Riegel's

Handbook of Industrial Chemistry

NINTH EDITION

Edited by

James A. Kent, Ph.D.

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Preface

The aim of this book is to present in a single volume an up-to-date account of the chemistry and chemical engineering which underlie the major areas of the chemical process industry. This most recent edition includes several new chapters which comprise important threads in the industry's total fabric. These new chapters cover waste minimization, safety considerations in chemical plant design and operation, emergency response planning, and statistical applications in quality control and experimental planning. Together with the chapters on chemical industry economics and wastewater treatment, they provide a unifying base on which the reader can most effectively apply the information provided in the chapters which describe the various areas of the chemical process industries.

The ninth edition of this established reference work contains the contributions of some fifty experts from industry, government, and academe. I have been humbled by the breadth and depth of their knowledge and expertise and by the willingness and enthusiasm with which they shared their knowledge and insights. They have, without exception, been unstinting in their efforts to make their respective chapters as complete and informative as possible within the space available. Errors of omission, duplication, and shortcomings in organization are mine.

Grateful acknowledgment is made to the editors of technical journals and publishing houses for permission to reproduce illustrations and other materials and to the many industrial concerns which contributed drawings and photographs.

Comments and criticisms by readers will be welcome.

James A. Kent
Stevensville, Maryland

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Economic Aspects of the Chemical Industry

F. E. Bailey, Jr.* and J. V. Koleske**

Within the formal departments of science at the traditional university, chemistry has grown to have a unique status because of its close correspondence with an industry and a branch of engineering—the chemical industry and chemical engineering. There is no biology industry, but drugs, pharmaceuticals, and agriculture are closely related disciplines. There is no physics industry although power generation, electricity, and electronics industries do exist. But connected with chemistry, there is an industry. This unusual correspondence probably came about because in chemistry one makes things from basic raw materials—chemicals—and the science and the use of chemicals more or less grew up together during the past century.

Since there is a chemical industry, which serves a major part of all industrialized economies, providing in the end synthetic drugs, fertilizers, clothing, building materials, paints, elastomers, etc., there is also the subject of "chemical economics"; and it is this subject, the economics of the chemical industry, that is the concern of this chapter.

DEFINITION OF THE CHEMICAL INDUSTRY

Early in the twentieth century, the chemical industry was considered to have two parts: the manufacture of inorganic chemicals and the manufacture of organic chemicals. Today, the Standard Industrial Classification (SIC Index) of the United States Bureau of the Census defines "Chemical and Allied Products" as comprising three general classes of products: "(1) basic chemicals such as acids, alkalis, salts, and organic chemicals; (2) chemicals to be used in further manufacture such as synthetic fibers, plastics materials, dry colors, and pigments; and (3) finished chemical products to be used for ultimate consumer consumption as architectural paints, drugs, cosmetics, and soaps or to be used as materials or supplies in other industries such as industrial paints, adhesives, fertilizers, and explosives."[1] An even broader description that is often considered is that of the "chemical

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process industries," major segments of which include: chemical and allied products and petrochemicals; pulp and paper; petroleum refining; rubber and plastics; and stone, clay, and glass products.

THE PLACE OF THE CHEMICAL INDUSTRY IN THE ECONOMY

Because the chemical industry is a major sector of any advanced national economy, a forecast of trends in the chemical industry must fall within certain general guidelines that are established by the national economy. A forecast for the chemical industry in the United States must be within the general boundaries set for the overall social and economic forecasts for the country.

It has been clear for many years that certain demographic and societal issues would have a dominant effect on the U.S. economy of the 1990s. It was evident, for example, that from the late 1980s through the year 2000 there would be a decline in the growth of the work force in the United States. There is a direct relation between the growth of the work force and the growth of the GNP (Gross National Product, the sum of all goods and services produced in a year); the decline in the growth of the work force in this period was determined by the number of women in the usual child-bearing age group (18 to 35) and by family-size decisions made in the 1960s. Therefore, this factor was set and calculable from census data obtained 20 years earlier.

A predicted decline in the growth of the GNP due to a declining work force can be offset if worker productivity increases or if the age of retirement from the work force is extended beyond the usual retirement age of 65. In the United States during the 1980s, there was little overall increase in worker productivity; and, in many industries, there was a move toward retirement before age 65. In many industries, the average age of retirement moved toward 60 from the long-accepted norm of 65. These trends, as well as a marked growth in the service sector of the economy as opposed to such growth in the manufacturing sector, have contributed to a shortage of technically trained chemists and engineers entering the work force. This shortage is expected to become severe in the latter part of the 1990s.

