26]
Exogeneous Demand	40	310	450	830	[5],[26],[20], [30],[31]

Ketene

Acetic anhydride manufacture consumes nearly all ketene produced. Another potentially large-volume use is the production of acrylic acid or its esters. Ketene can be produced commercially by the pyrolysis of either acetic acid or acetone. Though the acetic acid route is now more common, the acetone route is not considered obsolete.

Manufacturing Processes

187. Ketene via pyrolysis of acetic acid

Reaction: $CH_3COOH \rightarrow CH_2{=}CO + H_2O$

Comments: Reaction occurs at about 700-800 C and 200 mm Hg over a triethylphosphate catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetic Acid	-1.43	-1.59	[17]
Ketene	1.00	1.00	

---

188. Ketene via pyrolysis of acetone

Reaction: $CH_3COCH_3 \rightarrow CH_2{=}CO + CH_4$

Comments: Reaction occurs at about 650-670 C without a catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetone	-1.38	-1.60	[17]
Ketene	1.00	1.00	
Methane	.38	.38	

Demand Data

There is essentially no exogeneous demand.

Maleic Anhydride

The largest market for maleic anhydride is in the production of polyesters. It is also used to produce fumaric acid, alkyd resins, pesticides, plasticizers, and lubricants.

Since its emergence as a large-volume chemical, most maleic anhydride has been produced by oxidizing benzene. From time to time, processes oxidizing n-butylenes to maleic anhydride have also been used. Though this route dates back to the 1930s, there is continued interest in it today. There is also current interest in using a butane feedstock.

Manufacturing Processes

189. Maleic anhydride via oxidation of benzene

Reaction: $C_6H_6 + \frac{9}{2} O_2 \rightarrow$  $+ 2\ CO_2 + 2\ H_2O$

Comments: Reaction occurs in vapor phase at about 400-500 C and 1 atm. over a vanadium pentoxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.80	-1.30	[5],[17],[18],[20]
Maleic Anhydride	1.00	1.00	
Carbon Dioxide	.90	.90	

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190. Maleic anhydride via oxidation of n-butylenes

Reaction: $CH_3CH{=}CHCH_3$ or $CH_3CH_2CH{=}CH_2$ $+ 3\ O_2 \rightarrow$ $+ 3\ H_2O$

Comments: Reaction occurs at about 350-480 C and 1 atm. over a vandadium pentoxide-phosphorus pentoxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
n-Butylenes	-.57	-1.27	[5],[18],[19]
Maleic Anhydride	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	5	15	90	215	[24],[26]
Exogeneous Demand	5	15	90	215	[24],[26]

Methane

Aside from its use as fuel, methane is important primarily as a feedstock for synthesis gas production. It is also used to produce acetylene, carbon disulfide, hydrogen cyanide, and the chloromethanes. Natural gas is by far the most important source of methane. Substantial quantities are produced as a byproduct of ethylene manufacture but this is not is usually used as a feedstock.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from natural gas)	1000	4000	7000	16500	[34]

Methanol

Methanol has some market as a solvent but is used primarily as a chemical intermediate. Formaldehyde production consumes the largest amount of methanol; substantial amounts are also used to manufacture dimethyl terephthalate, acetic acid, methyl methacrylate, methyl amines, and methyl halides. Other outlets include its use as antifreeze and as fuel.

Methanol is produced by hydrogenating carbon monoxide, carbon dioxide, or mixtures thereof. The preferred feedstock is a synthesis gas containing one part carbon monoxide and two parts hydrogen by volume. Traditionally this process has been operated at quite high pressure (275-360 atm.), but recently processes using lower pressure (50-60 atm.) have been gaining favor. Some methanol is still produced by the destructive distillation of wood, but compared to the amounts produced synthetically this source has not been significant for decades.

Manufacturing Processes

191. Methanol via hydrogenation of carbon monoxide

Reaction: $CO + 2\ H_2 \rightarrow CH_3OH$

Comments: Reaction occurs at about 300-400 C and 275-360 atm. over a zinc oxide catalyst. Alternatively, reaction may occur at about 240-260 C and 50-60 atm. over a copper-based catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Monoxide	-.88	-1.00	[46]
Hydrogen	-.12	-.15	[46]
Methanol	1.00	1.00	

192. Methanol via hydrogenation of carbon dioxide

Reaction: $CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

Comments: Reaction may occur simultaneously with carbon monoxide hydrogenation to methanol.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Dioxide	-1.38	-1.57	estimate of yield
Hydrogen	-.19	-.24	based on yield of
Methanol	1.00	1.00	methanol from carbon monoxide

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production (synthetic)	300	900	1965	4930	[24],[26]
Exogeneous Demand	180	450	800	1700	[17],[18], [28-32]

Methyl Chloride

The two largest markets for methyl chloride are the production of tetramethyl lead for gasoline antiknock fluid and the production of methylchlorosilanes for silicone resins. Substantial quantities are also consumed in manufacturing the other chloromethanes, especially methylene dichloride and chloroform. It is also used as a solvent in butyl rubber manufacture, and at one time was important as a refrigerant.

Most methyl chloride is produced by the hydrochlorination of methanol. Methane can be chlorinated to methyl chloride; this may be favored if the manufacturer has an outlet for the hydrogen chloride that is coproduced and for the other chlrromethanes that can be coproduced.

Manufacturing Processes

193. Methyl chloride via chlorination of methane

Reaction: $CH_4 + C\ell_2 \rightarrow CH_3C\ell + HC\ell$

Comments: This is a flexible process that can be used to produce any chloromethane or mixtures thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.32	-.41	[30]
Chlorine	-1.40	-1.85	[30]
Methyl Chloride	1.00	1.00	
Hydrogen Chloride	.72	.72	

---

194. Methyl chloride via hydrochlorination of methanol

Reaction: $CH_3OH + HC\ell \rightarrow CH_3C\ell + H_2O$

Comments: Reaction occurs in vapor phase at about 350 C over a catalyst of alumina or zinc chloride.

Input-Output Coefficients:	Theoretical	Model	References
Methanol	-.63	-.70	[17],[20]
Hydrogen Chloride	-.72	-.80	[20]
Methyl Chloride	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	3	25	85	425	[24],[26]
Exogeneous Demand	3	25	85	425	[24],[26]

(Note: Published production statistics apparently do not account for the production of methyl chloride for conversion to other chloromethanes.)

Methyl Chloroform

The large-scale use of methyl chloroform did not begin until the 1950s, when it replaced carbon tetrachloride in many degreasing operations. Today its main use is still as a solvent in degreasing operations, particularly the cold cleaning of machinery and electronic assemblies.

Most methyl chloroform is manufactured from vinyl chloride via ethylidene chloride or from ethylene dichloride via vinylidene chloride. The vinylidene chloride route was used originally, but the ethylidene chloride route is most important today. Some methyl chloroform is also derived from ethane.

Manufacturing Processes

195. Methyl chloroform via chlorination of ethylene dichloride

Reactions:

$$CH_2ClCH_2Cl + Cl_2 \rightarrow CH_2ClCHCl_2 + HCl$$

$$CH_2ClCHCl_2 \rightarrow CH_2{=}CCl_2 + HCl$$

$$CH_2{=}CCl_2 + HCl \rightarrow CH_3CCl_3$$

Comments: First reaction occurs in liquid phase using a metal chloride catalyst. Third reaction occurs in liquid phase at about 25-35 C with a ferric chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-.74	-.82	[17]
Chlorine	-.53	-.55	
Methyl Chloroform	1.00	1.00	
Hydrogen Chloride	.27	.27	

---

196. Methyl chloroform via hydrochlorination of vinyl chloride

Reactions:

$$CH_2{=}CHCl + HCl \rightarrow CH_3CHCl_2$$

$$CH_3CHCl_2 + Cl_2 \rightarrow CH_3CCl_3 + HCl$$

Comments: First reaction occurs in the presence of a ferric chloride catalyst. Second reaction occurs in vapor phase at about 400 C and 1 atm.

Input-Output Coefficients:	Theoretical	Model	References
Vinyl Chloride	-.47	-.49	[32]
Chlorine	-.53	-.55	
Methyl Chloroform	1.00	1.00	

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197. Methyl chloroform via chlorination of ethane

Reaction: $CH_3CH_3 + 3\ C\ell_2 \rightarrow CH_3CC\ell_3 + 3\ HC\ell$

Comments: Reaction occurs at about 345 C and 40-80 psig.

Input-Output Coefficients:	Theoretical	Model	References
Ethane	-.23	-.37	[32]
Chlorine	-1.59	-2.02	[32]
Methyl Chloroform	1.00	1.00	
Hydrogen Chloride	.82	1.11	[32]
Ethylene		.07	[32]

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	150	365	[24],[26]
Exogeneous Demand	--	--	150	365	[24],[26]

Methylene Dichloride

Methylene dichloride is used primarily as a paint remover. Substantial quantities are also used in solvent degreasing and plastics processing. As a gas it is used as a propellant in aerosol formulations. There is also a sizable export market.

Methane or methanol-derived methyl chloride can be chlorinated to methylene dichloride. Both routes have been important, but today methane chlorination is dominant.

Manufacturing Processes

198. Methylene dichloride via chlorination of methane

Reaction: $CH_4 + 2\ C\ell_2 \rightarrow CH_2C\ell_2 + 2\ HC\ell$

Comments: This is a flexible process that can be used to produce any chloromethane or mixture thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methane	-.19	-.20	[17]
Chlorine	-1.67	-1.70	
Methylene Dichloride	1.00	1.00	
Hydrogen Chloride	.86	.86	

---

199. Methylene dichloride via chlorination of methyl chloride

Reaction: $CH_3C\ell + C\ell_2 \rightarrow CH_2C\ell_2 + HC\ell$

Comments: This is a flexible process that can be used to produce methylene dichloride, chloroform, carbon tetrachloride, or mixtures thereof.

