INTRODUCTION TO INDUSTRIAL CHEMISTRY

HOWARD L. WHITE

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HOWARD L. WHITE
CIBA-GEIGY Corporation (Ret.)

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To my wife Betty,
whose encouragement was vital in my
writing this book
and whose help in the detailed assembly
of the manuscript
was essential.
To my daughter, Joyce
(who suggested a word processor)
and to my sons Howie and Chris.

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HLW

Preface

A deficiency has developed in recent years in undergraduate chemistry programs taken by students heading toward a career in some branch of the chemical industry. To remedy the situation, students should enroll in a one-semester course in industrial chemistry using this textbook. This should be taken during their third or fourth year of study, after they have completed a general, an analytical, and an organic chemistry course. This book clarifies the career areas and technical problems to be considered when chemical reactions are carried out on a large scale. My twenty-two years in industrial chemical process development and experience in teaching industrial chemistry at the university level have been used in compiling this material.

Since World War II, understanding of chemistry fundamentals has increased at an extremely rapid rate. Undergraduate chemistry programs have consequently become much more theoretical. At the same time, a large number of consumer products based on chemical processes have come on the market. The research and development necessary for discovering these laboratory-scale processes and their conversion to an industrial scale have been carried out by industrial laboratories, but have usually not been described in university chemistry courses. New employees in the chemical industry have not been adequately prepared to deal with the parameters within which the chemical industry operates. This book should help with the indoctrination stage of their jobs.

The rapid increase in the volume of theoretical chemical data that undergraduates must cover has forced a reduction in the amount of descriptive chemistry taught, because of time limitations. However, many scientists now feel that too much of this kind of material has been removed from the curriculum. I wrote this book to give the basic background needed to handle a selected group of large-scale organic, fermentation, and inorganic processes. This type of material is necessary for a student who wishes to be adequately trained as a chemist. This book discusses these processes with modern mechanistic concepts in mind. This approach will help to hold the interest of the student who does not like highly theoretical treatments.

There has developed a distinct antiscience feeling among young people in recent years. For example, the preparation of chemical industry products such as pesticides and herbicides is seen as having caused severe pollution problems. This textbook discusses these types of problems by giving examples of how a product can be prepared in high yield with correspondingly low effluent. Bioconversion of product and effluent to innocuous products is discussed. In summary, the book discusses attack by chemical and biological means on these problems.

The all-important economic aspects of a process are emphasized in this book. Simple cost calculations to pinpoint factors that contribute to cost and to show how much it costs for pollution and effluent cleanup are explained. Selection of methods for cleanup at minimum cost is clarified.

This text does cover many monomers but does not get into polymers. The author believes polymer chemistry should be a separate one-semester course taken following this one. The principles of scale-up, cost, pollution, and so on discussed here will be readily applied in polymer work.

I believe that training in current B.S., M.S., and Ph.D. chemistry programs is strongly research oriented. Graduates are not generally aware that industrial chemistry has a wide range of careers that have not been mentioned in chemistry major programs. Also, discussions of chemical processes are usually omitted. I recommend enriching advanced courses through use of industrial material. This would have the result that students and faculty would get a more solidly based view of what to expect in various industrial careers in research and development, and in other careers needing a chemical background.

I also believe that industrial chemistry in the classroom should not be narrowly focused on vocational considerations, but should be taught to a much larger segment of the student population than just the industry-bound chemist.

Industrial chemistry should be a distinct portion of the curriculum, not just supplementary notes and comments. The difficulty is that academics lack appreciation of industrial concerns, and also that industrial chemists scold their academic colleagues for not teaching practical chemistry.

Industrial chemistry should be included in the curriculum of all students who are considering a chemical career. The material is of equal importance to that in the current course lists.

HOWARD L. WHITE

Warwick, Rhode Island
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The Chemical Industry and Large-Scale Chemical Manufacturing

We commence by describing those substances prepared by the group of companies that make up the chemical industry. We group these products according to how the public uses them in order to direct the reader's attention to those materials used in everyday living that originate from industrially manufactured chemicals. The many chemical process steps needed to show the connection between some of these useful substances and their raw materials are described. There are two general aims in view.

First, it is necessary to show how the reactions studied in previously taken chemistry courses have to be adapted in preparing these commonplace substances on a large scale. A discussion is presented to illustrate what problems arise when the scale of the process increases beyond what can be done in the laboratory up to the preparation of commercial quantities. Examples of these factors are regulation of environmental damage and safety and economic considerations.

