

Chemical Engineering

AN INTRODUCTION

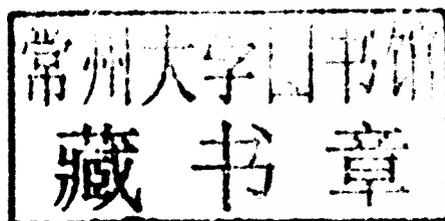
MORTON M. DENN

Chemical Engineering

AN INTRODUCTION

Morton M. Denn

The City College of New York



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CHEMICAL ENGINEERING

An Introduction

“Chemical engineering is the field of applied science that employs physical, chemical, and biochemical rate processes for the betterment of humanity.” This opening sentence of Chapter 1 is the underlying paradigm of chemical engineering. *Chemical Engineering: An Introduction* is designed to enable the student to explore the activities in which a modern chemical engineer is involved by focusing on mass and energy balances in liquid-phase processes. Applications explored include the design of a feedback level controller, membrane separation, hemodialysis, optimal design of a process with chemical reaction and separation, washout in a bioreactor, kinetic and mass transfer limits in a two-phase reactor, and the use of a membrane reactor to overcome equilibrium limits on conversion. Mathematics is employed as a language at the most elementary level. Professor Morton M. Denn incorporates design meaningfully; the design and analysis problems are realistic in format and scope. Students using this text will appreciate why they need the courses that follow in the core curriculum.

Morton M. Denn is the Albert Einstein Professor of Science and Engineering and Director of the Benjamin Levich Institute for Physico-Chemical Hydrodynamics at the City College of New York, CUNY. Prior to joining CCNY in 1999, he was Professor of Chemical Engineering at the University of California, Berkeley, where he served as Department Chair, as well as Program Leader for Polymers and Head of Materials Chemistry in the Materials Sciences Division of the Lawrence Berkeley National Laboratory. He previously taught chemical engineering at the University of Delaware, where he was the Allan P. Colburn Professor. Professor Denn was Editor of the *AIChE Journal* from 1985 to 1991 and Editor of the *Journal of Rheology* from 1995 to 2005. He is the recipient of a Guggenheim Fellowship; a Fulbright Lectureship; the Professional Progress, William H. Walker, Warren K. Lewis, Institute Lectureship, and Founders Awards of the American Institute of Chemical Engineers; the Chemical Engineering Lectureship of the American Society for Engineering Education; and the Bingham Medal and Distinguished Service Awards of the Society of Rheology. He is a member of the National Academy of Engineering and the American Academy of Arts and Sciences, and he received an honorary DSc from the University of Minnesota. His previous books are *Optimization by Variational Methods*; *Introduction to Chemical Engineering Analysis*, coauthored with T. W. Fraser Russell; *Stability of Reaction and Transport Processes*; *Process Fluid Mechanics*; *Process Modeling*; and *Polymer Melt Processing: Foundations in Fluid Mechanics and Heat Transfer*.

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Preface

“Chemical engineering is the field of applied science that employs physical, chemical, and biochemical rate processes for the betterment of humanity.” This opening sentence of Chapter 1 has been the underlying paradigm of chemical engineering for at least a century, through the development of modern chemical and petrochemical, biochemical, and materials processing, and into the twenty-first century as chemical engineers have applied their skills to fundamental problems in pharmaceuticals, medical devices and drug-delivery systems, semiconductor manufacturing, nanoscale technology, renewable energy, environmental control, and so on. The role of the introductory course in chemical engineering is to develop a framework that enables the student to move effortlessly from basic science and mathematics courses into the engineering science and technology courses that form the core of a professional chemical engineering education, as well as to provide the student with a comprehensive overview of the scope and practice of the profession. An effective introductory course should therefore be constructed around the utilization of rate processes in a context that relates to actual practice.