Another factor in the overall economy that must be considered is that the GNP represents a "volume" of goods and services measured in value or "dollars." This "dollar volume" is very sensitive to inflation (or deflation). To remove this sensitivity for forecasting purposes, GNP is expressed in "constant dollars," dollars "deflated" by the annual inflation rate to some base year such as 1982.

Against this brief discussion of the general demographic, societal, and economic factors that govern forecasting, Table 1.1 gives a general picture of the economy of the United States in terms of the GNP and chemical industry production.

The forecast for the early part of the 1990s, which is subject to all the uncertainties and unpredictabilities of social and international events, is for steady growth of the U.S. chemical industry, but growth at a rate lower than that experienced in the mid-1980s and moderated by an average annual inflation rate of about 5 percent per year. This forecast includes a gradual increase in the price of imported oil and petroleum products during the early 1990s compared with lower imported oil costs in the late 1980s. Changes such as that caused by the 1990–91 Persian Gulf crisis have not been considered although such events certainly can have a profound effect on prices. At present the price of oil appears to be fairly stable, at least for the short term.

This forecast is presented to highlight the sensitivity and the place of the chemical industry in the national economy. The importance of the cost of imported raw materials such as petroleum products in both the economy and the forecast highlights two important concerns. One is that the chemical industry is worldwide and interconnected; not only does the United States both import and export a wide variety of raw materials and chemical products, but major United States–based chemical companies have manufacturing and sales facilities abroad, and a large number

TABLE 1.1 U.S. Economy and the Chemical Industry[2]

	United States GNP		
Year	(Current dollars, billions)	(1982 dollars, billions)	Percent Change in Chemicals and Allied Products Annual Production Index
1987	4500	3800	6.1
1988	4900	4000	8.5
1989	5200	4100	4.9
1990 (estimate)	5500	4200	2.4
1995 (forecast)	8000	4700	2.8*

*Annual average for 1990–95.

of foreign-based companies have manufacturing and sales facilities in the United States. The other is that the United States economy is dependent on the balance of trade, the difference between the dollar value of exports and that of imports. A negative trade balance means that dollars spent abroad to import goods and services exceed the value of goods and services exported, a circumstance that effectively increases the cost of goods and services purchased in the United States—a net inflationary effect. To a large extent during the 1980s, this potentially inflationary effect was offset by foreign investment in the United States; however, this offsetting of a negative trade balance by investment cannot be depended on to continue through the 1990s. At some point, foreign investors will demand a return on their investment, in effect an export of dollars, with an inflationary result on the domestic economy.

In foreign trade, the performance of the chemical industry of the United States has been outstanding. While the overall balance of trade has been negative, the chemical industry has been one of the truly strong sectors in the U.S. economy; see Table 1.2. If the total world export market for chemicals is considered, that is, the sum of all of the chemicals exported by all the world's national economies, the U.S. chemical industry held about a 15 percent market share during the decade of 1979 to 1989.

Major segments in the U.S. chemical trade balance in 1989 were:

Organic chemicals— + \$3.6 billion
Plastics materials— + \$4.6 billion
Pharmaceuticals— + \$1.6 billion

The less favorable overall trade balance of the United States was due principally to imports of manufactured goods and petroleum products; see Table 1.3.

To support the U.S. chemical economy in 1989, there was a work force of more than one million, 600,000 of whom were occupied in chemical production. The largest single sector of this work force, about 20 percent,

TABLE 1.2 U.S. Balance of Trade

	Total Trade Balance (billions of dollars)			Chemical Trade (billions of dollars)		
Year	Export	Import	Balance	Export	Import	Balance
1979	181	206	−25	17	7	+10
1987	253	406	−153	26	16	+10
1989	364	473	−109	36	20	+16
1990	394	495	−101	39	22	+17

TABLE 1.3 U.S. Trade Balance in 1989 (billions of dollars)

Sector	*Import*	*Export*	*Balance*
Chemicals	20	36	+16
Machinery	206	148	−58
Other manufactured goods	139	60	−79
Fuels and petroleum products	53	9	−44

was involved in the manufacture of ethical drugs and pharmaceuticals. This group was closely followed by those workers involved in the manufacture of plastics and synthetic materials. To back up this immensely important part of the economy, the chemical industry (chemicals and allied products) employed about 75,000 scientists and engineers, which is about 10 percent of the total number of scientist and engineers employed by industry in the United States. On an average, the larger chemical companies (top 15 companies in chemical sales) invested approximately 4 percent of their gross sales in research and development activities to support growth and to maintain their market share.

