Shreve's Chemical Process Industries

Fifth Edition

GEORGE T. AUSTIN

International Student Edition

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Preface

It was a privilege to work with R. Norris Shreve, and I hope that his influence is reflected in this, the fifth edition. Dr. Joseph A. Brink, another of Professor Shreve's students and the editor of the fourth edition, has unfortunately also passed on. It is regrettable that his abilities and expertise are no longer available.

It has always been surprising to the author that many persons planning to work in the chemical process industries have little or no understanding of the technical and economic problems which manufacturing entails, of the equipment necessary for it to be done, or of the uses to which chemicals are actually put. Those engaged in some particular area of chemical manufacturing often have little knowledge of the chemical process industries as a whole. This is most unfortunate, for developments in one sector can cause profound changes in other areas. It is hoped that this work will aid young engineers, chemical, civil, mechanical, and electrical, as well as chemists, in understanding the value of chemicals, the type of problems met in their production, and the methods for solving these problems. Executives and supervisors should also find this material helpful in understanding the products with which they are involved, especially their economic relation to other chemicals.

Over 30 years of research and teaching, the complaint has frequently been heard that it is pointless to study processing because it is constantly changing. This, of course, is ridiculous since science, art, mathematics, medicine, and law are also changing rapidly, yet they are all considered worthy of study. In fact, constant study is necessary in any field that is active. At some time, every really effective laborer in the field of chemical processing must come to understand not only his immediate field, but those others which compete with and complement it. These studies need not be detailed; in fact, for comprehension, broad generalities are more important than details, and these are the types of facts presented here.

This book should be of great value to young chemical engineers and chemists who are just entering the field, but those already practicing will find much of interest and use for broadening their insight into fields in which they are only marginally informed. If used as a text, it is desirable to cover the entire book, rather than concentrating on a few chapters, for only by so doing will a perspective on the industry be obtained.

I wish to acknowledge the continued help and assistance of my wife, Helen, in preparing this edition. She worked on two previous editions, and her point of view and general assistance have been invaluable.

Norris Shreve gave encouragement and help to all his students. His enthusiasm for the subject of chemical processing was infectious, and I have retained the interest which he generated over these many years. This book is in part a memorial to his interest in processing.

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Acknowledgments

No one person can be both skilled and up-to-date in as many fields as this book covers. Dozens of persons have aided by volunteering their services to help revise this text. Their kindness in thus improving the modernity of the revision with their additional technical knowledge has contributed mightily to the quality of this work. Many companies have provided information, assistance, flowcharts, and photographs, which are acknowledged in the body of the text. For the fifth edition, the following persons have reviewed chapters, made suggestions, and in some cases helped extensively with the rewrite. If their companies appreciate this extracurricular activity as much as I do, they should all receive recognition from their companies for professional assistance above and beyond the call of duty. *Barnard and Burk Group*, Daniel J. Newman; *Battelle-Northwest Co.*, George A. Jensen; *Bolme and Associates*, Donald W. Bolme; *Calgon Corp.*, The Technology Department; *Chem Systems, Inc.*, Peter H. Spitz; *Chevron U.S.A., Inc.*, Thomas C. Austin; *Coors Porcelain Co.*, Michael J. Fenerty; *Diamond Shamrock Corp.*, Thomas E. Specht; *E. I. DuPont de Nemours and Co.*, Byron C. Sakiadis; *Eastman Kodak Co.*, George A. Massios; *Exxon Co., U.S.A.*, Ervin W. Squires; *General Electric Co.*, P. St. Pierre; *Great Lakes Research Corp.*, Harry L. Hsu; *Gulf Research and Development*, Gilbert A. Harris; *Hercules Inc.*, Clyde W. Eilo and Dr. Leo R. Gizzi; *J. M. Huber Co.*, Howard W. Renner; *Hydrocarbon Research, Inc.*, Derk T. A. Huibers; *International Minerals and Chemical Corp.*, James E. Lawver; *3M Company*, Dr. Norman Newman; *The M. W. Kellogg Co.*, L. J. Buividas et. al.; *Monsanto*, Charles E. Prince; *Monsanto Enviro-Chem*, J. R. Donovan; *National Association of Photographic Manufacturers*, Richard Hittner; *Oak Ridge National Laboratory*, Clifford A. Burchsted; *Purdue University*, Roy L. Whistler; *Salt Institute*, Frank O. Wood; *Superior Graphite Co.*, M. W. Goldberger; *Tennessee Valley Authority*, Ronald D. Young; *Texasgulf, Inc.*, Arthur Gloster; *Thorstensen Laboratory, Inc.*, Thomas C. Thorstensen; *Union Carbide Corp.*, R. L. Finicle; *U.S. Forest Products Laboratory*, Roger Gyger; *U.S. Forest Service Products Laboratory*, Harold Tarkow (Retired); *Washington State University*, Carl W. Hall, Robert K. Koppe, R. V. Subramanian; *Wellman Thermal Systems*, W. G. Coffeen, III.

