

*Processes and Systems
in
Industrial Chemistry*

H. P. MEISSNER

*Processes and Systems
in
Industrial Chemistry*

H. P. MEISSNER

*Professor of Chemical Engineering
Massachusetts Institute of Technology*

P R E N T I C E - H A L L , I N C .

Englewood Cliffs, N.J.

PRENTICE-HALL INTERNATIONAL, INC., *London*
PRENTICE-HALL OF AUSTRALIA, PTY. LTD., *Sydney*
PRENTICE-HALL OF CANADA, LTD., *Toronto*
PRENTICE-HALL OF INDIA PRIVATE LIMITED, *New Delhi*
PRENTICE-HALL OF JAPAN, INC., *Tokyo*

© 1971 by Prentice-Hall, Inc.
Englewood Cliffs, N.J.

All rights reserved. No part of this book
may be reproduced in any form or by any
means without permission in writing
from the publisher.

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

Library of Congress Catalog Card Number: 79-130374

13-723320-5

Printed in the United States of America

Processes and Systems
in
Industrial Chemistry

PRENTICE-HALL INTERNATIONAL SERIES
IN THE PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

NEAL R. AMUNDSON, EDITOR, *University of Minnesota*

ADVISORY EDITORS

ANDREAS ACRIVOS, *Stanford University*
JOHN DAHLER, *University of Minnesota*
THOMAS J. HANRATTY, *University of Illinois*
JOHN M. PRAUSNITZ, *University of California*
L. E. SCRIVEN, *University of Minnesota*

- AMUNDSON *Mathematical Methods in Chemical Engineering: Matrices and Their Application*
ARIS *Elementary Chemical Reactor Analysis*
ARIS *Introduction to the Analysis of Chemical Reactors*
ARIS *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*
BOUDART *Kinetics of Chemical Processes*
CROWE, ET AL. *Chemical Plant Simulation*
FREDRICKSON *Principles and Applications of Rheology*
HAPPEL AND BRENNER *Low Reynolds Number Hydrodynamics: With Special Applications to Particulate Media*
HIMMELBLAU *Basic Principles and Calculations in Chemical Engineering, 2nd Edition*
HOLLAND *Multicomponent Distillation*
HOLLAND *Unsteady State Processes with Applications in Multicomponent Distillation*
KOPPEL *Introduction to Control Theory with Applications to Process Control*
LEVICH *Physicochemical Hydrodynamics*
MEISSNER *Processes and Systems in Industrial Chemistry*
PETERSEN *Chemical Reaction Analysis*
PRAUSNITZ *Molecular Thermodynamics of Fluid-Phase Equilibria*
PRAUSNITZ AND CHUEH *Computer Calculations for High-Pressure Vapor-Liquid Equilibria*
PRAUSNITZ, ECKERT, ORYE, O'CONNELL *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*
WHITAKER *Introduction to Fluid Mechanics*
WILDE *Optimum Seeking Methods*

PRENTICE-HALL, INC.
PRENTICE-HALL INTERNATIONAL, INC., UNITED KINGDOM AND EIRE
PRENTICE-HALL OF CANADA, LTD., CANADA

Preface

Industrial chemistry deals with the methods and reactions for making the products of the process industries on a large scale. Study of this enormous field is generally undertaken in either of three ways, each having advantages and disadvantages. In one approach, which might be called encyclopedic, coverage of the entire field is attempted. This approach provides the broad background which is so necessary for effective action but runs the danger of being superficial. It is difficult to present a meaningful survey, because of both the enormous number of processes involved and the fact that each is complex, being the result of much ingenuity and invention often reflecting decades of technical evolution. In a second approach, a few processes are selected for study in depth. This method insures rigor but may become parochial, since opportunities for developing and illustrating principles of general applicability are limited. In the third approach, reactions are grouped into the so-called unit processes such as oxidations, hydrations, nitrations, etc. The patterns uncovered are again valid and helpful, but the focus is on the reactor rather than on the overall flowsheet. Often, important reactions are not readily amenable to such classification.

None of the three approaches described is to be disparaged, especially since professional activity in the field benefits from each. The student, however, continues to have difficulties in bringing order out of what he calls the chaos of industrial chemistry. To help reduce these difficulties, I have made an attempt in this book to indicate that processes might also be classified by similarities in (1) types of equilibria, (2) types of energy management problems, (3) types of rate problems (including catalysis), and finally (4) types of flow sheet patterns and materials handling problems. The

object here, of course, is only incidentally to classify and describe. Of primary importance is the development of a capacity to do effective and original thinking in the field, and such professional competence requires more than the absorption of a vast mass of factual material. Active work is essential on case-type problems in which are presented a little of the hurly-burly of the industrial world with its conflicting requirements, its superabundance of data or lack of data, and its need for judgment and invention. Some of the problems presented therefore call for analytical thinking; others require an imaginative approach to process thinking and to the solutions of process difficulties. These problems represent the heart of this book to which the text material is mainly supplementary.