Chemical engineering as an academic discipline has always suffered from the fact that the things that chemical engineers do as professionals are not easily demonstrated in a way that conveys understanding to the general public, or even to engineering students who are just starting to pursue their technical courses. (Every secondary school student can relate to robots, bridges, computers, or heart-lung machines, but how do you easily convey the beauty and societal importance of an optimally designed pharmaceutical process or the exponential cost of improved separation?) The traditional introductory course in chemical engineering has usually been called something like “Material and Energy Balances,” and the course has typically focused on flowsheet analysis, overall mass balance and equilibrium calculations, and process applications of thermochemistry. Such courses rarely explore the scope of the truly challenging and interesting problems that occupy today’s chemical engineers.

I have taken a very different approach in this text. My goal is to enable the student to explore a broad range of activities in which a modern chemical engineer might be involved, which I do by focusing on liquid-phase processes. Thus, the student

addresses such problems as the design of a feedback level controller, membrane separation and hemodialysis, optimal design of a process with chemical reaction and separation, washout in a bioreactor, kinetic and mass transfer limits in a two-phase reactor, and the use of a membrane reactor to overcome equilibrium limits on conversion. Mathematics is employed as a language, but the mathematics is at the most elementary level and serves to reinforce what the student has studied during the first university year; nothing more than a first course in calculus is required, together with some elementary chemistry. Yet we are able to incorporate design meaningfully into the very first course of the chemical engineering curriculum; the design and analysis problems, although simplified, are realistic in format and scope. Few students of my generation and those that followed had any concept of the scope of chemical engineering practice prior to their senior year (and perhaps not even then). Students enrolled in a course using this text will understand what they can expect to do as chemical engineering graduates, and they will appreciate why they need the courses that follow in the core curriculum.

There is more material in the text than can reasonably be covered in one semester. The organization is such that mass and energy balances can be given equal weight in a one-semester course if the instructor so desires. I prefer to emphasize the use of mass balances in order to broaden the scope of meaningful design issues; any negative consequences of deemphasizing thermochemistry in the introductory course, should the instructor choose to do so, are minimal. Much of what once formed the core of the traditional material and energy balances course is now covered in general chemistry, sometimes in a high school setting, and thermodynamics offerings in many chemical engineering departments have become more focused, with more emphasis on chemical thermodynamics than in the past.

Chemical Engineering: An Introduction incorporates material from an earlier textbook, *Introduction to Chemical Engineering Analysis* (1972), which Fraser Russell and I coauthored. I have added a great deal of new material, however, and removed a great deal as well. Much of what remains has been rewritten. Thus, this is not a new edition, but rather a new creation, with an important family resemblance to an earlier generation.

My PhD advisor was the late Rutherford Aris, whose insightful scholarship was matched by his strong commitment to education, which is reflected in his outstanding textbooks and monographs. Aris believed that students learn best when a subject is presented with rigor, and he wrote with a clarity and elegance that made the rigor accessible to everyone. I think that “Gus” would have approved of the approach presented in this textbook, even if his literary standards are unattainable, and I respectfully dedicate *Chemical Engineering: An Introduction* to his memory.

I am grateful to my colleagues at the City College of New York (CCNY), especially Raymond Tu and Alexander Couzis, for their encouragement and their willingness to use the evolving draft in the classroom, and I appreciate the willingness of the CCNY second-year students to work with us. I am, of course, grateful to Fraser Russell for his insights during our long collaboration and for his generosity in permitting me to use some of the fruits of our joint work. Peter Gordon of

Cambridge University Press enthusiastically supported this project, and Kim Dylla graciously permitted us to use her art on the cover. Finally, I am grateful to my colleagues at the Casali Institute of Applied Chemistry of the Hebrew University of Jerusalem, especially Gad Marom and Shlomo Magdassi, and to the Lady Davis Fellowship Trust, for hospitality and support while I was composing the final chapters of the book. My wife Vivienne's hand is hidden, but it is present throughout.