CHARACTERISTICS OF THE CHEMICAL INDUSTRY

Investment Trends

The chemical industry tends to be a high-investment business. Capital spending by the chemical and allied products industry in the United States has been a sizable percentage of the total spent for all manufacturing. Amounts spent in this industry and in certain facets of it are detailed in Table 1.4. The amount spent for all chemical process industries has been, of course, even larger; it totaled $68.9 billion in 1990, for example, a 5.3 percent increase over the amount spent in 1989. For perspective, annual expenditures for new plant and equipment in the United States for the chemical and allied products industry in recent years have averaged about 2.5 times

TABLE 1.4 New Capital Spending in the U.S. Chemical and Allied Products Industry and Comparison with That Spent a Decade Earlier[1]

	Billions of Dollars	
	1986	*1976*
Total chemical and allied products	7.9	7.1
Selected Segments		
Agricultural chemicals	0.52	1.05
Industrial inorganic chemicals	0.81	0.81
Industrial organic chemicals	1.84	2.69
Plastic materials, synthetic resins, and thermoplastic elastomers	1.90	1.37
Soap, detergents, perfumes, cosmetics, and other toilet products	0.74	0.29
Miscellaneous chemicals	0.51	0.32

the amount spent for iron and steel and about half of that invested in the petroleum industry. For the past decade a significant part of these capital investments have been made in pollution control and projects related to the environment.

Much of the capital investment in the chemical industry is spent for facilities used to produce major chemicals (Table 1.4) in truly enormous quantities. The volume produced is reflected in the size of plants being built to achieve the required economies of scale. That such economies are achieved is seen in the more modest increases in the chemical producers' price indices relative to the inflation levels in the general economy. (Economy of scale refers to the relative cost of building a larger plant; a rule of thumb is that the relative cost of building a smaller or a larger plant is the ratio of the productivities of the two plants being considered, raised to the 0.6 power. In other words, the unit cost of producing a chemical markedly decreases as the size of the plant producing it is increased, provided that the plant can be operated near capacity.)

Today, a typical, base petrochemicals plant will consume the equivalent of 30,000 barrels per day of naphtha to produce about one billion pounds of ethylene a year, plus 2.5

TABLE 1.5 Employment in Selected Parts of the Chemical Industry in 1990, 1987, and 1977[2]

	Thousands of Employees		
	1977	*1987*	*1990*
Chemical Industry			
Chemical and allied products	1,074	1,026	1,086
Segments			
Cosmetics, perfumes, etc.	53	70	N/A*
Drugs	181	212	239
Industrial inorganic chemicals	162	135	135
Industrial organic chemicals	166	152	153
Paints	66	63	63
Pharmaceutical preparations	145	169	N/A
Plastic materials	83	76	N/A

*N/A = not available.

billion pounds of coproducts. To be economically feasible, for example, plants for the production of monomers such as vinyl chloride and styrene for plastic products must be scaled in the billion-pound-per-year range.

Along with these very large plants and the associated enormous investment in them, most of the chemical industry is characterized by high investment versus low labor components in the cost of manufacture. The National Industrial Conference Board statistics list the chemical industry as one of the highest in terms of capital investment per production worker. The investment per worker in a base petrochemicals olefins plant may well exceed a quarter of a million dollars. Once again, however, such an index covers a spectrum of operations, and for a profitable chemical specialties manufacturer the investment may be on the order of 25,000 dollars per worker. Employment in selected parts of the chemical industry is given in Table 1.5.

Commercial Development and Competition Factors

In an earlier period of the chemical industry's development, chemical companies were generally production-oriented, exploiting a process to produce a chemical and then selling it in rapidly expanding markets. The plant sizes and investments required for participation were small fractions of what is needed to participate today. Raw materials often were purcharsed to produce chemical intermediates for sale. Small plants operating in small manufacturing complexes did not present the obvious problems of environmental pollution, which everyone has become increasingly aware of during the past decade. A new investment in chemical production today must include a significant proportion of the total outlay for abatement and control of environmental intrusion.