As in industry, the mathematical preparation required to deal with these problems is not formidable, extending no further than calculus. The reader should have a good background in physical chemistry and thermodynamics. A certain amount of review material is included, particularly in kinetics and electrochemistry, since these fields are usually not intensively discussed in courses in physical chemistry. Again, a passing familiarity with chemical plant equipment such as heat exchangers, stills, and the like is assumed, but no more familiarity than a college senior or graduate student might have is needed.

I have made an attempt in this book to provide enough background to prepare the student for the great differences between an industrial plant and a university laboratory. That is, the student is accustomed to the simplicity and versatility of beakers, Erlenmeyer flasks, glass filters, etc., and is always surprised by the high degree of specialization of industrial equipment and processes. The care with which each piece of industrial equipment is designed for its task reflects the pressure to attain lowest possible production costs, which must be at least comparable with those of competitors' plants. In consequence, the industrial chemist is vitally concerned with the material efficiency of his plant, which will consume thousands and even millions of dollars worth of raw material during its lifetime, and also require large expenditures for supplies of various types for labor, power, water, etc. Design of an efficient plant obviously requires a far-reaching knowledge of the basic chemistry, physical chemistry of the process including fluid flow behavior, mass and heat transfer rates, reaction rates, and whatever else may be directly relevant to the specific process under study. The cost of the research and development effort required to obtain such knowledge must be balanced against the potential profits in prospect and, especially for larger installations, the cost of such studies are easily justified.

The difficulties of integration of a process, so that all its parts are kept in proper balance, are again novel to the student. For example, in continuous production of a material like ethylene by propane cracking, the heat addition to the reactor must be in balance with the feed, which contains both fresh

and recycled raw material. These operations must all be properly matched to product cooling, to the stills for separating the product from the unconverted raw materials, etc. This is quite unlike a laboratory synthesis, where each stage is carried out in sequence and at leisure, receiving the full attention of the investigator. The preparation of a properly integrated flowsheet may be viewed as the chemical counterpart of the "systems engineering" function of the electrical and the mechanical industries.

The student often expects to find industrial chemistry to be somehow different than other kinds of chemistry. This is not the case, save that attention is focused on reactions which produce the products of industrial interest. Of course it often proves necessary to develop new reactions because of economic pressures to use new raw materials or to improve product characteristics. For example, the Solvay process for making soda ash was developed in a competition fostered by the French Government in the latter part of the eighteenth century for a process starting with limestone and common salt. Again, Haber's synthesis of ammonia from the elements by high pressure catalysis is an example of unorthodox operations which had not been studied previously. It was the increasing demand for ammonia and the inadequacy of the existing supply from coal distillation which provided the incentive for this pioneering effort. Similarly, the industrial chemist is always under pressure to find cheaper raw materials. To find a process for making ethylene glycol from ethylene which does not consume chlorine, the industrial chemist developed the ethylene oxide route, a direct oxidation which now competes successfully with the older ethylene chlorhydrin route. Often he develops a process which is basically not suited to small scale operation and so would not be used in the laboratory. The production of acetylene from hydrocarbons in a high temperature arc, followed by quench and recovery by scrubbing, is an obvious example.

The foregoing indicates that the industrial chemist often deals with reactions which are normally not of concern to the laboratory chemist. Many of the reactions of the so-called petrochemicals industry would not have been considered possible to the classic organic chemist of several decades ago. Examples here are the direct oxidation of cyclohexane to adipic acid, the chlorination of hydrocarbons with an oxygen-chlorine mixture to avoid the production of by-product hydrogen chloride, alkylation reactions such as the direct addition of ethylene to benzene to form ethyl benzene, and aromatizing reactions whereby normal paraffins are simultaneously dehydrogenated and converted to aromatics. The list can be extended to considerable length.

Often these reactions require a catalyst, especially in organic operations where the need for giving direction to reactions is particularly great. There is less need, or at any rate less use for, catalysis in inorganic industries, if the classic application of catalysis in SO_2 oxidation, ammonia synthesis, and

ammonia oxidation to the nitrogen oxides is excluded. Again, the field of process metallurgy has so far found little application for catalysis. This should not be interpreted as an indication of backwardness, since process metallurgy deals with reactions at high temperature or with ionic reactions in aqueous solution where rates are usually great. Catalysis, nevertheless, is industrial chemistry's most important frontier and accounts for the space devoted here to this subject.