Input-Output Coefficients:	Theoretical	Model	References
Methyl Chloride	-.59	-.62	estimate of yield
Chlorine	-.84	-.88	based on yield of
Methylene Dichloride	1.00	1.00	methylene dichloride
Hydrogen Chloride	.43	.43	from methane

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	4	40	115	400	[24],[26], [49]
Exogeneous Demand	4	40	115	400	[24],[26], [49]

Methyl Ethyl Ketone

Methyl ethyl ketone is used largely as a solvent for vinyl coatings, nitrocellulose, adhesives, and acrylic coatings. A variety of other solvent uses accounts for the remainder of the market.

Most methyl ethyl ketone is still produced by dehydrogenating s-butanol. However, the oxidation of butane today accounts for an increasing fraction of total methyl ethyl ketone production. The conversion of n-butylenes to methyl ethyl ketone using the Wacker process for olefin oxidation has also been practiced recently.

Manufacturing Processes

200. Methyl ethyl ketone via dehydrogenation of s-butanol

Reaction: $CH_3CH_2CHOHCH_3 \rightarrow CH_3CH_2COCH_3 + H_2$

Comments: Reaction occurs in vapor phase at about 350-550 C and 1 atm. over a zinc oxide or brass catalyst.

Input-Output Coefficients:	Theoretical	Model	References
s-Butanol	-1.03	-1.17	[17],[20]
Methyl Ethyl Ketone	1.00	1.00	
Hydrogen	.03	.03	

---

201. Methyl ethyl ketone via oxidation of n-butylenes

Reaction: $\begin{matrix} CH_3CH{=}CHCH_3 \\ \text{or} \\ CH_3CH_2CH{=}CH_2 \end{matrix} + \frac{1}{2} O_2 \rightarrow CH_3CH_2COCH_3$

Comments: Reaction occurs in liquid phase at about 120 C and 9-20 atm. using a catalyst of palladium chloride and cuprous chloride.

Input-Output Coefficients:	Theoretical	Model	References
n-Butylenes	-.78	-.90	[60]
Methyl Ethyl Ketone	1.00	1.00	

202. Methyl ethyl ketone via oxidation of n-butane

Reaction (not balanced): $CH_3CH_2CH_2CH_3 + O_2 \rightarrow CH_3CH_2COCH_3$ + various byproducts

Comments: The same process is used to produce acetic acid from butane. Compared to the acetic acid process less severe conditions are used to produce methyl ethyl ketone.

Input-Output Coefficients:	Model	References
n-Butane	-1.41	estimate of yield based on yield
Methyl Ethyl Ketone	1.00	of acetic acid from butane

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	45	125	200	480	[24],[26]
Exogeneous Demand	45	125	200	480	[24],[26]

Methyl Isobutyl Ketone

Most methyl isobutyl ketone is used as a solvent, primarily for nitrocellulose, vinyl coatings, and various other coatings and films. Methyl isobutyl ketone is derived from acetone via diacetone alcohol and mesityl oxide. Processes proceeding from acetone or isopropanol directly to methyl isobutyl ketone have recently been developed but apparently not yet commercialized.

Manufacturing Process

203. Methyl isobutyl ketone via dimerization of acetone

Reactions: $2\ CH_3COCH_3 \rightarrow (CH_3)_2COHCH_2COCH_3$

$(CH_3)_2COHCH_2COCH_3 \rightarrow (CH_3)_2C{=}CHCOCH_3 + H_2O$

$(CH_3)_2C{=}CHCOCH_3 + H_2 \rightarrow (CH_3)_2CHCH_2COCH_3$

Comments: First reaction occurs at about 0-5 C in a column packed with soda lime. Second reaction occurs at about 100-120 C using an acid catalyst. Third reaction occurs at about 120-200 C and 3-10 atm. using a copper or nickel catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetone	-1.16	-1.25	[17]
Hydrogen	-.02	-.02	
Methyl Isobutyl Ketone	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	25	75	140	200	[24],[26]
Exogeneous Demand	25	75	140	200	[24],[26]

Methyl Methacrylate

The largest market for methyl methacrylate is in the production of polymers such as Lucite and Plexiglas, which because of their clarity and strength are used as alternatives to glass in various situations. Methyl methacrylate polymers and copolymers are also used extensively as surface coatings, as oil additives, and as molding powders for automobile parts.

Methyl methacrylate is derived from acetone via acetone cyanohydrin. This was the original commercial route to methyl methacrylate and is the only route used today in the United States. An alternative process, developed in the late-1950s and used here in the 1960s, converts isobutylene to methyl methacrylate.

Manufacturing Processes

204. Methyl methacrylate via cyanation of acetone

Reaction $CH_3COCH_3 + HCN \rightarrow (CH_3)_2COHCN$

$(CH_3)_2COHCN + CH_3OH + H_2SO_4 \rightarrow CH_2=C(CH_3)COOCH_3 + NH_4HSO_4$

Comments: First reaction occurs at about 25-60 C and 1 atm. in the presence of caustic soda. Second reaction occurs at about 80 C using 98% sulfuric acid.

Input-Output Coeffcients:	Theoretical	Model	References
Acetone	-.58	-.72	[5],[17]
Hydrogen Cyanide	-.27	-.34	[5]
Methanol	-.32	-.57	[5]
Sulfuric Acid	-.98	-1.20	
Methyl Methacrylate	1.00	1.00	
Ammonium Bisulfate	1.15	1.15	

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205. Methyl methacrylate via oxidation of isobutylene

Reactions: $CH_2=C(CH_3)_2 + \frac{3}{2} O_2 \rightarrow CH_2=C(CH_3)COOH + H_2O$

$CH_2=C(CH_3)COOH + CH_3OH \rightarrow CH_2=C(CH_3)COOCH_3 + H_2O$

Comments: The oxidation step may employ nitric acid.

Input-Output Coefficients:	Theoretical	Model	References
Isobutylene	-.56	-1.00	[5]
Methanol	-.32	-.40	
Methyl Methacrylate	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	3	55	125	445	[24],[27], [50],[64]
Exogeneous Demand	3	55	125	445	[24],[27], [50],[64]

Naphtha

Naphtha is a liquid petroleum fraction (C_5-400°F) that can serve as a feedstock for the production of ethylene, acetylene, synthesis gas, and other chemicals. It has been important as a feedstock for petrochemicals in Europe and Japan for several years, and is increasingly important in the United States.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply	--	100	2000	10000	

Naphthalene

Production of phthalic anhydride has long been the largest market for naphthalene. Among smaller-volume naphthalene derivatives are insecticides, dyestuffs, and tanning agents. Until the early-1960s coal carbonization processes accounted for the entire naphthalene supply. Since then the dealkylation of refinery reformate streams containing methyl naphthalenes has become an equally important source.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from coal and petroleum)	160	290	520	700	[24],[26]

Nitric Acid

Fertilizer production is by far the largest market for nitric acid. Its other important derivatives are explosives such as TNT and petrochemicals such as aniline and toluene diisocyanate. Nearly all nitric acid is manufactured from ammonia by oxidation.

Manufacturing Process

206. Nitric acid via oxidation of ammonia

Reactions:

$$NH_3 + \frac{5}{4} O_2 \rightarrow NO + \frac{3}{2} H_2O$$

$$\frac{3}{2} NO + \frac{3}{4} O_2 \rightarrow \frac{3}{2} NO_2$$

$$\frac{3}{2} NO_2 + \frac{1}{2} H_2O \rightarrow HNO_3 + \frac{1}{2} NO$$

Comments: First reaction occurs at about 750 C and 100 psi over a platinum-rhodium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ammonia	-.27	-.29	[5],[20]
Nitric Acid	1.00	1.00	

Supply and Demand Data (in millions of pounds)

It is assumed that all nitric acid is produced within the petrochemical industry; thus there is no exogeneous supply.

	1940	1950	1960	1970	References
Total Production	500	2600	6600	15200	[20],[30], [32]
Exogeneous Demand	400	2400	6000	13700	[20],[30-32]

Nitrobenzene

Most nitrobenzene is hydrogenated to aniline. Other dye intermediates, such as benzidene, are also derived from nitrobenzene There are small-volumes uses for nitrobenzene as an intermediate in the production of pharmaceuticals, herbicides, and polyamide fibers. All nitrobenzene is manufactured by nitrating benzene with an aqueous solution of nitric and sulfuric acids.

Manufacturing Process

207. Nitrobenzene via nitration of benzene

Reaction: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

Comments: Reaction occurs at about 50-95 C in the presence of sulfuric acid.

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.63	-.65	[17],[18],[20]
Nitric Acid	-.51	-.53	[20]
Nitrobenzene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	70	130	160	550	[24],[26]
Exogeneous Demand	15	30	35	40	[20],[26], [30],[31]

Peracetic Acid

Peracetic acid is an intermediate in a route to caprolactam and in a route to glycerin. These are the only large-scale outlets. When used in these processes, peracetic acid is derived from acetaldehyde by oxidation. A process involving the reaction of acetic acid and hydrogen peroxide also exists, but to date has been used only to meet small-scale requirements for peracetic acid.