New York
February 2011

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1 Chemical Engineering

1.1 Introduction

Chemical engineering is the field of applied science that employs physical, chemical, and biochemical rate processes for the betterment of humanity. This is a sweeping statement, and it contains two essential concepts: *rate processes* and *betterment of humanity*. The second is straightforward and is at the heart of all engineering. The engineer designs processes and tangible objects that meet the real or perceived needs of the populace. Some civil engineers design bridges. Some mechanical engineers design engines. Some electrical engineers design power systems. The popular perception of the chemical engineer is someone who designs and operates processes for the production of chemicals and petrochemicals. This is an historically accurate (if incomplete) image, but it describes only a small fraction of the chemical engineers of the early twenty-first century.

Chemical engineering is the field of applied science that employs physical, chemical, and biochemical rate processes for the betterment of humanity.

Let us turn first to the concept of rate processes, which is the defining paradigm of chemical engineering, and consider an example. Everyone is familiar with the notion that medication taken orally must pass through the digestive system and across membranes into the bloodstream, after which it must be transported to the relevant location in the body (a tumor, a bacterial infection, etc.) where it binds to a receptor or reacts chemically. The residual medication is transported to an organ, where it is metabolized, and the metabolic products are transported across still more membranes and excreted from the body, perhaps in the urine. Each of these processes takes time, and the rate of each step plays an important role in determining the efficacy of the medication. Chemical engineers are concerned with all natural and man-made processes in which physicochemical processes that are governed by the rates at which the physical transport of mass, momentum, and energy and the

chemical and biochemical transformation of molecular species occur. The example of the fate of medication, and the logical extension to devising procedures that optimize the delivery of the drug to the active site, is an example of *pharmacokinetics*, which has been an area of chemical engineering practice since the 1960s and has led to many important advances. In the sections that follow we will briefly examine this and other areas in which the chemical engineer's interest in rate processes has resulted in significant societal benefit. We do this to illustrate the applications to which the material covered in the remainder of this introductory text and the courses that follow can be applied, although our scope of applications will be far more limited.

1.2 The Historical Chemical Engineer

Chemical engineering began as a distinct profession at the start of the twentieth century, although elements of what are now considered to be core chemical engineering have existed for centuries and more (fermentation, for example, is mentioned in the Bible and in Homer). The discipline began as something of an amalgam, combining chemistry having an industrial focus with the mechanical design of equipment. The early triumphs, which defined the profession in the public eye, had to do with large-scale production of essential chemicals. The invention of the fluid catalytic cracking (FCC) process by Warren K. Lewis and Edward R. Gilliland in the late 1930s was one such advance. A fluidized bed is a column in which a rising gas carries particles upward at the same average rate at which they fall under the influence of gravity, producing a particulate suspension in which the particles move about rapidly because of the turbulence of the gas stream. Crude oil contacts a granular catalyst in the FCC and is converted to a variety of low-molecular-weight organic chemicals (ethylene, propylene, etc.) that can be used for feedstocks and fuel. The cracking reactions are endothermic (i.e., heat must be added). Residual carbon forms on the catalyst during the cracking reaction, reducing its efficiency; this carbon is removed by combustion in an interconnected reactor, and the exothermic combustion reaction produces the thermal energy necessary to carry out the endothermic cracking reactions. The process is very energy efficient; its invention was crucial to the production of high-octane aviation gasoline during World War II, and it is still the centerpiece of the modern petroleum refinery.

As noted previously, fermentation processes have existed throughout human history. The first industrial-scale fermentation process (other than alcoholic beverages) seems to have been the production of acetone and butanol through the anaerobic fermentation of corn by the organism *Clostridium acetobutylicum*, a conversion discovered in 1915 by the British chemist Chaim Weizmann, who later became the first President of the State of Israel. The production of acetone by this route was essential to the British war effort in World War I because acetone was required as a solvent for nitrocellulose in the production of smokeless powder, and calcium acetate, from which acetone was normally produced, had become unavailable. The development of the large-scale aerobic fermentation process for the production of penicillin in

deep agitated tanks, which involves the difficult separation of very low concentrations of the antibiotic from the fermentation broth, was carried out under wartime pressure in the early 1940s and is generally recognized as one of the outstanding engineering achievements of the century. The production of chemicals by biological routes remains a core part of *biochemical engineering*, which has always been an essential component of chemical engineering. The discovery of recombinant DNA routes to chemical synthesis has greatly widened the scope of the applications available to the biochemically inclined chemical engineer, and biochemistry and molecular and cell biology have joined physical and organic chemistry, physics, and mathematics as core scientific foundations for chemical engineers.