A further general responsibility of the industrial chemist is the modification of materials to fit changing specifications and use requirements. Problems are especially challenging in the fields of polymeric materials, namely plastics, textile fibers, paper, etc., and also in the production of composites such as laminates, paints, lubricants, etc. However, no field seems free from the problems of product modification, since use specifications are constantly changing. These areas are left to consideration of texts more specialized than this one.

An industrial chemist, therefore, is concerned with the methods and reactions for making chemicals on a large scale. His academic training is usually either in chemistry or chemical engineering, but his success in the field is dependent not so much on background as on his resourcefulness, ingenuity, and capacity to improvise and invent. The field is remarkably dynamic, changing constantly, and derives much of its fascination from the continuing challenges presented by its new problems and opportunities.

H. P. MEISSNER

Nomenclature

- a* Stoichiometric coefficient in reactions (1-1), (2-2), and the like; also Activity, as defined in Eq. (2-1). Dimensionless.
- A* Reaction partner in reactions (1-1), (2-2), and the like; also Area, usually in sq ft.
- b* Stoichiometric coefficient in reactions (1-1), (2-2), and the like. Dimensionless.
- B* Reaction partner in reactions (1-2) and (2-2); a constant in Eq. (8-20).
- c* Heat capacity in cal/(g) (°C) or Btu/(lb) (°F); stoichiometric coefficient in reaction (1-1), etc.; c_A is concentration of any component *A* in units such as lb moles/cu ft or g moles/liter.
- C* Reaction partner in reactions (1-1) and (2-2).
- C* Number of Phase Rule components in Eq. (2-6).
- D* Reaction partner in reactions (1-1) and (2-2); diffusion coefficient in Eq. (8-22) in units such as cm²/sec.
- E* Activation energy, cal/g mole; cell voltage, with E° the standard state voltage.
- f* Fugacity; also fraction conversion as in example 5-4.
- F* Faraday number, namely 96,454 amp sec/g equivalent, 23,010 cal/(V) (g equivalent), or 12,163 amp hr/(lb equivalent).
- F* Feed rate to system, lb moles/sec.
- ΔF° Standard free energy change, usually in cal/g mole, or kcal/g mole, as in Eq. (1-10).
- G* Constant, Eq. (8-25).
- ΔH Enthalpy change, usually in kcal/g mole, as in Eq. (1-10); ΔH° is the standard enthalpy change of a chemical reaction.
- k* Reaction rate constant defined in Eqs. (6-4) and (7-9); also thermal conductivity as in Eq. (8-9), expressed in Btu/(hr) (sq ft) (°F)/ft.

- k' The effective coefficient of mass transfer through a porous solid, as defined in Eq. (8-3).
- K Equilibrium constant; K_a is the equilibrium constant expressed in terms of activities as in Eq. (1-2) and (2-3); K_p is expressed in terms of partial pressures, atm as in Eq. (1-6) and (2-4); K_B^A is the selectivity of an ion exchange resin as in Eq. (3-9).
- L Length, ft.
- m Stoichiometric coefficient for Eqs. (1-1) and (2-2).
- M Molecular weight; M_c referring to the core material of a solid particle as in Eq. (8-1); also reaction partner in reactions (1-1) and (2-2). MC_p is molal heat capacity.
- n Stoichiometric coefficient for reactions (1-1) and (2-2); also number of moles of a component present in a system, or flowing into a system, or formed within a system; \dot{n} is moles reacting on a surface per unit time as in Eq. (8-20).
- N Reaction partner as in Eqs. (1-1) and (2-2); also particle number in Eq. (8-27a).
- N Number of species in a system, as in the Phase Rule Eq. (2-6).
- p Partial pressure in atm; p_{ref} is partial pressure in the reference state; p° is vapor pressure of a pure material; p_c in Eq. (8-8) is the partial pressure of a component at the surface of a particle core; p_∞ is the partial pressure in the gas phase a great distance from the particle surface.
- P Number of phases in an equilibrium system, as in Eq. (2-6).
- q Heat flow rate, in Btu/hr. In Eq. (7-16), q_{chem} is heat generated "by an exothermal chemical reaction"; q_{sensible} is the sensible heat which must be supplied; q_{cool} is cooling rate as in Eq. (7-17).
- r Rate of reaction, in lb moles/(hr) (cu ft) as in Eq. (6-1), or in lb moles/(hr) (lb catalyst) as in Eq. (7-7); r_{surface} is reaction rate, lb moles/(unit surface area) (unit time).
- R_g Gas constant 1.987 Btu/(lb mole) ($^\circ\text{R}$), or 1546 ft lb/(lb mole) ($^\circ\text{R}$), or 1.987 cal/(g mole) ($^\circ\text{R}$), etc.
- R Radius of pores as in Eq. (7-1), or radius of pellets as in Eq. (8-1). R_0 indicates initial radius of a spherical particle, R_c is the radius of a core of unreacted solid within this particle at any time θ , while R_{cf} is the final core radius.
- R Number of independent chemical reactions in a system, Eq. (2-16).
- S Moles of a stream per mole of feed, after reaction occurs, as in Eq. (6-15).
- S Number of stoichiometric relations in a system, as in Eq. (2-6).
- SV Space velocity, defined in example 9-1.
- ΔS° Standard entropy change of a chemical reaction.
- t Steady state reactor temperature as in Eq. (7-15), in absolute degrees.
- T Absolute temperature, $^\circ\text{K}$ or $^\circ\text{R}$ as the case might be. T_{FW} is the value of feed and cooling fluid to a kettle, Eq. (7-20).
- U Overall heat transfer coefficient, Btu/(hr) (sq ft) ($^\circ\text{F}$).
- v Specific volume, cu ft/(lb mole).
- V Volume of system or reactor, cu ft.
- V Variance of a system, as in Eq. (2-7).