As the industry has grown, there has been a strong tendency toward integration, both forward and back. Petroleum producers have found opportunities based on their raw materials position to move into chemical manufacturing. Chemical companies, on the other hand, have moved to assure their access to low-cost raw materials. Similarly, producers of plastic materials have moved forward to produce fabricated products, such as films, fibers, and consumer items, while fabricators have installed equipment to handle and formulate the plastic materials to provide a supply at the lowest possible cost.

With ever higher investment needs and increasing cross-industry competition, much greater sophistication has been required in marketing analysis and selection of investment opportunity. The enormity of the investment now required for successful participation does not allow multiple approaches for the private investor. Consequently, a high degree of market orientation tends to predominate in the chemical industry, along with increasingly focused research and development programs.

A major trend in industrial chemistry has been an emphasis on improved processes for the production of major chemicals. The need for higher-efficiency, lower-cost processes has been accentuated by relatively slow growth rates in overall production of major industrial chemicals in recent years, as described in Table 1.6 for inorganic chemicals and Table 1.7 for organic chemicals. Thus profitability growth has had to be achieved from higher efficiencies in production.

For plastics materials, there also was relatively slow growth—except for a few bright spots such as high-density polyethylene

TABLE 1.6 U.S. Production of Major Inorganic Chemicals in 1990 and the Average Annual Production Growth Rate, 1980–90[3]

Chemical	*1990 Production Amount, 1980–90 (billion of pounds)*	*Annual Growth Rate (percent per year)*
Sulfuric acid	88.6	0
Nitrogen	57.3	5.1
Oxygen	39.0	0.9
Lime	34.8	−0.9
Ammonia	33.9	−1.5
Phosphoric acid	24.4	1.2
Sodium hydroxide	23.4	0.1
Chlorine	21.9	−0.4
Sodium carbonate	19.9	1.8
Urea	15.8	0.1
Nitric acid	15.5	−1.7
Ammonium nitrate	14.2	−2.5
Carbon dioxide	11.0	6.2
Ammonium sulfate	5.0	1.6
Hydrochloric acid	4.7	−2.1
Potash (K_2O basis)	3.6	−3.1
Carbon black	2.9	1.2
Aluminum sulfate	2.4	−0.6
Titanium dioxide	2.2	4.2
Sodium silicate	1.8	0.9
Sodium sulfate	1.5	−4.3
Calcium chloride	1.4	−3.5

TABLE 1.7 U.S. Production of Major Organic Chemicals in 1990 and Average Annual Growth Rate, 1980–90[3]

Chemical	*1990 Production Amount, 1980–90, (billion of pounds)*	*Annual Growth Rate (percent per year)*
Ethylene	37.5	2.7
Propylene	22.1	4.9
Ethylene dichloride	13.3	1.8
Benzene	11.9	−2.2
Vinyl chloride	10.7	5.1
Ethyl benzene	9.0	1.6
Styrene	8.0	1.6
Methanol	8.0	1.1
Terephthalates	7.7	2.4
Formaldehyde	6.4	1.4
Toluene	6.1	1.9
Xylene	5.7	−1.4
Ethylene oxide	5.6	0.7
Ethylene glycol	5.0	1.4
Phenol	3.5	3.2
Acetic acid	3.5	2.4
Propylene oxide	3.2	6.1
Butadiene	3.2	1.2
Acetone	2.2	0.7
Vinyl acetate	2.6	2.8
Cyclohexane	2.5	2.3

TABLE 1.8 U.S. Production of Major Plastics Materials in 1990 and Annual Growth Rate, 1980–90[3]

Plastic Material	Annual Production (billion of pounds) 1990	1980	Production Growth Rate 1980–90
Polyethylene			
Low density	11.2	7.3	1.9
High Density	8.3	4.4	6.6
Poly(vinyl chloride)*	9.1	5.5	5.2
Polypropylene	8.3	3.7	8.6
Polystyrene	5.0	3.5	3.6
Unsaturated polyester	1.2	1.0	2.6
Epoxide	0.50	0.32	5.0

*Includes copolymers of vinyl chloride.

and polypropylene—over the decade of 1979–89; see Table 1.8. Toward the end of the 1980s, growth decreased as increasing emphasis was placed on the recycling of packaging materials, and as new construction, a major use area for plastics materials, declined. As the 1990s began, recycling was showing strong growth, and there was no reason to think recycling would decrease during the nineties.

In the plastic and synthetic materials sector, in which useful fabricated articles are produced directly, for example, from polymers such as polyethylene, polypropylene, and poly(vinyl chloride), there is now major emphasis on the reuse of plastic instead of discarding it, particularly as packaging of various sorts, in trash for landfill. The major problems are not so much technical as they are ones of logistics and the development of a new kind of infrastructure to accommodate recycling.