War is, unfortunately, a recurring theme in identifying the great chemical engineering advances in the twentieth century. The Japanese conquest of the rubber plantations of southeast Asia at the start of World War II necessitated the industrial development of synthetic rubber, and a U.S.-government-sponsored industrial-academic consortium set out in 1942 to produce large amounts of GR-S rubber, a polymer consisting of 75% butadiene and 25% styrene. The chemists and chemical engineers in the consortium improved the production of butadiene, increased the rate of polymerization of the butadiene-styrene molecule, controlled the molecular weight and molecular-weight distribution of the polymer, and developed additives that enabled the synthetic rubber to be processed on conventional natural rubber machinery. By 1945, the United States was producing 920,000 tons of synthetic rubber annually. The synthetic rubber project was the forerunner of the modern synthetic polymer industry, with a range of materials that are ubiquitous in every aspect of modern life, from plastic bags and automobile hoods to high-performance fibers that are stronger on a unit weight basis than steel. Chemical engineers continue to play a central role in the manufacture and processing of polymeric materials.

This short list is far from complete, but it serves our purpose. The chemical engineer of the first half of the twentieth century was generally concerned with the large-scale production of chemicals, usually through classical chemical synthesis but sometimes through biochemical synthesis. The profession began to expand considerably in outlook during the second half of the century.

1.3 The Chemical Engineer Today

Chemical engineers play important roles today in every industry and service profession in which chemistry or biology is a factor, including semiconductors, nanotechnology, food, agriculture, environmental control, pharmaceuticals, energy, personal care products, finance, medicine – and, of course, traditional chemicals and petrochemicals. More than half of the Fourteen Grand Challenges for Engineering in the accompanying block posed by the National Academy of Engineering in 2008 require the active participation and leadership of chemical engineers. Rather than attempt to give a broad picture, we will focus on a small number of applications areas and key individuals. Chemical engineers have traditionally been involved in both the design

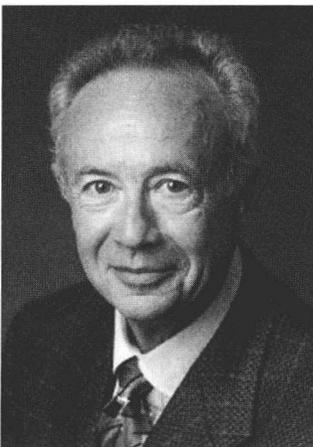
of *processes* and the design of *products* (although sometimes the product cannot be separated from the process). We include chemical engineers involved with both products and processes, but the entrepreneurial nature of businesses makes it easier to single out individuals who have contributed to products.

The Fourteen Grand Challenges for Engineering

as posed by the U.S. National Academy of Engineering in 2008, prioritized through an online survey.

1. Make solar energy economical
2. Provide energy from fusion
3. Provide access to clean water
4. Reverse-engineer the brain
5. Advance personalized learning
6. Develop carbon sequestration methods
7. Engineer the tools of scientific discovery
8. Restore and improve urban infrastructure
9. Advance health informatics
10. Prevent nuclear terror
11. Engineer better medicines
12. Enhance virtual reality
13. Manage the nitrogen cycle
14. Secure cyberspace

1.3.1 Computer Chips



Andrew Grove

The production of semiconductors is driven by chemical engineers, who have devised many of the processes for the manufacture of computer chips, which are dependent on chemical and rate processes. No one has been more influential in this world-changing technology than Andrew Grove, a chemical engineer who was one of the three founders of the Intel Corporation and its CEO for many years. Grove was selected in 1997 as *Time Magazine's* "Man of the Year." One of the most interesting aspects of Grove's career is that his chemical engineering education at both the BS and PhD levels was a classical one that took place before semiconductor technology could form a part of the

chemical engineering curriculum, as it does today in many schools. Hence, it was the fundamentals that underlie the education of a chemical engineer (and, of course, his extraordinary ability) that enabled him to move into a new area of technology and to become an intellectual leader who helped to change the face of civilization.