W	Weight of solid, either reagent or catalyst, usually in lb.
X	Abscissa on Janecke diagram, such as Fig. 3-4.
x	Mole fraction often referring to liquid phase, as in Eq. (3-13).
y	Mole fraction, often referring to the vapor phase, as in Eq. (3-13).
Y	Moles of key component present at any time in a reacting system, often based on 1 mole of feed; also abscissa on Janecke diagram, such as Fig. 3-4.
Z	Compressibility factor, namely $R_g T/pV$. Dimensionless.

Greek Symbols

α	Empirical exponent of Eq. (6-5).
β	Empirical exponent of Eq. (6-5).
γ	Activity coefficient, as in Eq. (10-8) etc.; empirical exponent of Eq. (6-5).
Δ	Finite difference between final and initial quantity, such as enthalpy or free energy.
δ	Change in the number of moles of a reaction, defined by Eq. (1-7).
ξ	Defined in Eq. (1-13).
η	Effectiveness factor in Eq. (7-5); also empirical exponent of Eq. (6-10).
ρ	Density, as in lb/cu ft of catalyst.
π	Total pressure, atm.
Σ	Summation.
τ	Residence time, Eq. (6-34).
θ	Time in sec, min, or hr depending on circumstances.
ψ	Temperature interval over which reaction rate doubles, usually in °C, as in example 6-1.
μ	Empirical exponent of Eq. (6-10).

Contents

1.	Equilibrium in Homogeneous Systems	1
2.	Heterogeneous Reaction Equilibria	24
3.	Liquid-Solid Equilibria Involving Ions	46
4.	Management of Materials	72
5.	Management of Heat Energy	89
6.	Homogeneous Reaction Rates	111
7.	Catalytic Reactions and Reactors	138

8.	Reactions between Gases and Solids	159
9.	Chemical Reactors	179
10.	Reactions Having an Unfavorable ΔF°	195
11.	Industrial Electrochemical Operations	212
	Notes to Problems	235
	Problems	237
	Subject Index	383
	Problem Index	385

Equilibrium in Homogeneous Systems

1

Industrial chemistry is the study of the large-scale manufacture of materials whose production involves chemical reactions. The field is vast, for it includes not only the so-called industrial chemicals, but also plastics, paper, the metals, glass, synthetic fibers, and others. Industrial chemistry is therefore the study of the process industries.

In industrial chemistry, attention is focused on both the processes operated and the systems of apparatus used in manufacture. A process may be defined as an integrated series of reactions and associated operating steps, such as mixing, separation by distillation, and the like, whereby available raw materials are converted into a desired product. A process is carried out in a system of apparatus, through which materials travel in accordance with the processing plan. A schematic representation of the route so traveled is called a flow sheet, while the aggregation of equipment itself constitutes a plant. The creation, modification, and analysis of processes and their associated systems of equipment form the subject matter of this book, with illustrations and examples largely drawn from the field of industrial chemicals.