Manufacturing Process

208. Peracetic acid via oxidation of acetaldehyde

Reactions: $2\ CH_3CHO + O_2 \rightarrow CH_3COOOCHOHCH_3$

$CH_3COOOCHOHCH_3 \rightarrow CH_3COOOH + CH_3CHO$

Comments: First reaction occurs in liquid phase and may be catalyzed by ultraviolet light, ozone, or heavy metal salts. Second reaction occurs at about 100 C and 0.3 atm.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-.58	-.64	[19]
Peracetic Acid	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Perchloroethylene

Most perchloroethylene is used in dry cleaning. It has smaller markets as a solvent for vapor degreasing and as a chemical intermediate for fluorocarbon production.

For many years most perchloroethylene was produced by chlorinating acetylene-derived trichloroethylene. Today most perchloroethylene is derived from ethylene dichloride by chlorination or oxychlorination. The chlorination and oxychlorination reactions are often run simultaneously. Substantial quantities of perchloroethylene are also produced by the chlorinolysis of various hydrocarbons or chlorohydrocarbons. Ethane now seems to be the usual feed to the chlorinolysis reactor, but propane, propylene, and propylene dichloride have all been used. Carbon tetrachloride is produced as a byproduct in the chlorinolysis process; this can be pyrolyzed to make additional perchloroethylene. Methane can also be used as a feedstock; it is chlorinated to carbon tetrachloride which is simultaneously pyrolyzed to perchloroethylene.

Manufacturing Processes

209. Perchloroethylene via chlorination of trichloroethylene

Reactions:

$$CHC\ell{=}CC\ell_2 + C\ell_2 \rightarrow CHC\ell_2CC\ell_3$$

$$CHC\ell_2CC\ell_3 + \frac{1}{2}\,Ca(OH)_2 \rightarrow CC\ell_2{=}CC\ell_2 + \frac{1}{2}\,CaC\ell_2 + H_2O$$

Comments: First reaction occurs in liquid phase at about 70-80 C using a metal chloride catalyst. Second reaction employs a boiling slurry of lime.

Input-Output Coefficients:	Theoretical	Model	References
Trichloroethylene	-.79	-.86	[20]
Chlorine	-.43	-.47	[20]
Calcium Hydroxide	-.22	-.23	
Perchloroethylene	1.00	1.00	
Calcium Chloride	.33	.33	

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210. Perchloroethylene via chlorinolysis of propane

Reaction (not balanced): $CH_3CH_2CH_3 + Cl_2 \rightarrow CCl_2{=}CCl_2 + CCl_4 + HCl$

Comments: This is a flexible process that can also be operated to produce a predominance of carbon tetrachloride.

Input-Output Coefficients:	Model	References
Propane	-.25	[46]
Chlorine	-2.71	[46]
Perchloroethylene	1.00	
Carbon Tetrachloride	.54	[46]
Hydrogen Chloride	1.29	[46]

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211. Perchloroethylene via chlorinolysis of propylene dichloride

Reaction (not balanced): $CH_3CHClCH_2Cl + Cl_2 \rightarrow CCl_2{=}CCl_2 + CCl_4 + HCl$

Comments: This is a flexible process that can be used also to produce a predominance of carbon tetrachloride.

Input-Output Coefficients:	Model	References
Propylene Dichloride	-.66	estimate of yields based on
Chlorine	-2.22	yields for chlorinolysis of
Perchloroethylene	1.00	propylene
Carbon Tetrachloride	.54	
Hydrogen Chloride	1.20	

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212. Perchloroethylene via chlorination of ethylene dichloride

Reaction: $CH_2ClCH_2Cl + 3\ Cl_2 \rightarrow CCl_2{=}CCl_2 + 4\ HCl$

Comments: This is a flexible process that can also be used to produce trichloroethylene. Frequently ethylene dichloride is chlorinated and oxychlorinated simultaneously.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-.60	-.63	[45]
Chlorine	-1.28	-1.33	[45]
Perchloroethylene	1.00	1.00	
Hydrogen Chloride	.88	.88	

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213. Perchloroethylene via oxychlorination of ethylene dichloride

Reaction: $CH_2C\ell CH_2C\ell + 2\ HC\ell + \frac{3}{2}\ O_2 \rightarrow C\ell_2C=CC\ell_2 + 3\ H_2O$

Comments: This is a flexible process that can also be used to produce trichloroethylene. Frequently ethylene dichloride is chlorinated and oxychlorinated simultaneously.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-.60	-.67	[45]
Hydrogen Chloride	-.44	-.45	
Perchloroethylene	1.00	1.00	

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214. Perchloroethylene via chlorinolysis of ethane

Reaction (not balanced): $CH_3CH_3 + C\ell_2 \rightarrow C\ell_2C=CC\ell_2 + CC\ell_4 + HC\ell$

Comments: This is a flexible process that can also be operated to produce a predominance of carbon tetrachloride.

Input-Output Coefficients:	Model	References
Ethane	-.25	estimates of yields based on
Chlorine	-2.71	yields for chlorinolysis of
Perchloroethylene	1.00	propane
Carbon Tetrachloride	.54	
Hydrogen Chloride	1.29	

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215. Perchloroethylene via chlorinolysis of propylene

Reaction (not balanced): $CH_3CH=CH_2 + C\ell_2 \rightarrow C\ell_2C=CC\ell_2 + CC\ell_4 + HC\ell$

Comments: This is a flexible process that can be used also to produce a predominance of carbon tetrachloride.

Input-Output Coefficients:	Model	References
Propylene	-.25	[46]
Chlorine	-2.63	[46]
Perchloroethylene	1.00	
Carbon Tetrachloride	.54	[46]
Hydrogen Chloride	1.20	[46]

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216. Perchloroethylene via pyrolysis of carbon tetrachloride

Reaction: $2\ CC\ell_4 \rightarrow CC\ell_2{=}CC\ell_2 + 2\ C\ell_2$

Comments: Reaction occurs in vapor phase at about 800-900 C.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Tetrachloride	-1.86	-2.00	estimate of yield
Perchloroethylene	1.00	1.00	based on yield for
Chlorine	.86	.86	chlorinolysis processes

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	12	95	210	705	[24],[26]
Exogeneous Demand	12	95	210	705	[24],[26]

Phenol

Phenolic resins, especially phenol-formaldehyde, account for about half the demand for phenol. There is also a substantial market for phenol as an intermediate for the production of bisphenol-A and cyclohexanol. Among other phenol derivatives are a variety of surfactants, antioxidants, pesticides, and plasticizers.

The oldest commercial routes to phenol involve the sulfonation of benzene and the alkaline hydrolysis of chlorobenzene. In 1940 a process in which chlorobenzene is catalytically hydrolyzed with steam was introduced, but did not exhibit substantial growth until the 1950s. The hydrochloric acid coproduced in this process is recycled to chlorobenzene production. A process oxidizing cumene to phenol and acetone was commercialized in 1955, and soon assumed a dominant position. Since the early-1960s some phenol has also been derived from toluene via benzoic acid. From time to time, processes oxidizing benzene directly to phenol have been operated, but these did not prove successful. There has also been some interest in the commercial production of phenol from cyclohexanol.

Manufacturing Processes

217. Phenol via oxidation of cumene

Reactions:

$$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH$$

$$C_6H_5C(CH_3)_2OOH \rightarrow C_6H_5OH + CH_3COCH_3$$

Comments: First reaction occurs at about 130 C using a catalyst of copper, manganese, or cobalt salts. Second reaction occurs at 45-65 C on contact with 10% sulfuric acid.

Input-Output Coefficients:	Theoretical	Model	References
Cumene	-1.28	-1.42	[17]
Phenol	1.00	1.00	
Acetone	.62	.60	[17]

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218. Phenol via decarboxylation of benzoic acid

Reaction: $C_6H_5COOH + \frac{1}{2} O_2 \rightarrow C_6H_5OH + CO_2$

Comments: Reaction occurs at about 230 C and 20-25 psi using a cupric benzoate catalyst promoted by manganese.

Input-Output Coefficients:	Theoretical	Model	References
Benzoic Acid	-1.30	-1.44	[20]
Phenol	1.00	1.00	
Carbon Dioxide	.47	.47	

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219. Phenol via dehydrochlorination of chlorobenzene

Reaction: $C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$

Comments: Reaction occurs at about 425-500 C using calcium phosphate catalyst on silica.

Input-Output Coefficients:	Theoretical	Model	References
Chlorobenzene	-1.20	-1.32	[20]
Phenol	1.00	1.00	
Hydrogen Chloride	.39	.39	

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220. Phenol via alkaline hydrolysis of chlorobenzene

Reactions: $C_6H_5Cl + 2\ NaOH \rightarrow C_6H_5ONa + NaCl + H_2O$

$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$

Comments: First reaction occurs at about 360 C and 4000-5000 psi.

Input-Output Coefficients:	Theoretical	Model	References
Chlorobenzene	-1.20	-1.25	[17],[20]
Sodium Hydroxide	-.85	-1.37	[20]
Hydrogen Chloride	-.39	-.51	[20]
Phenol	1.00	1.00	
Sodium Chloride	1.24	1.25	

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221. Phenol via sulfonation of benzene

Reactions:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$$

$$C_6H_5SO_3H + \frac{1}{2} Na_2SO_3 \rightarrow C_6H_5SO_3Na + \frac{1}{2} SO_2 + \frac{1}{2} H_2O$$

$$C_6H_5SO_3Na + 2\ NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

$$C_6H_5ONa + \frac{1}{2} SO_2 + \frac{1}{2} H_2O \rightarrow C_6H_5OH + \frac{1}{2} Na_2SO_3$$

Input-Output Coefficients:	Theoretical	Model	References
Benzene	-.83	-1.11	[17]
Sulfuric Acid	-1.04	-1.36	[20]
Sodium Hydroxide	-.85	-1.70	[20]
Phenol	1.00	1.00	
Sodium Sulfite	1.34	2.60	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	70	290	730	1710	[24],[26]
Exogeneous Demand	40	220	560	1100	[18-20], [27-31]

Phosgene

Phosgene had no large-scale commercial use until the mid-1950s, when the manufacture of isocyanates for polyurethane production began. Isocyanates still account for most of the demand for phosgene. Other important phosgene derivatives are polycarbonate resins and the insecticide Sevin. The only commercial route to phosgene is the reaction of chlorine and carbon monoxide.