Some 20 years ago, there was a proposal in Germany to reuse "virgin" poly(vinyl chloride) blow-molded beer bottles sold in the larger football (soccer) stadiums by regrinding the plastic bottles and extruding the ground product as pellets for use in flooring applications. The concept was that a large number of empty bottles could be collected at one point and reprocessed essentially "on the spot." This proposal was not successful; but it illustrates the major recycling problems of collection, sorting by material, and reprocessing for reuse. The proposal also presaged many active new ventures being started in the 1990s, such as the Du Pont effort to reprocess polyethylene and polyester polymers into fencing, fence posts, and garden furniture, and the new ventures by Mobil Chemical and Union Carbide to reprocess polyethylene packaging, film, and wrap. American National Can Company has demonstrated, with the help of the Center for Plastics Recycling Research at Rutgers University, that a blow-molded, layered polypropylene bottle could not only be reprocessed into shampoo and detergent bottles but also into automobile bumper fascia. Today supermarkets are collection depots for plastic grocery bags, and many municipalities are requiring separation of trash into recyclable components. Even more desirable are the voluntary separation and proper disposal of selected trash items that have been undertaken by many individuals.

The principal recycling problems that must be overcome to make plastic-material recycling feasible on a significant scale include the development of commercial pathways for consumer disposal, collection, and reprocessing. A technical problem remains in the collection–reprocessing step of sorting by material type. In the examples of the poly(vinyl chloride) bottle for stadium beer in Germany and polyethylene shopping bags and wrap, identification and collection are relatively simple if the collection is done at the point of sale, or if material is collected later at the place of original sale. However, it must be realized that different polymeric materials usually are not compatible with one another. Two incompatible materials generally will not mix or blend together sufficiently to yield a product with any utilizable strength properties, and are useful only for their fuel value. The process of sorting items into separate materials (e.g., poly(vinyl chloride), polyester, polypropylene), by the consumer–home owner or at a community-operated collection center, is still difficult. A recent solution to this problem has been to mark shaped plastic articles with a code that permits easy identification by classification or type.

Technological Orientation

The chemical industry is a high-technology industry, even though it is now more marketing-oriented and competitive than it was in its earlier period of development. This orientation is shown by the number of scientists and engineers employed in research and development in the chemical industry relative to other industries (Table 1.9). In general, the chemical industry is among the largest employers of scientists and engineers, and it puts a sizable percentage of the total U.S. business investment in research and development.

The contemporary scientist or engineer engaged in research and development in the chemical industry represents individually a high-investment occupation. Since the mid-1950s, chemistry has become increasingly an instrumental science. The instruments now routinely used are both highly sophisticated and costly. A major research project would not be undertaken today without access to a variety of spectrophotometers, spectrometers, chromatographs, etc., as well as the necessary physical/chemical instruments for molecular structure determinations and reaction kinetics. Pilot plants are highly automated and instrumented. Both the basic researcher and the pilot plant engineer require access to computer facilities. In 1978, the average annual cost to maintain an operating R&D scientist or engineer in the chemical industry was about $75,000. Today, it may be three or four times that amount. Impressive as these statistics may be in representing the business investment in chemicals R&D in the United States, R&D spending in the chemicals industry as a percent of sales declined from about 4 percent in 1970 to about 2.5 percent in 1980, although today it remains about 4 percent in the largest chemical companies. This relatively low level is a concern because reinvestment in R&D in other industrialized countries, particularly in West Germany and Japan, has remained at a higher level as measured by this index.

TABLE 1.9 Scientists and Engineers in Research and Development in the United States in 1990 and a Decade Earlier[2]

	Thousands of Employees		
	1990	*1987*	*1980*
Chemicals and Allied Products	78.4	75.2	51.4
Segments			
Industrial Chemicals	23.0	22.4	20.9
Drugs	33.0	32.6	21.6
Other Chemicals	22.4	20.2	8.9