Shreve's Chemical Process Industries

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Chapter 1

Chemical Processing

This book considers the chemical processing of raw materials into useful and profitable products. These products are used both as consumer goods and as intermediates for further chemical and physical modification to yield consumer products. About one-quarter of the total chemical output is utilized in the manufacture of other chemicals, so the chemical industry is unique in being its single best customer.

Chemical engineers, chemists, entrepreneurs, managers, and business people engaged in chemical manufacture will find this overview of the process industries helpful in understanding the current state of the art. Chemical engineering and industrial chemistry must both be critically concerned with profit, for without profit a business cannot operate. Rapid changes in methods characterize the chemical business, which currently is responding to large changes in energy costs; however, whenever the cost of a chemical entity increases by as little as 10 percent, in many cases it risks replacement as much as if it were a new substance.

Chemical engineering emerged as a separate discipline about 1910 when professors at Massachusetts Institute of Technology realized that neither mechanical engineering nor chemistry offered sound approaches to chemical plant design. They characterized the physical operations necessary for manufacturing chemicals as "unit operations" (heat transfer, fluid flow, distillation, filtration, etc.). Although originally they were largely descriptive, these *unit operations* have been the object of vigorous study and can now be used with sound mathematical procedures for plant design predictions. About 1930, P. H. Groggins suggested a somewhat similar approach to classifying chemical operations as "unit processes." Such processes include nitration, sulfonation, oxidation, chlorination, etc. This concept has not proved as useful as the unit operations idea nor have its concepts been reduced to mathematical procedures, but it is frequently useful.

Recently, the field of unit operations has expanded to include many new types of operations. Probably the best compilation of the current state of the art is in Perry's *Chemical Engineers' Handbook* (now in the fifth edition).

This book emphasizes *chemical conversions,* which may be defined as chemical reactions applied to industrial processing (Table 1.1). The basic chemistry is set forth along with some discussion of the equipment in which reactions take place. Consideration is consistently given to the costs of the reaction materials, the energy used in the process, and the effect of efficiency—in short, the problems concerned in arriving at efficient and profitable operation. This is, of course, not as scientifically and quantitatively formulated as the unit operations—which are not discussed here. There is a considerable body of opinion that studies of this type are of small value because of the constantly changing nature of the approach to chemical processing solutions, but it is for precisely this reason that chemical processing needs to be studied very broadly since changes in one sector of the chemical industry rapidly affect all sectors. Today's new development in soap manufacture may well strongly change paint formulation tomorrow. Because of the diversity and complexity of chemical processing, a broad

Table 1.1 Principal Chemical Conversions

Acylation	Double decomposition	Ion exchange
Alcoholysis	Electrolysis	Isomerization
Alkylation	Esterification	Neutralization
Amination by reduction	Fermentation	Nitration
Ammonolysis	Fischer-Tropsch reaction	Oxidation (controlled)
Aromatization or cyclization	Friedel-crafts (reactions)	Polymerization
Calcination	Halogenation	Pyrolysis or cracking
Carboxylation	Hydroformylation (oxo)	Reduction
Causticization	Hydrogenation, hydrogenolysis	Silicate formation
Combustion (uncontrolled oxidation)	Hydrolysis and hydration (saponification, alkali fusion)	Sulfonation and sulfation
Condensation		
Dehydration		
Dehydrogenation		
Diazotization and coupling		

study gives a powerful approach of wide usefulness in designing new manufacturing processes.

The characteristics of chemical conversions applied to the manufacture of chemicals may be summarized as follows.

1. Each chemical conversion is one of a family of numerous individual reactions that are similar in energy change, reaction pressure and/or temperature, reaction time, equilibrium, or raw materials.
2. Frequently there is factory segregation wherein a building or section is devoted to making many different products by means of a single type of chemical conversion such as hydrogenation, nitration, or diazotization. Providing protection against similar hazards to safety or toxicity can often be simplified by such procedures.
3. There is often a close relationship among the types of equipment used for making many different products by means of a single type of chemical conversion. For example, a well-agitated reactor with good cooling coils is generally used for nitrations with mixed sulfuric-nitric acid mixtures and is commonly called a nitrator. The same equipment may be used to nitrate benzene, toluene, naphthalene, or substituted aromatics to yield such desired products (intermediates) as nitrobenzene, trinitrotoluene, nitronaphthalenes, or chloronitrobiphenyls.
4. Where production is small or products variable, *equipment* may be conveniently and economically transferred from the making of one chemical to that of another based on the same chemical conversion. It is the aim of a production manager to keep all the equipment constantly in use. To do this, frequently it is necessary to make first one chemical, then another in the same general reactor—a sulfonator, for example. This *multiple use of equipment* is most easily managed with chemical-conversion segregation. Large-scale specialized plants are wholly committed to one product, and duplicate uses are not economically possible.
5. The chemical-conversion classification enables a chemical manufacturer to move from group performance to that of a new individual chemical in the related class. It is necessary chiefly to know and to remember *principles* rather than specific performances. This method of approach, rarely stressed in organic and inorganic chemistry courses, greatly facilitates the making of any chemical by having available past knowledge regarding the generalized data of a specific conversion. This procedure obviates memorizing individual observations. The principal conversions considered are listed in Table 1.1.
6. Since the basis of chemical-conversion classification is a chemical one, stress is placed on the *chemical reaction*. Despite large increases in energy costs, materials remain substantially