Manufacturing Process

222. Phosgene via reaction of chlorine and carbon monoxide

Reaction: $CO + C\ell_2 \rightarrow COC\ell_2$

Comments: Reaction occurs at about 200 C over an activated carbon catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Monoxide	-.28	-.29	[20]
Chlorine	-.72	-.72	[20]
Phosgene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	35	600	[24],[26]
Exogeneous Demand	--	--	10	200	[24],[26],[5]

Phthalic Anhydride

About half the total production of phthalic anhydride is used to manufacture plasticizers. Other major markets are the production of polyesters and alkyd resins. Phthalic anhydride is produced commercially by oxidizing either naphthalene or o-xylene. Although some phthalic anhydride has been derived from o-xylene since 1945, it was not until substantial quantities of o-xylene became available in the late-1950s that the process became important. o-Xylene is now the preferred feedstock, but it did not overtake naphthalene until the early-1970s.

Manufacturing Processes

223. Phthalic anhydride via oxidation of o-xylene

Reaction: $C_6H_4(CH_3)_2 + O_2 \rightarrow C_6H_4(C)_2O + 3\ H_2O$

Comments: Reaction occurs at about 550 C in the vapor phase over a vanadium-pentoxide-based catalyst.

Input-Output Coefficients:	Theoretical	Model	References
o-Xylene	-.72	-1.00	[18],[20]
Phthalic Anhydride	1.00	1.00	

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224. Phthalic anhydride via oxidation of naphthalene

Reaction: $C_{10}H_8 + \frac{9}{2}\ O_2 \rightarrow C_6H_4(CO)_2O + 2\ CO_2 + 2\ H_2O$

Comments: Reaction occurs in vapor phase at about 400-460 C over a vanadium-pentoxide-based catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Naphthalene	-.87	-1.05	[5],[17],[18]
Phthalic Anhydride	1.00	1.00	
Carbon Dioxide	.59	.59	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	60	215	400	735	[24],[26]
Exogeneous Demand	60	215	400	735	[24],[26]

Propane

Aside from its use as fuel, propane is important primarily as a feedstock for ethylene manufacture, though it can also be used to produce acetylene, synthesis gas, perchloroethylene, and other chemicals. Natural gas is the source of most of the propane consumed by the petrochemical industry; refinery gas streams account for the remainder.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply					
from natural gas	} 150	} 1700	} 5500	9100	} [25]
from refineries				4200	

Propylene

Aside from fuel production (propylene is fed to refinery alkylation and polymerization units), most propylene is used as a chemical intermediate. Isopropanol, acrylonitrile, cumene, propylene oxide, n-butyraldehyde, and allyl chloride are its major derivatives. From these is produced a wide range of other chemicals, including acetone, phenol, n-butanol, 2-ethylhexanol, glycerin, epichlorohydrin, propylene glycol, and adiponitrile. Large quantities of propylene are polymerized to polypropylene, a lightweight plastic, and to propylene trimer and tetramer, feedstocks for synthetic detergent manufacture. Propylene is also polymerized with ethylene to yield elastomers.

Refinery cracking units are the major suppliers of propylene. Large quantities are also recovered as a byproduct of ethylene manufacture.

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply (from refineries)	200	1100	2700	5100	[18],[26]
Exogeneous Demand	--	200	1000	2750	[18],[26], [29]

Propylene Dichloride

Propylene dichloride is produced as a byproduct in the chlorohydrin route to propylene oxide. It has a small market as a solvent and as a lead scavenger in leaded gasoline. Since the amount produced far exceeds this demand, it is usually disposed by converting it to perchloroethylene and carbon tetrachloride by chlorinolysis. Should the need arise, propylene dichloride could also be produced by chlorinating propylene.

Manufacturing Process

225. Propylene dichloride via chlorination of propylene

Reaction: $CH_3CH{=}CH_2 + C\ell_2 \rightarrow CH_3CHC\ell CH_2C\ell$

Comments: Reaction occurs in liquid phase at about 45 C and 25-50 psi using an iron oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Propylene	-.37	-.41	[23]
Chlorine	-.63	-.70	
Propylene Dichloride	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Propylene Glycol

The largest market for propylene oxide is the production of polyester resins. Other important outlets are cellophane production, tobacco processing, and plasticizer production. Propylene glycol is produced commercially by hydrating propylene oxide. New technologies in which propylene glycol is derived directly from propylene are being developed.

Manufacturing Process

226. Propylene glycol via hydration of propylene oxide

Reaction: $CH_2\underset{\underset{O}{|}}{CH}CH_3 + H_2O \rightarrow CH_3CHOHCH_2OH$

Comments: Some dipropylene glycol is also produced.

Input-Output Coefficients:	Theoretical	Model	References
Propylene Oxide	-.76	-.85	[17]
Propylene Glycol	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	1	80	150	430	[24],[26]
Exogeneous Demand	1	80	150	430	[24],[26]

Propylene Oxide

The two major markets for propylene oxide are the production of propylene glycol for polyester resins and the production of polypropoxyethers or polyols for polyurethane foams. It also has various small-scale uses as a solvent and as a chemical intermediate.

Until recently all propylene oxide manufactured commercially was produced from propylene via propylene chlorohydrin in a process similar to that once used to make ethylene oxide. In a process commercialized in the late-1960s, isobutane is oxidized to t-butyl hydroperoxide, which is then used to oxidize propylene to propylene oxede. In the process the t-butyl hydroperoxide is converted to t-butanol. Since there is little use for the latter, it is routinely dehydrated to isobutylene. Ethylbenzene has been used in place of isobutane; in this case styrene replaces isobutylene as the coproduct.

Manufacturing Processes

227. Propylene oxide via chlorohydration of propylene

Reactions:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

$$CH_3CH{=}CH_2 + HOCl \rightarrow CH_3CHOHCH_2Cl$$

$$CH_3CHOHCH_2Cl + \frac{1}{2}\,Ca(OH)_2 \rightarrow \underset{\underset{O}{\lfloor\!\rfloor}}{CH_2CHCH_3} + \frac{1}{2}\,CaCl_2 + H_2O$$

$$HCl + \frac{1}{2}\,Ca(OH)_2 \rightarrow \frac{1}{2}\,CaCl_2 + H_2O$$

Comments: Process is similar to the chlorohydrin route to ethylene oxide.

Input-Output Coefficients:	Theoretical	Model	References
Chlorine	-1.22	-1.59	[32]
Propylene	-.72	-.94	[32],[17]
Calcium Hydroxide	-1.28	-1.44	[32]
Propylene Oxide	1.00	1.00	
Calcium Chloride	1.91	2.15	[32]
Propylene Dichloride		.10	[32],[17]

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228. Propylene oxide via oxidation of propylene with t-butyl hydroperoxide

Reactions:

$$2\ (CH_3)_2CHCH_3 + O_2 \rightarrow (CH_3)_2COOHCH_3 + (CH_3)_2COHCH_3$$

$$CH_3CH{=}CH_2 + (CH_3)_2COOHCH_3 \rightarrow CH_2\underset{\underset{O}{|}}{\overset{\overset{2}{|}}{}}CHCH_3 + (CH_3)_2COHCH_3$$

$$2\ (CH_3)_2COHCH_3 \rightarrow 2\ (CH_3)_2C{=}CH_2 + 2\ H_2O$$

Comments: First reaction occurs in liquid phase at about 125-150 C and 500 psi. Second reaction occurs in liquid phase at about 110 C and 550 psi using a catalyst based on tungsten, vanadium, or molybdenum.

Input-Output Coefficients:	Theoretical	Model	References
Isobutane	-2.00	-2.50	[5]
Propylene	-.72	-.80	[5]
Propylene Oxide	1.00	1.00	
Isobutylene	1.94	2.00	

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229. Propylene oxide via oxidation of propylene with ethylbenzene hydroperoxide

Reactions:

$$2\ C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5CHOOHCH_3 + C_6H_5CHOHCH_3$$

$$CH_3CH{=}CH_2 + C_6H_5CHOOHCH_3 \rightarrow CH_2\underset{\underset{O}{|}}{\overset{\overset{2}{|}}{}}CHCH_3 + C_6H_5CHOHCH_3$$

$$2\ C_6H_5CHOHCH_3 \rightarrow 2\ C_6H_5CH{=}CH_2 + 2\ H_2O$$

Comments: First reaction occurs in the liquid phase. Second reaction occurs in liquid phase at about 90 C and 16-65 atm. using a molybdenum naphthenate catalyst. Third reaction occurs in vapor phase at about 180-280 C over a titanium dioxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylbenzene	-3.66	-4.58	estimate of yields
Propylene	-.72	-.80	based on yields for
Propylene Oxide	1.00	1.00	t-butyl hydroper-
Styrene	3.58	3.72	oxide process

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	1	65	310	1180	[24],[26]
Exogeneous Demand	--	--	180	815	[24],[26]

Pyrolysis Gasoline

A light hydrocarbon liquid (C_5-400°F) known as pyrolysis gasoline is produced as a byproduct when hydrocarbons are pyrolyzed to ethylene. This liquid is rich in aromatics and in isoprene. As used here, the term pyrolysis gasoline refers to the liquid fraction remaining after extraction of these valuable components. Large quantities of pyrolysis gasoline are produced when naphtha or gas oil is used for ethylene manufacture. Marketing this byproduct may be difficult unless the ethylene manufacturer is allied with a petroleum refinery where the pyrolysis gasoline can be blended in motor gasoline or used in other operations.