Second, we discuss these processes so that university graduates will have an introductory background for careers such as state and federal regulators, or other careers affected by the preparation of these products in enormous quantities, as well as for chemical industry jobs.

The chemical industry's product groups used in the monograph *Chemistry in the Economy* (Harris and Tishler, 1973, pp. vii–viii) are as follows:

Fertilizers
Ferrous metals
Glass
Other inorganic chemicals
Petroleum refining products
Natural and synthetic rubber
Plastics and resins
Textile fibers

Soaps and detergents
Protective coatings
Pharmaceuticals
Personal care products
Pesticides
Food processing chemicals
Pulp and paper chemicals
Photographic products
Electronic equipment products
Electrical equipment products
Other organic chemicals
Products of the nuclear industry

A few selected products from the preceding categories have been chosen for detailed discussion. Some are inorganic products and some are organic chemicals. Others could have been used just as easily to illustrate the principles to be discussed. The aim is to lead you to think about the details of *any* chemical process by seeing how these particular materials are prepared.

The previous laboratory experiences of most chemistry students have probably only included the preparation of, at the most, a hundred grams of a selected group of chemicals. The lecturer may have referred to a few equations for some industrial processes. This book shows the many opportunities for the use of a chemist's background knowledge in the development and scale-up stages for preparing a large-scale process for a useful chemical product. Merely having prepared in the laboratory a substance that has been shown to have an exciting end use does not mean that the large-scale stage will be easily reached.

1.1 BACKGROUND FACTORS IN LARGE-SCALE PROCESSES

In this chapter we introduce various topics relating to large-scale processes that are not considered at all in laboratory work at most universities. The syntheses, at least the equations, may well have been encountered in other courses. In some cases the process chemistry was discovered many years ago, but necessary improvements are still being made because of questions of cost, environmental damage, and so on.

1.1.1 Raw Materials

It probably does not occur to the typical student that all the chemicals in the university laboratory have a basic natural source, for example, a mineral, petroleum, an agricultural crop, or an atmospheric gas. When millions of kilograms of a product are to be prepared, it is important to determine the availability of the raw material in the area slated for manufacture. All prospective chemists should realize that only a small number of chemicals made for use as laboratory reagents are prepared in commercial quantities. When a source of raw material for a new process is being considered, it is necessary to think about the limited supply of our earth's resources, which, of course, controls the quantities of basic source material available. Then, to limit the quantity of raw material needed, organic and inorganic process development chemists have to become involved in recycling products from waste streams, conversion of chemical by-products from a process to make additional useful materials, and the devising of one process to make two commercially useful products at once. Background of this sort is discussed in Chapters 4, 5 and 6.

Both inorganic and organic raw materials are used in sequential reactions in which substances are converted to products that are sold, or, in other cases, converted to different commercial products. Chenier (1983) shows this in tabular form for some inorganic chemicals existing in nature. His data are shown in adapted form in Figure 1.1.

These data indicate that certain substances on the list of the commodity chemicals (those produced in enormous quantities) are produced from naturally

Nature's Raw Materials	Other Raw Materials		Products	
Air		→	$O_2 + N_2$	(1)
$CH_4 + H_2O$		→	$CO + H_2$	(2)
N_2 (as air) +	H_2	→	NH_3	(3)
O_2 (as air) +	NH_3	→	HNO_3	(4)
O_2 (as air) + S + H_2O		→	H_2SO_4	(5)
Al_2O_3 +	H_2SO_4	→	$Al_2(SO_4)_3$	(6)
$CaF_2 \cdot 3[Ca_3(PO_4)_2]$ +	H_2SO_4	→	H_3PO_4	(7)
NaCl + H_2O		→	$NaOH + Cl_2 + H_2$	(8)
	$H_2 + Cl_2$	→	2HCl	(9)
Alkanes +	Cl_2	→	Cl-alkanes + HCl	(10)
$CaCO_3$		→	$CaO + CO_2$	(11)
$CaCO_3$ + NaCl		→	$CaCl_2 + Na_2CO_3$	(12)
SiO_2 +	Na_2CO_3	→	$Na_2O \cdot SiO_2$	(13)
	$CO_2 + NH_3$	→	NH_2CONH_2	(14)
TiO_2 (as air) +	$Cl_2 \rightarrow TiCl_4$	→	TiO_2	(15)

FIGURE 1.1 Summary of preparations of several commodity chemicals. From P. J. Chenier, *J. Chem. Ed.* **60,** 412 (1983). Reprinted with permission.

occurring materials. The "other" raw materials are those previously prepared from natural raw materials in a separate synthesis as shown in this figure.