more expensive than energy, so slight improvements in chemical yield materially improve the profit of the manufacturing sequence. Energy or power savings may be less profitable.

7. The design of equipment can often be simplified by the generalizations arising from a like chemical-conversion arrangement rather than by considering each reaction as unique. That which experience has indicated for a number of reactions allied under a like chemical conversion is an excellent guide for a new reaction in this same grouping. In handling chemical conversions, the more that is understood about the underlying physical chemistry and kinetics, the better will be the plant conception. Generally speaking, conditions that increase the rate of a reaction decrease the equilibrium conversion. This relationship between equilibrium and rate is frequently the major design problem. For example, in the manufacture of sulfuric acid by the contact process, the sulfur dioxide converter consists of two (sometimes more) parts, a hot part of small size in which the reaction proceeds rapidly, approaching an unfavorable equilibrium, which results in an incomplete conversion leaving some unreacted SO_2. This is followed by a larger, cooler section (or sections) in which the reaction proceeds slowly, but nearly all the remaining SO_2 is converted to SO_3. Without the low temperature section, material costs would be prohibitively high and the air pollution would be unacceptable because much unconverted material would be lost.

Extensive use of *flowcharts* is made in this book because they allow a great deal of information to be collected and examined in a small space. There are a great many types of flowcharts used: some show simple flows, others show material balances, and some few are so complete that drains, fire lines, and special start-up lines are included. The flowcharts used here have been reduced to maximum simplicity and are designed to show principles rather than details.

Because of space limitations, very little has been included pertaining to the chemical industries outside the United States. No attempt is made here to supply the names of companies in various branches of the chemical industry, although there is an occasional reference to a specific company. A full listing of such companies is obtainable from a number of trade directories and from the pages of various chemical publications such as the annual *Chemical Engineering Equipment Buyers' Guide* (CEEBG) and the *Chemical Engineering Catalog*, which is also a good source of information about equipment.

Most chemical producers do not have intimate contact with more than one industry. This text, therefore, emphasizes broad principles of systems rather than details. These should be part of the working knowledge of chemists, engineers, and all manufacturing personnel, even specialists, for it is often possible to translate such general procedures from one field to another. For the growing number of chemical engineers who enter sales, executive, or management positions, a broader acquaintance with the chemical industry in its entirety is essential. For all these, the specialist, the salesperson, and the manager, the flowcharts will present in a connected logical manner an overall viewpoint of many processes.

All chemical manufacturers should be familiar with the current selling prices of the principal chemicals with which they are concerned. Prices per pound are frequently misleading, molal or equivalent costs being far more significant. Prices are quoted weekly in the comprehensive *Chemical Marketing Reporter* and limited data are in *Chemical Week* and *Chemical and Engineering News* among others. Where costs are included in the text, they must be used with great caution and corrected for inflationary changes. Costs in this edition are generally corrected to the year 1981.

Students using the flowchart approach for the first time should find it possible to visualize a series of rational connected steps for a process, greatly reducing the memorization so frequently required by the academic chemical reaction approach. Here the attempt is made to emphasize the *why* rather than the *how* of industrial procedures.

In such a lively business, the use of current journals is essential for study beyond this book's materials. The texts and the advertising pages of *Chemical Engineering, Chemical Engineering Progress, Chemical Week, Chemical and Engineering News, Hydrocarbon Processing,* and the many specialized journals such as *Adhesives Age, Sugar,* and *Modern Plastics* should be consulted for recent changes.

INFORMATION SOURCES

Libraries are the best source of information for those seeking to study chemical processing. Engineers are particularly inclined to ignore this great source and attempt to find information among personal contacts while ignoring better, written information. *Chemical Abstracts* and the *Engineering Index* are indexes to almost all current periodicals and save much searching time.