Obsolescence and Dependence on Research

The high technology level that characterizes the chemical industry, and which is reflected in heavy investments in R&D, generally concerns discovery and development of new products and improvements in the manufacture of known products. The first area is more conspicuous: the pharmaceutical for a specific disease; the narrow-spectrum, transient pesticide; the new superperformance, composite system for an internal combustion engine; or a thermoset polymer/graphite fiber-composite material for a high-technology military aircraft, such as the "stealth" bomber or fighter. The second area, however, makes viable the circumstances outlined earlier, where increasing investments can be made to produce larger quantities of materials. The development of a new, lower-cost process for a commercial product can permit the development of a profitable opportunity, or can spell disaster for a company with existing investment in a now-obsolete plant. Major reductions in manufacturing cost can be achieved, for example, by reducing the number of reaction steps required, changing to a lower-cost or more available raw material, or eliminating coproducts, costly separations, and environmental intrusions. The ability of a process scheme to contain or avoid a pollutant can be a deciding factor in the continuance of a manufacturing operation. Examples of the above situations will make the economic consequences clear.

Acetic acid production in the United States has increased about eightfold in the last 40 years. From the 1930s, acetic acid was produced by a three-step synthesis from ethylene; acid hydrolysis to ethanol, then catalytic dehydrogenation to acetaldehyde, then direct liquid-phase oxidation to acetic acid and acetic anhydride as coproducts:

$$CH_2{=}CH_2 \xrightarrow{H_2SO_4/H_2O} C_2H_5OH \xrightarrow{Cu/Cr} CH_3CHO$$

$$CH_3CHO \xrightarrow{[O],Co} CH_3CO{-}O{-}OCCH_3 + CH_3COOH$$

In the 1940s a major process change was introduced—direct oxidation of butane to acetic acid and coproducts (such as methylethylketone):

$$C_4H_{10} \xrightarrow{[O]} CH_3COOH + CH_3COC_2H_5 + \text{others}$$

Having fewer steps in the synthesis was reflected in lower cost and investment. In 1969, another advance was announced, synthesis of acetic acid from methanol and carbon monoxide with essentially no coproducts:[4,5]

$$CH_3OH + CO \xrightarrow{I/Rh} CH_3COOH$$

The absence of coproducts reduces production costs and investment in distillation and other separation systems. These are very attractive process features in an industry where the principally accepted measure of business quality is return-on-investment.

Acetic anhydride is required as a process intermediate in acetylations. To obtain acetic anhydride from acetic acid, acetic acid is first pyrolyzed to ketene, which then reacts with recovered acetic acid to yield the anhydride:

$$CH_3COOH \xrightarrow{Heat} CH_2{=}C{=}O$$

$$CH_2{=}C{=}O + CH_3COOH \longrightarrow CH_3CO{-}O{-}OCCH_3$$

In 1980, the Tennessee Eastman unit of Eastman Kodak announced that it would begin construction of a plant to make acetic anhydride from coal.[6,7] This decision reflected a changing of the raw materials base of much of the chemical industry due to such factors as the rising cost of natural gas and petroleum and the large coal reserves of the United States.

In the new process, synthesis gas (carbon monoxide and hydrogen) is made from coal. Then, methanol is produced from the synthesis gas. (Previously, methanol had been produced chiefly from natural gas methane.)

$$CO + 2H_2 \rightarrow CH_3OH$$

Methanol can then react with acetic acid to give methyl acetate:

$$CH_3OH + CH_3C(=O)OH \longrightarrow CH_3C(=O){-}OCH_3$$

Acetic anhydride is then obtained from the catalytic carbonylation of methyl acetate with carbon monoxide:[5]

$$CH_3COO{-}CH_3 + CO \rightarrow CH_3CO{-}O{-}OCCH_3$$

The attractiveness of this process is twofold: (1) the raw materials base of synthesis gas from coal and (2) the avoidance of energy-consuming manufacture of ketene by pyrolyzing acetic acid.

The increase in the production of vinyl chloride, the principal monomer for poly(vinyl chloride) plastics, which are used in vinyl flooring, phonograph records, shower curtains, raincoats, carseat upholstery, house siding, pipe, and so on, has been even more spectacular. Production in the United States has increased from 250 million pounds in 1950 (when it was declared by many industry economic forecasters to be a mature chemical commodity) to over one billion pounds in 1960, to about 3.5 billion pounds in 1970, to over 7 billion pounds in 1980, and to almost 11 billion pounds in 1990.