Demand Data

There is no exogeneous demand, though pyrolysis gasoline may be an output of the petrochemical industry.

Sodium

Metallic sodium is consumed in an obsolete process for making hydrogen cyanide; this is its only petrochemical application as a raw material. Metallic sodium is produced by the electrolysis of molten sodium chloride.

Supply Data

The supply of sodium to the petrochemical industry is not constrained in the model.

Sodium Chloride

Sodium chloride is produced in processes currently used to manufacture chloroprene and glycerin, as well as in obsolete processes for phenol and vinyl chloride. The sodium chloride so produced is usually electrolyzed to recover the chlorine. Of course, the usual source of sodium chloride is sea water or other natural brines.

Demand Data

There is no exogeneous demand, though sodium chloride may be an output of the petrochemical industry.

Sodium Hydroxide

Sodium hydroxide is consumed in current processes for manufacturing chloroprene and glycerin and in obsolete processes for phenol and vinyl chloride. This represents a very small fraction of the total demand for this chemical. The electrolysis of sodium chloride accounts for most of the sodium hydroxide supply.

Supply Data

The supply of sodium hydroxide to the petrochemical industry is not constrained in the model.

Sodium Sulfate

Sodium sulfate is produced in an obsolete process for making hydrogen cyanide. Usually sodium sulfate is recovered from natural brines or manufactured from sodium chloride and sulfuric acid. It is used mainly in the kraft pulp industry.

Demand Data

There is no exogeneous demand, though sodium sulfate may be an output of the petrochemical industry.

Sodium Sulfite

Sodium sulfite is produced in an obsolete process for making phenol. It is usually produced by the reaction of sulfur dioxide and sodium carbonate. It is used mainly for bleaching and as a preservative for foods and beverages.

Demand Data

There is no exogeneous demand, though sodium sulfite may be an output of the industry.

Styrene

Production of polystyrene accounts for about half the market for styrene. Most of the remainder is used to produce copolymers, of which the most important are styrene-butadiene, acrylonitrile-butadiene-styrene, and styrene-acrylonitrile. There is also a substantial export market.

Nearly all styrene is manufactured from ethylbenzene by dehydrogenation. An alternative process oxidizes ethylbenzene to acetophenone, which is then reduced to phenyl ethyl alcohol for dehydration to styrene. This process has been operated in the United States, but now is used only in Europe. Another source of styrene is the pyrolysis gasoline produced in ethylene manufacture. Also styrene is coproduced in one process for propylene oxide production.

Manufacturing Processes

230. Styrene via dehydrogenation of ethylbenzene

Reaction: $C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$

Comments: Reaction occurs at about 600-700 C under reduced pressure using a metallic oxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylbenzene	-1.02	-1.13	[17],[20]
Styrene	1.00	1.00	
Hydrogen	.02	.02	

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231. Styrene via oxidation of ethylbenzene

Reactions: $C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5COCH_3 + H_2O$

$C_6H_5COCH_3 + H_2 \rightarrow C_6H_5CHOHCH_3$

$C_6H_5CHOHCH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2O$

Comments: First reaction occurs in liquid phase at about 125 C and 30 psi with a manganese acetate catalyst. Second reaction occurs in liquid phase at about 150 C and 150 psi using a copper-chromium-iron catalyst. Third reaction occurs in vapor phase at about 200-250 C using a titanium dioxide catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Ethylbenzene	-1.02	-1.30	[17]
Hydrogen	-.02	-.02	
Styrene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	2	540	1750	4335	[24],[26]
Exogeneous Demand	2	540	1750	4335	[24],[26]

Sulfur

Elemental sulfur is consumed by the petrochemical industry in producing carbon disulfide and in preparing hydroxylamine sulfate for caprolactam production. These are its only large-scale petrochemical applications as a raw material. Elemental sufur is obtained from natural deposits or from naturally occurring hydrogen sulfide gas.

Supply Data

The supply of sulfur to the petrochemical industry is not constrained in the model.

Sulfuric Acid

Sulfuric acid is consumed in current processes for manufacturing caprolactam and methyl methacrylate, and is used in an auxiliary capacity in many petrochemical operations. These applications account for a very small fraction of the total demand for sulfuric acid. Most sulfuric acid is produced by the stepwise oxidation of sulfur to sulfur trioxide, which is then contacted with water to yield sulfuric acid.

Supply Data

The supply of sulfuric acid to the petrochemical industry is not constrained in the model.

Terephthalic Acid

Terephthalic acid (TPA) and its dimethyl ester (DMT) are used almost entirely for the production of polyethylene terephthalate, a polyester first prepared commercially in the United States in the early-1950s. Because TPA was less readily purified than DMT, it was not used directly for polyester manufacture until the mid-1960s, when purification processes were sufficiently improved. Since then the fraction of polyethylene terephthalate manufactured directly from TPA has gradually increased.

In the United States all TPA is produced by oxidizing p-xylene with either nitric acid or oxygen. Nitric acid was originally used, but the oxygen-based process has been predominant since the mid-1960s. There are three variants of the oxygen-based process; they differ primarily in whether bromine, methyl ethyl ketone, or acetaldehyde is used as a catalyst promoter. Some of the methyl ethyl ketone or acetaldehyde used as a promoter is converted to acetic acid in the process. TPA can also be derived from benzoic acid obtained from toluene or phthalic anhydride. This process is important in Japan, where there are insufficient supplies of p-xylene. A recently developed process involves the ammonolysis of p-xylene to terephthalonitrile, followed by hydrolysis to TPA.

Manufacturing Processes

232. Terephthalic acid via oxidation of p-xylene

Reaction: $C_6H_4(CH_3)_2 + 3\ O_2 \rightarrow C_6H_4(COOH)_2 + 2\ H_2O$

Comments: Reaction occurs in liquid phase at about 200 C and 200 psi using a cobalt acetate catalyst promoted with sodium bromide or hydrogen bromide. Methyl ethyl ketone or acetaldehyde can also be used as promoters; in this case some of the promoter is converted to acetic acid.

Input-Output Coefficients:	Theoretical	Model	References
p-Xylene	-.64	-.67	[17],[18]
Terephthalic Acid	1.00	1.00	

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233. Terephthalic acid via disproportionation of benzoic acid

Reaction: $2\ C_6H_5COOH \rightarrow C_6H_4(COOH)_2 + C_6H_6$

Comments: Reaction occurs at about 410-430 C and 10-15 atm. with a cadmium salt catalyst. The potassium salt of benzoic acid is the usual reactant.

Input-Output Coefficients:	Theoretical	Model	References
Benzoic Acid	-1.47	-1.69	[5]
Terephthalic Acid	1.00	1.00	
Benzene	.47	.50	[5]

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234. Terephthalic acid via oxidation of p-xylene with nitric acid

Reactions: $C_6H_4(CH_3)_2 + 4\ HNO_3 \rightarrow C_6H_4(COOH)_2 + 4\ NO + 4\ H_2O$

$6\ NO + 3\ O_2 \rightarrow 6\ NO_2$

$6\ NO_2 + 2\ H_2O \rightarrow 4\ HNO_3 + 2\ NO$

Comments: Reaction occurs in liquid phase at about 165 C and 140 psi.

Input-Output Coefficients:	Theoretical	Model	References
p-Xylene	-.64	-.73	[5],[17],[18]
Nitric Acid		-2.00	[5],[18],[19]
Terephthalic Acid	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	--	--	--	420	[26]

Toluene

The traditional markets for toluene, blending in gasoline and production of explosives (TNT), are now secondary to benzene production, which in 1970 accounted for over half the demand for toluene in the United States. Of the various other chemicals derived from toluene, benzoic acid and toluene diisocyanate are the most important. Toluene also has some use as a solvent.

Refinery reforming units are the major suppliers of toluene. Coal carbonization processes, once the primary source of toluene, still account for some of the toluene supply. Toluene also occurs as a byprocuct in ethylene manufacture, particularly when naphtha or gas oil is the feedstock.

Supply and Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply	150	300	1000	5050	[18],[26], [27-29]
Exogeneous Demand	150	300	970	1100	[20],[27-31]

Toluene Diamine

The only major market for toluene diamine is the production of toluene diisocyanate for making polyurethane plastics. The usual commercial product, an 80:20 mixture of the 2,4 and 2,6 isomers, is prepared by the catalytic hydrogenation of the corresponding mixture of dinitrotoluene isomers.

Manufacturing Process

235. Toluene diamine via hydrogenation of dinitrotoluene

Reaction: $CH_3C_6H_3(NO_2)_2 + 6\ H_2 \rightarrow CH_3C_6H_3(NH_2)_2 + 4\ H_2O$

Comments: Reaction occurs at about 80 C and 75 psi using a palladium catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Dinitrotoluene	-1.49	-1.57	[17]
Hydrogen	-.10	-.10	
Toluene Diamine	1.00	1.00	

Demand Data

There is essentially no exogeneous demand.