Alternatives in manufacture. Characteristically, a product can be made industrially by any of several alternative processes involving different reactions and systems of apparatus, depending on the raw materials available and the chemical route chosen. To illustrate the use of alternative raw materials with a single example, acetaldehyde is made from acetylene by hydra-

tion using an aqueous solution of mercury salts as catalyst, from ethylene by oxidation using an aqueous solution of palladium salts as catalyst, and from butane by partial oxidation. Similarly, two different chemical routes from the same raw material to the same product and therefore involving different reactions and different processing systems may be illustrated by ethanol manufacture from ethylene. The conversion to alcohol is carried out directly by passing a mixture of ethylene and steam at high pressure over a phosphoric acid catalyst. Alternatively, ethylene combines at low pressure with sulfuric acid to form ethyl hydrogen sulfate, which is then hydrolyzed to the alcohol. Finally, there are often many possible alternatives in the systems of apparatus used in carrying out conversion of a given raw material into a given product by a given set of chemical reactions. Thus, in making ammonia from hydrogen-nitrogen gas mixtures at high pressure, the reacting gases are passed through a series of adiabatic catalyst beds. Cooling between stages is necessary since this reaction is vigorously exothermal. One such method of cooling is by inserting water-cooled heat exchanger surfaces in the ducts between the reactors to generate process steam, while another involves injecting suitable quantities of cold fresh feed gas into the hot gases between reactors.

The existence of alternatives such as the ones mentioned is characteristic of industrial chemistry, and their discovery and elaboration afford extensive opportunities for innovation, ingenuity, and invention. Moreover, because of continual changes in technology and raw material costs in a dynamic economy the best processing system for manufacture at any given location today does not necessarily remain the best. Thus, the recent development of the catalytic one-step conversion of propylene, ammonia, and air into acrylonitrile has made the older syntheses from acetylene and hydrogen cyanide and from ethylene via the cyanohydrin intermediate appear much less attractive. The advent of this new acrylonitrile process illustrates the general trend in the petrochemicals industry toward the use of cheaper feedstocks and simpler but more sophisticated chemical processes. Analogous changes are, of course, occurring throughout the field of industrial chemistry.

Reactions of industrial chemistry. While the study of a processing system is conveniently started with the chemical reactions occurring, the key difficulties of the operation do not necessarily lie in the reactors. That is, a typical process might involve purification and mixing of raw materials, followed by reaction and then by recovery, separation, and purification of products. There are always problems associated with the process such as supplying or removing energy, recycling unused reagents in the product stream from the reactor, and others. It is not uncommon to find that the investment in product recovery and purification equipment in a plant is manyfold greater than for the reactors. The broad challenge is to assemble

and arrange an equipment system of high efficiency which will respond sensitively and without excessive demands of attention to unavoidable variations in raw material compositions, in temperatures of coolants and heat sources, in throughput, etc.

Basically, no new chemical or physical principles are encountered in industrial chemistry. The reactions of this area, however, are often not suitable as simple illustrations for a systematic development of general inorganic or organic chemistry, and so are not discussed in detail in elementary texts. Thus, ethylene is made in enormous quantities industrially by cracking light naphthas, but because of the complexity of both the reactions and product recovery, naphtha cracking is not a good introductory example to simple dehydrogenation. Again, the reactions of industrial chemistry are often not easily performed on a laboratory scale. In the ethylene process just mentioned, serious difficulties are encountered both in controlling the residence time of the reacting stream at elevated temperature and in product recovery; consequently, simpler preparative methods are preferred for bench scale studies, such as the dehydration of ethanol with sulfuric acid. Finally, particularly in the organic chemistry field, the student is frequently not familiar with the catalytic processes being operated which sometimes involve highly unorthodox chemistry, such as in the direct oxidation of ethylene with air over a silver catalyst to ethylene oxide.

Novelty in the field of industrial chemistry lies primarily in its focus on reactions of commercial interest and the associated physical chemistry of the mixing and separation processes. The intensity with which these matters are studied in industry is often surprising to the newcomer, but such studies of general chemistry, equilibria, thermal effects, kinetics, etc., is essential for the design and operation of a processing system having lowest costs of construction and operation. These detailed technical studies are costly, but are readily justified if even small improvements in performance are attainable. A chemical plant often represents a multimillion dollar investment and it will be supplied during its lifetime with many more millions of dollars of raw material, along with associated large expenditures for labor, operating supplies, power, and fuel. The benefits of studies leading to optimum system design are thus obvious.

Initial orientation. Study of a processing system is usually begun with the chemical reactions occurring, since these help fix much of the system's stoichiometry. Three key questions are asked:

1. Over what range of temperature, pressure, and reactant feed compositions are the chemical equilibria such that a favorable concentration of the desired product is attainable in the reactor outlet streams?
2. Within this range of conditions, where do reaction rates become favorable?