1.3.2 Controlled Drug Release

Polymer gels that release a drug over time have been investigated since the 1960s. The key issues in timed release are the solubility of the drug in the gel, the uniformity of the rate of release, and, of course, the biocompatibility for any materials placed in the body. One of the leaders in developing this field was chemical engineer Alan Michaels, who was the President of ALZA Research in the 1970s, where he developed a variety of drug delivery devices, including one for transdermal delivery (popularly known as “the patch”). More recently, in 1996, the U.S. Food and Drug Administration (FDA) approved a controlled release therapy for glioblastoma multiforme, the most common form of primary brain cancer, developed by chemical engineer Robert Langer and his colleagues. In this therapy, small polymer wafers containing the chemotherapy agent are placed directly at the tumor site following surgery. The wafers, which are made of a new biocompatible polymer, gradually dissolve, releasing the agent where it is needed and avoiding the problem of getting the drug across the blood-brain barrier. This therapy, which is in clinical use, was the first new major brain cancer treatment approved by the FDA in more than two decades and has been shown to have a positive effect on survival rates. The methodologies used by Michaels, Langer, and their colleagues in this area are the same as those used by chemical engineers working in many other application fields.



Alan Michaels



Robert Langer

1.3.3 Synthetic Biology

Chemical engineers have always been involved in chemical synthesis, but the new field of synthetic biology is something quite different. Synthetic biology employs the new access to the genetic code and synthetic DNA to create novel chemical building blocks by changing the metabolic pathways in cells, which then function as micro-chemical reactors. One of the leading figures in this new field is chemical engineer Jay Keasling, whose accomplishments include constructing a practical and



Jay Keasling

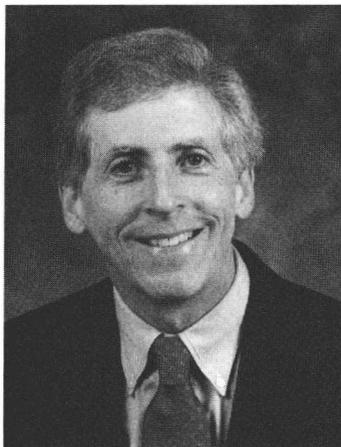
inexpensive synthetic biology route to *artemisinin*, which is the medication of choice for combating malaria that is resistant to quinine and its derivatives. Keasling's synthetic process is being implemented on a large scale, and it promises to provide widespread access to a drug that will save millions of lives annually in the poorest parts of the globe. Keasling is now the head of the U.S. Department of Energy's Joint BioEnergy Institute, a partnership of three national laboratories and three research universities, where similar synthetic biology techniques are being brought to bear on the manufacture of new fuel sources that will emit little or no greenhouse gas.

1.3.4 Environmental Control

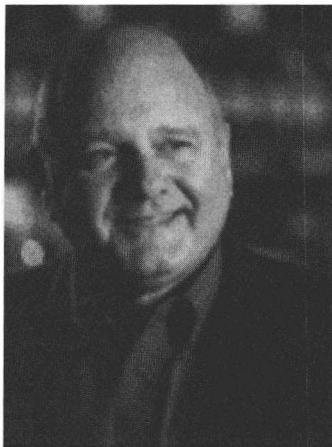
Control of the environment, both through the development of "green" processes and improved methods of dealing with air and water quality, has long been of interest to chemical engineers. Chemical engineer John Seinfeld and his colleagues developed the first mathematical models of air pollution in 1972, and they have remained the leaders in the development of urban and regional models of atmospheric pollution, especially the processes that form ozone and aerosols. The use of Seinfeld's modeling work is incorporated into the U.S. Federal Clean Air Act.