Toluene Diisocyanate

Toluene diisocyanate is used primarily to produce polyurethanes, polymers which were first commercialized in 1955. The usual commercial product, an 80:20 mixture of 2,4 and 2,6 toluene diisocyanate, is manufactured by the phosgenation of the corresponding mixture of toluene diamine isomers.

Manufacturing Process

236. Toluene diisocyanate via phosgenation of toluene diamine

Reactions:

$$CH_3C_6H_3(NH_2)_2 + COCl_2 \rightarrow CH_3C_6H_3(NH_3Cl)(NHCOCl)$$

$$CH_3C_6H_3(NH_3Cl)(NHCOCl) + COCl_2 \rightarrow CH_3C_6H_3(NHCOCl)_2 + 2\ HCl$$

$$CH_3C_6H_3(NHCOCl)_2 \rightarrow CH_3C_6H_3(NCO)_2 + 2\ HCl$$

Comments: First reaction occurs in liquid phase at about 20-50 C. Second reaction occurs in liquid phase at about 185 C. Third reaction occurs at about 110-115 C.

Input-Output Coefficients:	Theoretical	Model	References
Toluene Diamine	-.70	-.83	[17]
Phosgene	-1.14	-1.30	[17]
Toluene Diisocyanate	1.00	1.00	
Hydrogen Chloride	.84	.84	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	--	--	45	310	[24]
Exogeneous Demand	--	--	45	310	[24]

Trichloroethylene

Trichloroethylene is used largely in the vapor degreasing of fabricated metal parts. It has various other uses as a solvent.

Today most trichloroethylene is derived from ethylene dichloride by chlorination or oxychlorination. In practice the chlorination and oxychlorination reactions are often made to occur simultaneously. In the original route to trichloroethylene, acetylene was chlorinated to 1,1,2,2 tetrachloroethane, which was dehydrochlorinated with lime. Later many manufacturers switched to a catalytic dehydrochlorination process, therby avoiding the loss of chlorine as calcium chloride. In 1970 the acetylene-based processes were used to produce about half the trichloroethylene. Today however these processes are not commercially important in the United States.

Manufacturing Processes

237. Trichloroethylene via chlorination of acetylene (catalytic dehydrochlorination)

Reactions: $CH{\equiv}CH + 2\ C\ell_2 \rightarrow CHC\ell_2CHC\ell_2$

$CHC\ell_2CHC\ell_2 \rightarrow CHC\ell{=}CC\ell_2 + HC\ell$

Comments: First reaction occurs in liquid phase at about 80 C using a ferric chloride or antimony trichloride catalyst. Second reaction occurs in vapor phase at about 250-300 C over a barium chloride catalyst.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.20	-.21	[17],[20]
Chlorine	-1.08	-1.20	[20]
Trichloroethylene	1.00	1.00	
Hydrogen Chloride	.28	.28	

---

238. Trichloroethylene via chlorination of acetylene (alkaline dehydrochlorination)

Reactions: $CH{\equiv}CH + 2\ Cl_2 \rightarrow CHCl_2CHCl_2$

$CHCl_2CHCl_2 + \frac{1}{2}\ Ca(OH)_2 \rightarrow CHCl{=}CCl_2 + \frac{1}{2}\ CaCl + H_2O$

Comments: First step occurs at about 80 C in the liquid phase over a ferric chloride or antimony trichloride catalyst. Second reaction employs a boiling slurry of lime.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.20	-.22	[31]
Chlorine	-1.08	-1.20	[31]
Calcium Hydroxide	-.28	-.33	[31]
Trichloroethylene	1.00	1.00	
Calcium Chloride	.42	.42	

---

239. Trichloroethylene via chlorination of ethylene dichloride

Reaction: $CH_2ClCH_2Cl + 2\ Cl_2 \rightarrow CHCl{=}CCl_2 + 3\ HCl$

Comments: This is a flexible process that can also be used to produce perchloroethylene. Frequently ethylene dichloride is chlorinated and oxychlorinated simultaneously.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-.75	-.79	estimate of yield
Chlorine	-1.08	-1.14	based on yield of
Trichloroethylene	1.00	1.00	perchloroethylene
Hydrogen Chloride	.83	.83	from ethylene dichloride

---

240. Trichloroethylene via oxychlorination of ethylene dichloride

Reaction: $CH_2ClCH_2Cl + HCl + O_2 \rightarrow CHCl{=}CCl_2 + 2\ H_2O$

Comments: This is a flexible process that can also be used to produce perchloroethylene. Frequently ethylene dichloride is chlorinated and oxychlorinated simultaneously.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-.75	-.83	[45]
Hydrogen Chloride	-.83	-.85	
Trichloroethylene	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	55	215	350	610	[24],[26]

(Note: Published production statistics apparently do not account for the amount of trichloroethylene chlorinated to perchloroethylene.)

Trichlorofluoromethane

Most trichlorofluoromethane (fluorocarbon 11) is used either as a refrigerant or as a propellant in aerosol formulations. Its use as a propellant is currently the subject of some controversy (see p. 62). Fluorocarbon 11 is produced by the reaction of carbon tetrachloride and hydrogen fluoride. There has been some interest recently in processes that simultaneously chlorinate and fluorinate methane to mixtures of chlorofluoromethanes.

Manufacturing Process

241. Trichlorofluoromethane via reaction of carbon tetrachloride and hydrogen fluoride

Reaction: $CCl_4 + HF \rightarrow CCl_3F + HCl$

Comments: Reaction occurs in liquid phase using an antimony pentachloride catalyst. Dichlorodifluoromethane can be coproduced.

Input-Output Coefficients:	Theoretical	Model	References
Carbon Tetrachloride	-1.12	-1.40	[20]
Hydrogen Fluoride	-.15	-.19	
Trichlorofluoromethane	1.00	1.00	
Hydrogen Chloride	.27	.27	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	5	30	70	245	[24],[26]
Exogeneous Demand	5	30	70	245	[24],[26]

Triethylene Glycol

Natural gas dehydration is the major market for triethylene glycol. It is also important as a humectant for tobacco, as a solvent for printing inks, and as a solvent for extracting aromatics from petroleum refinery streams. Polyester and polyurethane resins and vinyl plasticizers are important derivatives.

Triethylene glycol is produced as a byproduct when ethylene oxide is hydrated to ethylene glycol. The quantities so produced have not been sufficient to satisfy demand, so additional triethylene glycol is produced from the reaction of ethylene oxide and diethylene glycol. It is this reaction that is responsible for the formation of byproduct triethylene glycol; the extent to which it occurs can be increased by decreasing the water to ethylene oxide ratio in the feed to the hydration process. However, this also increases the amount of byproduct diethylene glycol, for which there may be no market. Thus the demand for additional triethylene glycol is not met by increasing byproduct formation, but by reacting diethylene glycol and ethylene oxide in a separate process.

Manufacturing Process

242. Triethylene glycol via reaction of diethylene glycol and ethylene oxide

Reaction: CH_2CH_2O + $CH_2OHCH_2OCH_2CH_2OH$ → $CH_2OHCH_2OCH_2CH_2OCH_2CH_2OH$

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Oxide	-.29	-.35	estimate of yield
Diethylene Glycol	-.71	-.85	based on yield of
Triethylene Glycol	1.00	1.00	ethylene glycol from ethylene oxide

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	1	5	35	90	[24],[26]
Exogeneous Demand	1	5	35	90	[24],[26]

Urea

Most urea is consumed as a fertilizer or as animal feed. Important non-agricultural markets include the production of melamine and the production of plastics such as urea-formaldehyde or urea-melamine. Since the 1930s all urea manufactured in the United States has been derived from ammonia and carbon dioxide.

Manufacturing Process

243. Urea via reaction of ammonia and carbon dioxide

Reactions: $2\ NH_3 + CO_2 \rightarrow NH_2COONH_4$

$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$

Comments: First reaction occurs in liquid phase at about 160-220 C and 180-350 atm. There are a number of variations of this process.

Input-Output Coefficients:	Theoretical	Model	References
Ammonia	-.57	-.58	[5],[17],[45]
Carbon Dioxide	-.73	-.76	[5],[17],[45]
Urea	1.00	1.00	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	135	300	1500	6240	[20],[30]
Exogeneous Demand	135	300	1500	6240	[20],[30]

Vinyl Acetate

Virtually all vinyl acetate is consumed in polymerized form as polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, and other polymers and copolymers. Polyvinyl acetate is used primarily in water-base paints and adhesives; polyvinyl alcohol is used in textile and paper processing; and polyvinyl butyral is used as an interlayer in safety glass.

For many years the usual route to vinyl acetate was the reaction of acetylene and acetic acid. Within the last decade, however, this process has been largely replaced by a process that combines ethylene and acetic acid. The ethylene route was first commercialized in 1966 and by 1970 accounted for over forty percent of the vinyl acetate capacity in the United States. Originally a liquid-phase process was used, but severe corrosion problems were encountered, forcing shut-down in favor of a vapor-phase process. Another route to vinyl acetate involves the reaction of acetaldehyde and acetic anhydride. This process was operated in the United States from 1953 to 1969.