The numbers in the following list refer to Figure 1.1.

1. Oxygen and nitrogen are prepared by the distillation of liquid air.
2. Syngas (a mixture of carbon monoxide and hydrogen) is made from methane (or other hydrocarbons) with steam. (See Section 2.3.1.A, B.)
3. Ammonia is synthesized from nitrogen and hydrogen. (See Section 2.3.2.)
4. Nitric acid is prepared from ammonia by catalytic oxidation with oxygen. (See Section 2.5.)
5. Sulfuric acid is made from sulfur, oxygen and water in a three-step process. Sulfur is mined or recovered from petroleum. (See Section 2.4.)
6. Aluminum sulfate is prepared from sulfuric acid and aluminum oxide (alumina), which is mined.
7. Phosphoric acid is prepared from phosphate rock, a mineral called fluoroapatite, a calcium fluoride–calcium phosphate double salt, and sulfuric acid. (See Section 2.1.)
8. Soduium hydroxide and chlorine are prepared by the electrolysis of sodium chloride solution. (See Section 2.6.)
9. Hydrogen and chlorine combine directly to give hydrogen chloride.
10. Hydrogen chloride is more commonly made from the reaction of various alkanes (from petroleum) with chlorine. The chloroalkanes are discussed in Section 4.8.3.C.
11. Lime is made from the mineral limestone by heating.
12. Sodium carbonate (soda ash) is made from the minerals limestone and salt with the aid of ammonia and coke. This is the solvay process. It is also mined as a component of the mineral Trona.
13. Sodium silicate (glass) is made from sand, lime, and soda ash.
14. Carbon dioxide reacts with 2 moles of ammonia to give ammonium carbamate, which decomposes to urea and water.
15. Titanium dioxide, a product used in paints, is made from the mineral rutile (TiO_2), which is purified by distillation of the tetrachloride.

To obtain a similar outlook on organic raw materials, see Chapters 3 and 4.

1.2 REVIEW OF MAJOR TOPICS

We now examine in synopsis form the highlights of the book:

Type of process discussed. Examples of inorganic, fermentation, and organic processes are examined. Chemically simple processes have been included, along with a few more elaborate ones.

Scale-up. The techniques used in changing a laboratory process to large scale are discussed in Chapter 5. These are problems that are of little or no importance to the laboratory chemist.

Costs. As we consider a process, we need a procedure for deciding which are technically the most difficult factors so as to properly direct our research and development work. The student would probably think about problems strictly related to the laboratory, such as long reaction time and wasteful recrystallization. On a large scale, other problems could be, for example, the use of an expensive piece of equipment, or a difficult-to-prepare raw material, or troublesome waste disposal. To decide where to aim the development work, a simplified cost calculation is prepared. The method used is given in Chapter 6. The most technically difficult stage is shown as the most costly step in this preliminary process computation. Future process work will then be directed toward simplifying the process, with resulting cost reduction.

Energy Requirements. In the laboratory, electric heaters are used for supplying energy and ice baths are used for removing heat. For large-scale work, it is necessary to keep energy costs as low as possible. For example, it is sometimes technically straightforward to transfer energy emitted by a reaction to another process step where it is needed. Energy costs are reduced by the use of catalysts and by utilizing heat of reaction in various ways. (See Chapters 2, 8 and 11.)

Chemical Control. It is necessary to have chemical analyses done at various points in a process and to understand the chemistry of the product and of the by-products that is occurring at each stage. This is necessary to determine quickly when the yield is at the maximum, and to minimize the quantity of effluent and other factors. (See Chapters 2, 4, and 5.)

Use of Catalysts. The great majority of large-scale industrial processes, particularly the continuous ones, require catalysts. These substances are used to cause other substances to react quickly with reduction or elimination of solvent and by-product and with resulting cost reduction. From the needs of the chemical industry, particularly the petrochemical industry, new synthetic reactions have been achieved using special catalyst mixtures. These reactions are rather unusual synthetic steps. The impetus for discovering these reactions was the preparation of products having great industrial importance at minimum cost. This book briefly discusses some detailed mechanistic work used to plan the most cost effective final process. (See Chapters 2, 4 and 11.)