David Boger, a chemical engineer who specializes in the flow of complex liquids (colloidal suspensions, polymers, etc.), attacked the problem of disposing of bauxite residue wastes from the aluminum manufacturing process, which are in the form of a caustic colloidal suspension known as "red mud" that had been traditionally dumped into lagoons occupying hundreds of acres. Boger and his colleagues showed that they could turn the suspension into a material that will flow as a paste by tuning the flow properties (the *rheology*) of the suspension, permitting recovery of most of the water for reuse and reducing the volume of waste by a factor of two. The aluminum industry in Australia alone saves US\$7.4M (million) annually through this process, which is now employed in much of the industry worldwide. An environmental disaster in Hungary in 2010, in which the retaining walls of a

lagoon containing a dilute caustic red mud suspension collapsed, devastating the surrounding countryside, could probably have been averted or mitigated if Boger's technology had been employed.



John Seinfeld



David Boger

1.3.5 Nanotechnology

Nanotechnology, the exploitation of processes that occur over length scales of the order of 100 nanometers (10^{-7} meters) or less, has been the focus of scientific interest since the early 1990s, largely driven by the discovery of carbon nanotubes and “buckyballs” and the realization that clusters containing a small number of molecules can have very different physical and chemical properties from molar quantities (10^{23} molecules) of the same material. The nanoscale was not new to chemical engineers, who had long been interested in the catalytic properties of materials and in interfacial phenomena between unlike materials, both of which are determined at the nanoscale.

One area in which nanotechnology holds great promise is the development of chemical sensors. As a sensor element is reduced in size to molecular dimensions, it becomes possible to detect even a single analyte molecule. Chemical engineer Michael Strano, for example, has pioneered the use of carbon nanotubes to create nanochannels that only permit the passage of ions with a positive charge, enabling the observation of individual ions dissolved in water at room temperature. Such nanochannels could detect very low levels of impurities such as arsenic in drinking water, since individual ions can be identified by the time that it takes to pass through the nanochannel. Strano has also used carbon nanotubes wrapped in a polymer that is sensitive to glucose concentrations to develop a prototype glucose sensor, in which the nanotubes fluoresce in a quantitative way when exposed to near-infrared light. Such a sensor could be adapted into a tattoo “ink” that could be injected into the skin of suffers of Type 1 diabetes to enable rapid blood glucose level readings without the need to prick the skin and draw blood.

Chemical engineer Matteo Pasquali and his colleagues have found a way to process carbon nanotubes to produce high-strength fibers that are electrically conductive; such fibers could greatly reduce the weight of airplane panels, for example, and could be used as lightweight electrical conductors for data transmission (USB cables) as well as for long-distance power delivery. Pasquali's process is similar to that used for the production of high-strength aramid (e.g., KevlarTM and TwaronTM) fibers, which are used in applications such as protective armor but which are nonconductive. He showed that the carbon nanotubes are soluble in strong acids, where the stiff rodlike molecules self-assemble into an aligned nematic liquid crystalline fluid phase. Nematic liquid crystals flow easily and can be spun into continuous fibers with a high degree of molecular orientation in the axial direction, which imparts the high strength, modulus, and conductivity, then solidified by removing the acid. Pasquali and his team have partnered with a major fiber manufacturer to improve and commercialize the spinning process.

Few commercial applications of nanotechnology have been implemented at the time of writing this text. One of the most prominent is the invention and commercialization of the Nano-CareTM process by chemical engineer David Soane, in which cotton fibers are wet with an aqueous suspension of carbon nanowhiskers that are between 1 and 10 nm in length. Upon heating, the water evaporates and the nanowhiskers bond permanently to the cotton fibers. The resulting fibers are highly stain resistant, causing liquids to bead up instead of spreading. The technology is now in widespread use, as are similar technologies developed by Soane for other applications.



Michael Strano



Matteo Pasquale



David Soane

1.3.6 Polymeric Materials

As we noted in Section 1.2, chemical engineers play a significant role in the synthetic polymer industry, both with regard to the development of new materials and their processing to make manufactured objects. Gore-TexTM film, which was invented by chemical engineer Robert Gore, is a porous film made from