Manufacturing Processes

244. Vinyl acetate via reaction of acetylene and acetic acid

Reaction: $CH{\equiv}CH + CH_3COOH \rightarrow CH_3COOCH{=}CH_2$

Comments: Reaction occurs in vapor phase at about 350-400 C using a catalyst of zinc acetate on carbon.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.30	-.33	[17],[20]
Acetic Acid	-.70	-.72	[17],[20]
Vinyl Acetate	1.00	1.00	

245. Vinyl acetate via reaction of ethylene and acetic acid

Reaction: $CH_2{=}CH_2 + CH_3COOH + \frac{1}{2}O_2 \rightarrow CH_3COOCH{=}CH_2 + H_2O$

Comments: Reaction occurs in vapor phase at about 175-200 C and 5-10 atm. using a palladium catalyst on silica or alumina.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene	-.33	-.35	[32]
Acetic Acid	-.70	-.71	[32]
Vinyl Acetate	1.00	1.00	

---

246. Vinyl acetate via reaction of acetaldehyde and acetic anhydride

Reactions: $CH_3CHO + (CH_3CO)_2O \rightarrow CH_3CH(OCOCH_3)_2$

$CH_3CH(OCOCH_3)_2 \rightarrow CH_3COOCH{=}CH_2 + CH_3COOH$

Comments: Both reactions are acid-catalyzed.

Input-Output Coefficients:	Theoretical	Model	References
Acetaldehyde	-.51	-.57	
Acetic Anhydride	-1.19	-1.32	
Vinyl Acetate	1.00	1.00	
Acetic Acid	.70	.70	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	10	60	250	800	[24],[26],[31]
Exogeneous Demand	10	60	250	800	[24],[26],[31]

Vinyl Chloride

Nearly all vinyl chloride is polymerized; polyvinyl chloride is the usual product, but copolymers such as vinyl chloride-vinyl acetate or vinyl chloride-vinylidene chloride (Saran) are also important.

Vinyl chloride is manufactured commercially from acetylene or from ethylene via ethylene dichloride. The acetylene route was once dominant but has gradually been replaced by the ethylene dichloride route.

Manufacturing Processes

247. Vinyl chloride via dehydrochlorination of ethylene dichloride

Reaction: $CH_2ClCH_2Cl \rightarrow CH_2{=}CHCl + HCl$

Comments: Reaction occurs in vapor phase at about 480-510 C and 5 atm. using a catalyst of pumice or charcoal.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-1.58	-1.67	[17],[20]
Vinyl Chloride	1.00	1.00	
Hydrogen Chloride	.58	.58	

---

248. Vinyl chloride via hydrochlorination of acetylene

Reaction: $CH{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$

Comments: Reaction occurs in vapor phase at about 90-140 C over a catalyst of mercuric chloride on charcoal.

Input-Output Coefficients:	Theoretical	Model	References
Acetylene	-.42	-.44	[5],[17],[18]
Hydrogen Chloride	-.58	-.60	[18]
Vinyl Chloride	1.00	1.00	

---

249. Vinyl chloride via alkaline dehydrochlorination of ethylene dichloride

Reaction: $CH_2C\ell CH_2C\ell + NaOH \rightarrow CH_2{=}CHC\ell + NaC\ell + H_2O$

Comments: Reaction occurs at about 140-150 C and 10 atm.

Input-Output Coefficients:	Theoretical	Model	References
Ethylene Dichloride	-1.58	-1.76	[20]
Sodium Hydroxide	-.64	-.70	
Vinyl Chloride	1.00	1.00	
Sodium Chloride	.93	.93	

Demand Data (in millions of pounds)

	1940	1950	1960	1970	References
Total Production	10	275	1040	4040	[20],[24], [26],[31]
Exogeneous Demand	10	275	1000	3950	[20],[24], [31],[32]

m-Xylene

The only large-scale use for pure m-xylene is the production of isophthalic acid. Mixed xylenes have various solvent uses. Refinery reforming operations supply most of the xylene consumed by the petrochemical industry. m-Xylene is the most abundant isomer in reformate but is also the least demanded. Thus it is usually isomerized to a mixture of the other isomers; this is usually an integral part of isomer separation plants.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply	--	--	40	100	[24]

o-Xylene

The only large scale use of pure o-xylene is the production of phthalic anhydride. Mixed xylenes have various solvent uses. Refinery reforming operations supply most of the xylene consumed by the petrochemical industry. m-Xylene is the most abundant isomer in reformate but is also the least demanded. Thus additional o-xylene is usually produced from m-xylene by isomerization; this operation is usually an integral part of isomer separation plants.

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Supply	--	50	140	800	[24],[26]

p-Xylene

The only large-scale use for p-xylene is the production of terephthalic acid or its dimethyl ester. Mixed xylenes have various solvent uses. Refinery reforming operations supply most of the xylene consumed by the petrochemical industry. m-Xylene is the most abundant isomer in reformate but is also the least demanded. Thus additional p-xylene is usually produced from m-xylene by isomerization; this operation is usually an integral part of isomer separation plants.

Manufacturing Process

250. p-Xylene via isomerization of m-xylene

Reaction (not balanced): (m-) $C_6H_4(CH_3)_2$ → (o-) $C_6H_4(CH_3)_2$ + (p-) $C_6H_4(CH_3)_2$ + $C_6H_5CH_2CH_3$

Input-Output Coefficients:	Model	References
m-Xylene	-3.10	[45]
o-Xylene	1.00	
p-Xylene	1.00	
Ethylbenzene	1.00	

Supply Data (in millions of pounds)

	1940	1950	1960	1970	References
Exogeneous Demand	--	--	210	1600	[24], [26]

APPENDIX 2

In this appendix the optimal values of the p_i, q_i, and x_j are listed for the bounding industries for 1940, 1950, 1960, and 1970. In addition, the results of a sensitivity analysis are given. The techniques involved in the sensitivity analysis of a linear programming problem are discussed in practical terms by Driebeek[9].

In Table A.1 the optimal values of the p_i and q_i are given. The q_i that are simply equal to the corresponding d_i are not listed. The sensitivity analysis indicates that the optimal solution is quite insensitive to changes in the supply and demand parameters. Detailed results of this part of the sensitivity analysis are not given.

In Table A.2 the optimal values of the x_j are given. Also, for each process in the bounding industry, we list the amount by which carbon consumption per unit weight of product can be increased without changing the optimal industry. This sensitivity analysis indicates that the optimal solution is quite insensitive to changes in the carbon consumption, and thus the input-output coefficients, for some processes.

Table A.1. The optimal values of the p_i and q_i for the bounding industries for 1940, 1950, 1960, and 1970. Only the q_i not equal to the corresponding d_i are listed. All figures are in millions of pounds.

	Optimal p_i for:			
Chemical	1940	1950	1960	1970
Benzene	250	1356	2987	6300
Bromine	10	73	150	258
n-Butane	100	91	1518	2692
n-Butanol	90	50	30	30
n-Butylenes	63	1000	1500	2300
Calcium Hydroxide	306	376	2471	5229
Calcium Hypochlorite	0	0	0	0
Carbon	299	0	0	0
Chlorine	633	2385	5726	17422
Cyclohexane	0	80	200	400
Ethane	150	600	3200	11500
Ethanol	600	380	160	100
Ethylbenzene	0	0	100	480
Fuel Oil	0	0	0	0
Gas Oil	0	0	0	0
Hydrogen Chloride	0	0	0	0
Hydrogen Fluoride	7	39	81	200
Hydrogen Peroxide	0	0	93	73
Iron	88	160	192	640
Isobutane	0	0	0	800
Isobutylene	10	125	275	547
Isopentenes	0	0	33	0
Methane	586	3367	6303	11676
Naphtha	0	0	0	0
Naphthalene	63	173	269	0
Propane	150	314	3269	13300
Propylene	200	631	1703	4813
Sodium	0	0	0	0
Sodium Hydroxide	26	145	434	856

Table A.1 (continued)

Chemical	Optimal p_i for: 1940	1950	1960	1970
Sulfur	138	335	452	484
Sulfuric Acid	6	67	217	534
Toluene	148	296	970	2374
m-Xylene	0	0	40	100
o-Xylene	0	50	140	726
p-Xylene	0	0	84	1118

Chemical*	Optimal q_i for: 1940	1950	1960	1970
Ammonium Bisulfate	6	63	144	512
Ammonium Sulfate	†	†	225	†
Butadiene	7	†	†	†
Calcium Chloride	380	490	3172	6905
Carbon Dioxide	481	†	3042	13301
Diethylene Glycol	16	†	†	†
Hydrogen Chloride	23	701	407	3836
Iron Oxide	103	187	224	748
Isobutyraldehyde	†	27	61	141
Propylene Dichloride	†	7	†	†
Pyrolysis Gasoline	9	20	194	840
Triethylene Glycol	1	†	†	†

* only chemicals for which output exceeds exogeneous demand are listed

† indicates that output does not exceed exogeneous demand in the bounding industry for that year

Table A.2. The optimal values of the x_j for the bounding industries for 1940, 1950, 1960, and 1970. Also given are the results of sensitivity analyses for each decade. Δ_u indicates the amount by which the carbon consumption for a process can be raised without changing the optimal industry. Δ_ℓ indicates the amount by which the carbon consumption for a process can be lowered without changing the optimal industry. A dagger (†) indicates that carbon consumption can be lowered to zero without a change in the optimal industry. The values for the x_j are given in millions of pounds of product. The values of the Δ_u and Δ_ℓ are given in pounds of carbon per pound of product.