During the early development period of vinyl polymers in the 1930s, vinyl chloride was produced via catalytic addition of hydrogen chloride to acetylene:

$$CH{\equiv}CH + HCl \xrightarrow{HgCl} CH_2{=}CHCl$$

Later, a so-called balanced process was introduced, in which, by addition of chlorine to ethylene, ethylene dichloride was produced:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{[O]/Cu} CH_2ClCH_2Cl$$

Ethylene dichloride could then be cracked to vinyl chloride and HCl, with the hydrogen chloride recycled to produce vinyl chloride from acetylene:

$$CH_2ClCH_2Cl \xrightarrow{Heat} CH_2{=}CHCl + HCl$$

At that time, vinyl chloride was being produced from chlorine, acetylene, and ethylene. More recently, catalytic oxychlorination has been developed, in which vinyl chloride is produced from ethylene and hydrogen chloride:[8]

$$CH_2{=}CH_2 + HCl \xrightarrow{[O]/Cu} CH_2{=}CHCl + H_2O$$

The hydrogen chloride can be obtained via cracking of ethylene dichloride. The oxychlorination process freed vinyl chloride from the economics of the more costly raw material, acetylene. (Deliberate acetylene manufacture is energy-intensive. Although by-product acetylene from gas cracking is less expensive than the raw material, it has not been available in sufficient supply for the large, near billion-pound-per-year, vinyl chloride units.)

During the long period of development of poly(vinyl chloride) into one of the major plastics material, several basic processes for making PVC evolved. In all of these processes vinyl chloride was handled as a liquid under pressure. Despite the relative ease with which it could be polymerized by free radical initiators, the monomer, vinyl chloride, was regarded as an innocuous, relatively inert chemical. A number of producers of PVC resins were caught by total surprise in the 1970s when it was found that long-term (20-year) exposure to vinyl chloride monomer could cause rare forms of tumors.[9]

During the 1960s, vinyl chloride sold in the United States for five to six cents per pound. In the presence of traces of air (oxygen), it would form low concentrations of peroxide, which could collect in compressors and on occasion rapidly decompose to blow out compressor seals. Rather than recover and compress the inexpensive monomer for recycle from stripping and drying operations at the end of the polymerization process, some manufacturers vented it into the atmosphere. After the discovery that vinyl chloride was a carcinogen, venting was not permissible; containment and recovery were mandatory. Some older processes and manufacturing facilities could not be economically modified to incorporate monomer containment, so operations were discontinued. This case is but one example of the impact that necessary environmental controls can have on manufacturing processes and operations.

Propylene oxide is another basic chemical, used in manufacturing intermediates for urethane foams (used in cushioning and insulation) and brake and hydraulic fluids. The volume of propylene oxide produced increased from 310 million pounds in 1960 to 3.2 billion pounds in 1990. The classical industrial synthesis has been the reaction of chlorine with propylene to produce the chlorohydrin, followed by dehydrochlorination with caustic to produce the epoxide, propylene oxide, plus salt. In this case, both the chlorine and the caustic used to effect this synthesis are discarded as a valueless salt by-product:

$$CH_3CH{=}CH_2 + Cl_2 + H_2O \longrightarrow CH_3CH(OH)CH_2Cl$$

$$CH_3CH(OH)CH_2Cl \xrightarrow{\text{Caustic}} CH_3CH{-}CH_2\ (\text{ring through } O) + \text{salt}$$

A more economical process has been commercialized. In one version, a hydroperoxide is produced by catalytic air-oxidation of a hydrocarbon such as ethylbenzene. Reaction of this hydroperoxide with propylene yields propylene oxide as a coproduct. This direct peroxidation can be carried out with other agents to give different coproducts such as *t*-butanol or benzoic acid.[10,11]

$$\text{Aryl-}C_2H_5 \xrightarrow{[O]/V} \text{Aryl-}CH(CH_3)OOH$$

$$\text{Aryl}{-}CH(CH_3)OOH + CH_3CH{=}CH_2 \longrightarrow CH_3\text{-}CH{-}CH_2\ (\text{ring through } O) + \text{Aryl}{-}CH(CH_3)OH$$

When the economics are balanced, a significant cost reduction is achieved by eliminating the coproduct salt, which is of low value and presents a disposal problem. Further, a process can be designed to produce a coproduct that can be used or sold as a chemical intermediate. In the case of using isobutane as the starting hydrocarbon, the by-product is *t*-butanol, which can then be converted to methyl *t*-butyl ether, which is the gasoline additive used to replace lead in "lead-free" gasoline.