The field of chemistry has by far the best index to its literature of all the sciences. The Chemical Abstracts Service (CAS) is an outgrowth of the general index and summary of the chemical literature, *Chemical Abstracts,* a magazine published by The American Chemical Society. *Chemical Abstracts* gives short summaries of all the world's literature even remotely related to chemistry as published in approximately 40,000 journals. The material can be accessed by means of yearly and decennial indexes of subject, author, patent, formula, etc. Publications since 1967 can be searched rapidly by computers. The material is held in so-called *data bases,* which are just computer-based record-keeping systems. Almost any information can be searched out as desired in rough outline, titles only, full abstracts, and in some cases complete articles. Interactive computer systems enable the search to be made roughly (hence cheaply), then refined to search out the most relevant details. Such searches are low in cost and very time conserving. No knowledge of computers is required, for reference librarians are available to help, and some facility is readily obtained.

A list of periodicals most frequently used by chemical engineers and others interested in chemical processing follows. Note particularly the abbreviations which will be used for references throughout the text. A selected group of books of general interest is also included. When *Chemical Engineers' Handbook* is referred to in footnotes, "Perry" is used as the abbreviation, and the *Encyclopedia of Chemical Technology* is abbreviated as ECT. Previous editions of the book are cited as CPI along with the relevant edition number.

PERIODICALS

American Chemical Society (ACS), P.O. Box 3337, Columbus, Ohio 43210.

Industrial and Engineering Chemistry (Ind. Eng. Chem.)
Industrial and Engineering Chemistry Process Design and Development (Ind. Eng. Chem. Process Des. Dev.)
Industrial and Engineering Chemistry Fundamentals (Ind. Eng. Chem. Fundam.)
Industrial and Engineering Chemistry Product Research and Development (Ind. Eng. Chem. Prod. Res. Dev.)
Journal of Chemical and Engineering Data (J. Chem. Eng. Data)
Chemical and Engineering News (Chem. Eng. News)
CHEMTECH
Chemical Week (Chem. Week)

American Institute of Chemical Engineers (AIChE), 345 East 47th St., New York, N.Y. 10017.
Chemical Engineering Progress (Chem. Eng. Prog.)
AIChE Journal (AIChE J.)
International Chemical Engineering (Int. Chem. Eng.)

Gulf Publishing Company, P.O. Box 2608, Houston, Tex. 77001.
Hydrocarbon Processing (Hydrocarbon Process.)

McGraw-Hill Publications, 1221 Avenue of the Americas, New York, N.Y. 10020.
Chemical Engineering (Chem. Eng.)

SELECTED REFERENCES

Chemical Engineering Catalog, annual.
Chemical Engineering Thesaurus, AIChE, 1963 (8000 chemical engineering terms).
Dean, J. A.: *Lange's Handbook of Chemistry*, 12th ed., McGraw-Hill, New York, 1978.
Facts and Figures for the Chemical Process Industries, Supplement to *Chem. Eng. News*, yearly.
Handbook of Chemistry and Physics, Chemical Rubber Co., 19
Himmelblau, D. M.: *Basic Principles and Calculations in Chemical Engineering*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1982.
Kent, J. A. (ed.): *Riegel's Industrial Chemistry*, 7th ed., Reinhold, New York, 1974.
Kirk, R. E. and D. F. Othmer: *Encyclopedia of Chemical Technology*, 3d ed., Wiley-Interscience, New York, 1982.
Lowenheim, F. A. and M. K. Moran: *Industrial Chemicals*, 4th ed., Wiley-Interscience, New York, 1975.
McGraw-Hill Encyclopedia of Science and Technology, 5th ed., McGraw-Hill, New York, 1982.
Perry, R. H. et al. (eds.): *Chemical Engineers' Handbook*, McGraw-Hill, New York, 1973.

Chapter 2

Chemical Processing and the Work of the Chemical Engineer

By 1980 there were about 60,000 chemical engineers and 250,000 chemists gainfully employed in the United States. There are a modest number of self-trained persons and transfers from other fields of science and engineering who have entered chemical manufacturing, so probably around 200,000 professional persons are engaged in chemical manufacturing in some fashion. Most chemical engineers work for private industry. In 1981, surveys by the American Institute of Chemical Engineers (AIChE) showed over 90 percent so employed in the following functional areas.

Area	%
Process	23.4
Research and development	23.0
Administration	9.3
Production	7.7
Design	5.0
Consulting	4.9
Project management—construction	4.5
Environmental engineering	4.1
Education	4.8
Product engineering	1.3
Maintenance	0.9
Quality control	0.7
Other	4.6

SOURCE: AIChE Report, August 1981.

This wide spectrum of application shows that chemical engineers must be trained to function in any phase of chemical manufacturing.

Commercial chemical processing involves *chemical conversions* and *physical operations*, and presupposes factory scale equipment and chemical engineering experience. To keep the factory from corroding away, resistant construction materials must be selected. Efficient plant operation requires instruments for recording and controlling processing variables. Harmful impurities in raw materials must be controlled and product purities monitored. Instruments that perform these functions have largely replaced analytical chemists, mainly because of lower cost and far greater speeds.