	1940			1950			1960			1970		
Process	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u
1							242	.009	.048	607	.071	.053
2				25	.008	.017						
3	185	.081	.013									
6	189	.172	.186									
8	334	.060	.160									
9										5889	.048	.007
11				2277	.015	.021	3020	.020	.020			
12	260	.233	.389	910	.003	.199	1330	.089	.033	1510	.078	.268
15	196	.010	.022									
20				383	.049	.046	516	.044	.032	1426	.101	.015
21	86	.455	.235									
22	143	†	1.469	130	.067	.012	361	.035	.152	66	.012	.173
23				136	.078	.072						
34							146	.031	.043	15	.070	.212
37				13	.115	.055						
38							59	†	.145	262	†	.192

Table A.2 (continued)

Process	1940 x_j	1940 Δ_ℓ	1940 Δ_u	1950 x_j	1950 Δ_ℓ	1950 Δ_u	1960 x_j	1960 Δ_ℓ	1960 Δ_u	1970 x_j	1970 Δ_ℓ	1970 Δ_u
40	2	.146	.065									
41										1623	.579	.007
43	1	.326	∞	17	.051	.029	433	.516	.001			
46							125	.133	.007	380	.192	.007
47	6	.007	.158	30	.002	.176						
48	2	1.243	.940									
49				37	†	.056						
50							186	†	.192	572	†	.190
51							138	.032	.044			
53				2	.049	.038				115	.075	.039
54				46	.033	.128	62	.029	.024	323	.376	.047
55	768	†	.172	3205	.219	.389	10658	.057	.005	28415	.048	.477
59	55	†	.082	100	†	.058	120	†	.082	400	†	.079
60										971	.038	.009
62							10	.131	.127	60	.068	.127
65							50	†	∞	200	†	∞
66				624	.378	.062	928	.043	.042	1349	.069	.101
67							723	.013	.009	974	.101	.014
73				95	.009	.136	260	.036	.057			
74	10	.164	.087									

Table A.2 (continued)

Process	1940			1950			1960			1970		
	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u
75										435	.046	.036
76	55	.073	3.648	154	.088	.205	246	.106	.031	35	.106	∞
78				169	.008	.132	451	.035	.056	596	.035	.050
79	12	.084	.177									
81							50	.040	.218			
82										500	†	.157
86				360	.023	.059	450	.023	.148	520	.023	.148
87	150	.148	∞									
88	146	.023	.002	475	.003	.001	339	.003	.002	612	.001	.002
95	30	.071	.032	178	.013	.036	502	.001	.046	1128	.004	.014
97	65	.065	.088	392	.075	.082	1128	.030	.088	1904	.035	.008
98				20	†	.005						
101	3	†	.002				75	†	.002	240	†	.002
103										370	†	.011
104	10	†	∞	130	.266	∞	300	.027	∞			
105										100	†	.008
107	22	1.191	∞									
109				70	.041	.099				922	.200	.044
111	4	.057	.173	22	.050	.122						
112										701	.288	.045

Table A.2 (continued)

Process	1940 x_j	1940 Δ_ℓ	1940 Δ_u	1950 x_j	1950 Δ_ℓ	1950 Δ_u	1960 x_j	1960 Δ_ℓ	1960 Δ_u	1970 x_j	1970 Δ_ℓ	1970 Δ_u
113										668	.302	.009
114							133	.036	.049			
115	15	†	∞	80	†	∞	165	†	∞	375	†	∞
116				44	†	.501	120	†	.642	376	†	.862
117							150	†	.122	1450	†	.122
119							59	†	∞	404	†	∞
120				37	.026	.068	50	.055	.025	130	.026	.060
122				38	.007	.019	896	.009	.005	1159	.001	.019
123	94	.030	.159									
124				90	†	.091	105	†	.065	160	†	.114
125	75	†	.042									
126	1	†	∞	10	†	∞	50	†	∞	210	†	∞
127	2	.316	23.22	610	.049	4.883	1872	.026	.651	4414	.028	.400
128	125	.145	.022									
129				355	†	.011				680	†	.001
130							545	†	.003			
131	120	.369	.094	341	.028	.074	2560	†	.009	8933	.002	.134
132	65	†	.326	137	.007	.026	1403	.007	.001	5725	.030	.050
133										355	.008	.026
140	12	†	∞	85	†	∞	175	†	∞	300	†	∞

Table A.2 (continued)

Process	1940			1950			1960			1970		
	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u	x_j	Δ_ℓ	Δ_u
141	53	.394	.022	572	.010	.009	2224	.008	.009	8412	.019	.009
143	135	1.058	∞									
144				551	†	.059	1384	†	.076	3304	†	.102
146	136	.180	.080	124	.044	.025	954	.102	.001	1650	.034	.226
147	2	†	∞	25	†	∞	100	†	∞	460	†	∞
148	65	.129	.010	668	.356	.011	1569	.205	.010	4075	.194	.010
150				35	.027	.178						
151							190	†	.058	150	†	.027
153	2	†	∞	40	†	∞	200	†	∞	615	†	∞
155	119	.046	.035	943	.081	.139	2395	.046	.014	6019	.046	.035
167	25	.379	.497				163	.025	.201	734	.185	.097
170	10	.292	.129	67	.077	.026	375	†	.002	89	.011	.082
176				15	†	.728	50	†	.670	7	†	.243
177	5	†	∞									
179										339	.091	.007
180							35	†	∞	110	†	∞
181							25	.046	.173			
183										350	†	.046
185	263	.140	.146	310	.041	.045						
186							602	.028	.040	830	.065	.112

Table A.2 (continued)

Process	1940 x_j	1940 Δ_ℓ	1940 Δ_u	1950 x_j	1950 Δ_ℓ	1950 Δ_u	1960 x_j	1960 Δ_ℓ	1960 Δ_u	1970 x_j	1970 Δ_ℓ	1970 Δ_u
187	73	.095	.255	391	.008	.169	612	.208	.077	827	.182	.162
188	39	.255	.238									
189				6	.062	.060	90	†	.217	215	†	.103
190	5	†	.104	9	.060	.062						
191	239	.008	.006	2490	.010	.031	4701	.008	.006	10894	.008	.006
192				166	.031	.010						
194	7	.005	.004	25	.008	.058	189	.005	.004	779	.005	.004
196							150	†	.001	365	†	.001
198				40	†	.005						
199	4	†	.005				115	†	.005	400	†	.005
200	45	.085	4.268	125	.103	.240	200	.124	.036			
201										480	†	.124
203	25	†	∞	75	†	∞	140	†	∞	200	†	∞
204	3	.405	∞	55	†	.113	125	†	.223	445	†	.306
206	455	†	.141	2523	†	.158	6321	†	.108	14959	†	.138
207	91	†	.120	169	†	.127	202	†	.120	596	†	.134
208										480	.275	.164
210							163	.012	.009	526	.017	.003
211							47	.028	.005	179	.022	.007
216	12	†	.150	95	.009	.001						

Table A.2 (continued)

Process	1940 x_j	1940 Δ_ℓ	1940 Δ_u	1950 x_j	1950 Δ_ℓ	1950 Δ_u	1960 x_j	1960 Δ_ℓ	1960 Δ_u	1970 x_j	1970 Δ_ℓ	1970 Δ_u
220	44	.082	.084	241	.094	.077	735	.037	.084	1363	.043	.010
222							68	†	∞	603	†	∞
223				50	3.194	.050	144	.255	.026	735	.375	.077
224	60	.077	∞	165	.050	3.194	256	.026	.255			
226	1	†	∞	80	†	∞	150	†	∞	430	†	∞
227	1	1.371	.132	68	.144	.226	307	.150	.266	1180	.114	.274
230	2	†	.104	540	†	.089	1750	†	.103	4335	†	.111
232							130	†	.140	1681	†	.140
235							37	†	∞	257	†	∞
236							45	†	∞	310	†	∞
237				215	.084	.015						
238	55	.028	∞									
239							350	.026	.011	610	.030	.011
241	5	†	∞	30	†	∞	70	†	∞	245	†	∞
242				5	†	6.345	35	†	8.254	90	†	11.08
243	135	†	∞	300	†	∞	1500	†	∞	6240	†	∞
244	10	.160	.465	60	.174	.005						
245										800	†	.103
246							250	.118	.044			
247	10	†	.002	275	.464	.007	1073	†	.001	4129	†	.001
250							4	.651	.036	5	.400	.028

APPENDIX 3

Table A.3. Estimated demand parameters for the Mexican petrochemical industry in 1970. Estimates are based on observed values of production and importation[40-42]. All figures are in metric tons and represent exogeneous demand.

Chemical	Demand	Chemical	Demand
Acetone	4650	Methyl Chloroform	1000
Acrylonitrile	7800	Methylene Dichloride	3000
Ammonia	400000	Methyl Methacrylate	3150
Aniline	1000	Nitric Acid	160000
Butadiene	27350	Perchloroethylene	5450
Caprolactam	25150	Phenol	6000
Chloroform	1500	Phthalic Anhydride	12700
Dimethyl Terephthalate	10600	Propylene	8900
Ethyl Chloride	9600	Propylene Glycol	6000
Ethylene	66000	Styrene	32500
Ethylene Dibromide	1350	Toluene Diisocyanate	3000
Ethylene Glycol	6700	Trichloroethylene	5000
2-Ethylhexanol	6150	Urea	150000
Formaldehyde	7200	Vinyl Acetate	9150
Maleic Anhydride	1950	Vinyl Chloride	36750

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TITLE OF THESIS A Systems Study of the Petrochemical Industry

Major Professor Professor Dale F. Rudd

Major Department Chemical Engineering

Minor(s) Chemistry

Full Name Mark Allen Stadtherr

Place and Date of Birth Austin, Minnesota 15 May 1950

Colleges and Universities: Years attended and degrees

University of Minnesota 1968-1972 B. Ch. E.

University of Wisconsin 1972-1976 Ph. D.

Membership in Learned or Honorary Societies

American Institute of Chemical Engineers

American Chemical Society

Publications M. A. Stadtherr, W. A. Gifford, and L. E. Scriven, "Efficient Solution of Sparse Sets of Design Equations," Chem. Eng. Sci. 29 1025 (1974)

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Date 26 May 1976