If a company is in the business of making and selling products such as acetic acid, vinyl chloride, propylene oxide, or other chemicals and has plans to stay in business and to expand its facilities to serve growing markets, it at least must have economically competitive processes. Today this means being competitive with not only any new processes developed in the United States, but also with any new process technology developed in Western Europe, Japan, and Russia—for the chemical industry is a worldwide industry. This is readily apparent from the data in Tables 1.10, 1.11, and 1.12, which describe the sales for the largest chemical producers in the United States, Western Europe, and Japan, respectively. Further, the processes that are operative must be environmentally compatible—all toxic or carcinogenic by-products or waste must be contained and disposed of harmlessly. Even a relatively innocuous by-product such as salt must be disposed of so as not to intrude on the environment.

The profound effect of environmental concerns on the manufacture of a chemical is

TABLE 1.10 Largest U.S. Chemical Producers[2,12]

	Chemical Sales Millions of Dollars			
Company	*1969*	*1979*	*1989*	*1990*
Du Pont	*3,655*	*12,572*	*15,249*	*15,571*
Dow Chemical	*1,876*	*9,255*	*14,179*	*14,690*
Exxon	*1,004*	*5,807*	*10,559*	*11,153*
Union Carbide	*2,933*	*9,177*	*7,962*	*7,621*
Monsanto	*1,939*	*6,193*	*5,782*	*5,711*
Hoechst Celanese	*1,250*	*3,010*	*5,658*	*5,499*
General Electric	—	—	*4,929*	*5,167*
Occidental Petroleum	—	—	*5,203*	*5,040*
BASF (U.S.A. only)	—	—	*4,461*	*4,366*
Amoco	—	—	*4,274*	*4,087*

TABLE 1.11 Largest Western European Chemical Producers

Company	Country	Chemical Sales Millions of Dollars 1969	1979	1988
BASF	Germany	2,430	15,018	24,925
Hoechst	Germany	2,550	15,870	23,275
Bayer	Germany	2,550	15,079	22,993
ICI	United Kingdom	3,250	11,389	20,817
Ciba-Geigy	Switzerland	—	—	12,087
Rhone-Poulenc	France	1,840	7,940	10,962
Montedison	Italy	2,620	8,224	10,846
Norsk Hydro	Norway	—	—	9,207
Akzo	The Netherlands	—	—	8,374
Degussa	Germany	—	—	7,730

1988 data from "Facts and Figures for the Chemical Industry," *Chemical and Engineering News*, p. 81, June 19, 1989.

TABLE 1.12 Largest Japanese Chemical Producers

Company	Chemical Sales Millions of Dollars 1979	1988
Asahi Chemical Industry	2,359	6,384
Mitsubishi Kasei	2,967	6,132
Takeda Chemical Industry	—	4,567
Sumitomo Chemical	2,716	4,341
Toray Industries	2,094	4,317
Sekisui Chemical	1,300	3,936
Showa Denko	1,706	3,679
Dainippon Ink & Chemicals	1,416	3,440
Mitsui Toatsu Chemicals	1,767	3,082
Mitsubishi Petrochemical	1,558	2,654

1988 data from "Facts and Figures for the Chemical Industry," *Chemical and Engineering News*, p. 83, June 19, 1989.

TABLE 1.13 Aerosol, Pressurized Product Sales in the United States in 1978

Use	Percent of Sales
Personal products and toiletries	33%
Household products	28
Coatings and finishes	14
Automotive	7
Food products	6
Insect sprays	6
Industrialized products	5
Animal products	1
Miscellaneous	0.5

reflected in the history of aerosol pressurized products. These products are familiar to the consumer in aerosol spray cans containing hair sprays, deodorants, dessert toppings, or insect sprays (Table 1.13). The market for these products grew enormously in the 1960s, with rapid consumer acceptance of packaged convenience products.[13,14]

The aerosol spray product is a pressurized formulation with a propellant gas. During the rapid growth of these products, the major propellant gases were chlorofluorocarbons. Then, in 1973, the uncontrolled release of chlorofluorocarbons into the atmosphere was linked to possible depletion of the ozone layer in the earth's atmosphere. Since stratospheric ozone provides significant protection at the earth's surface from ultraviolet radiation from the sun, depletion of the ozone layer could be forecast to lead to skin cancers, reductions in seafood and grain crops, and alteration of the carbon dioxide level in the atmosphere. Carbon dioxide is thought to be a potential culprit in "global warming."

Popular concern over "global warming" has now spread from its origin mainly in the large developed economies, which were the principal users of halocarbon propellants, to virtually all countries. The release into the atmosphere of contaminants that can affect the ozone layer, particularly the "ozone hole"