



ANGELO J. PERNA

of the
New Jersey
Institute of Technology



Computation of Multiple Reaction Equilibria . . .

MYERS

An Introduction to Equilibrium Thermodynamics . . .

WILLIAMS, GLASSER

Developing a Course in Chemical Engineering Ethics WATTERS, ZOELLER

A Course in Immobilized Enzyme and Cell Technology LEE

Principles of Stagewise Separation Process Calculations CRITTENDEN

Undergraduate Education: Where Do We Go From Here? GRISKEY

Crystallization: An Interesting Experience in the ChE Laboratory

GRABER, TABOADA

A Second-Year Undergraduate Course in Applied Differential Equations

FAHIDY

Removal of Chlorine From the Chlorine-Nitrogen Mixture in a Film of Water . . .

SANDHU

Purdue-Industry Computer Simulation Modules

SQUIRES, REKLAITIS, YEH, MOSEY, KARIMI, ANDERSEN

. . . . and ChE at

UCLA

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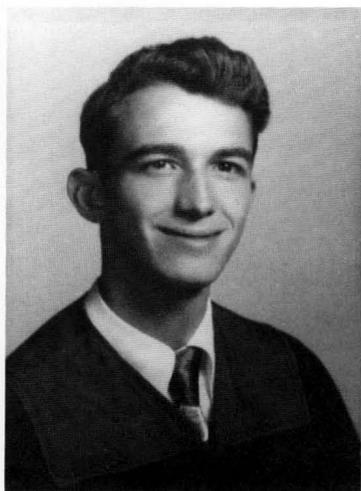
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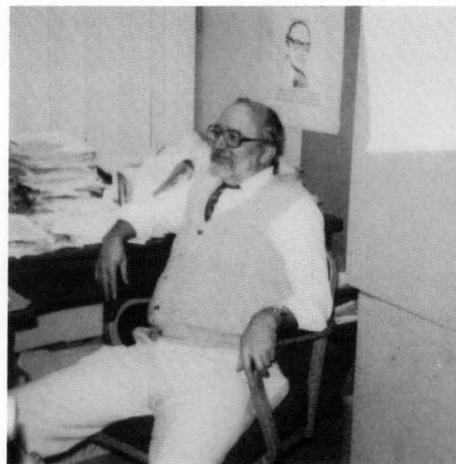
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ANGELO J. PERNA

*of the
New Jersey
Institute of
Technology*



↑ *First . . . the student (1950) — and then . . . the teacher (1991)* →

DERAN HANESIAN

*New Jersey Institute of Technology
Newark, NJ 07102*

Angelo J. Perna (or Angie, as he is more familiarly known to friends and colleagues) was born in Brooklyn, New York, in 1931, to Vito and Marie Perna, who had immigrated to the United States from Italy. He was the fourth child in a family of eight children.

Although Angie's early years paralleled the great depression in the United States, the Perna family was never unduly affected since Vito was self-employed and was able to continuously provide for his family. Education was always highly stressed in the Perna household, and the children were encouraged to help one another to excel in academics.

Angie enjoyed, and was accomplished in, both academics and sandlot sports as he was growing up. He participated in baseball and football activities and was on several championship teams in each sport. He says that he always knew he would eventually go to college and become a teacher, but during his early years he was undecided whether to pursue engineering or history as a career—although he enjoyed chemistry and mathematics, it was in history that he received early academic recognition.

When Angie was a junior in high school his father passed away after a long bout with cancer. The

lengthy siege of illness had created such a serious financial drain on the family resources that when Angie graduated from high school the following year, he had to postpone his plans for college and join the workforce instead. He worked first for the Motion Picture Association of America and later in the garment industry before being drafted into the United States Army in January of 1952.

Angie was sent to Camp Breckenridge, Kentucky, for basic training before being sent to Korea in June of 1952, where he served with Company K of the 279 RCT attached to the 45th Division until August of 1953. While in Korea he rose to the rank of staff sergeant and earned several battle stars and the Combat Infantryman's Badge.

Angie was honorably discharged in November of 1953 and through the GI assistance program he was finally able to begin his postponed college education. It is interesting to hear how he made the decision to attend Clemson and take up chemical engineering:

When I got out of the service I felt I could not go to a school in the immediate area and live at home. I really wanted to go to Brooklyn Poly, but since all of my friends were now working, I knew I would be socializing with them, and I could never have undertaken a course of study while continuing to intermingle with my friends; therefore, the school I attended had to be one which was far enough away so that I had to live

there instead of at home. In addition, it had to be inexpensive enough so that my savings and my GI support could see me through the studies. Insofar as to why I chose chemical engineering—this was simple. I happened to read an article in the New York Times which gave a salary survey for all engineers, and chemical engineers were paid the most. This fact appealed to me, and since I had done fairly well in chemistry, my field of study was now fixed. As for Clemson, a cousin of mine had gone there prior to the second world war and a high school classmate of mine was currently attending—and both of them were enthusiastic about the place. So I thought, "Why not?" In addition, I remembered they had a pretty good football team (even in those days). I saw in the college catalog that they offered chemical engineering and that it was fairly inexpensive, so I applied for admission, and I was accepted. I entered the school in January of 1954. These decisions were the most fortuitous ones I have ever made, and I have been thankful to the fates ever since. I found a school I respect, a profession I love, and I met not only a great group of classmates, but also Dr. Charles E. Littlejohn.

Dr. Littlejohn was a dedicated teacher who instilled a sense of pride and professionalism in his students, and he had a marked effect on Angie's life. Even in the face of all of Angie's eventual technical accomplishments in teaching and research, it is the area of service to his colleagues and his profession in which he places the greatest value. He credits Charley Littlejohn with instilling in him a sense of responsibility toward both his chosen field of endeavor and its related professional organizations.

After graduation from Clemson, Angie joined Union Carbide where he worked at the Y-12 plant in Oak Ridge, Tennessee. While there he worked as a production engineer, as a research-development engineer, and finally as a production scheduler. He found himself working on innovative powdered metallurgy techniques and isostatic pressing—interesting work, but classified since it dealt with thermo-nuclear weapons.

After more than three years at Union Carbide he decided to return to school to work on his Master's degree and to continue with his plan to enter the teaching profession, so in September of 1960 he returned to Clemson and became a member of the initial graduate class in chemical engineering.

During this period of time Angie became interested in the environmental area through his inter-

action with George Meenahan, a professor in chemical engineering, and Gene Rich, chairman of the civil engineering department and author of *Unit Operations of Sanitary Engineering*. Angie helped Dr. Rich by reviewing his book and (together with a classmate, Bill Huffman) by solving the text problems. This period of time had a great influence on his strong belief that chemical engineers are ideally suited by their training to be a force in solving the challenges that the environment presents. It was

Even in the face of all of Angie's eventual technical accomplishments in teaching and research, it is the area of service to his colleagues and his profession in which he places the greatest value.

during this time that Angie also began his association with the unit operations laboratory when, as a graduate assistant, he was given the responsibility for the lab.

After obtaining his Master's in 1962, he went to VPI to teach metallurgy for a year before going on to the University of Connecticut for his PhD degree. His classmates at UConn were an unusual group since, like Angie himself, all of them had been out of college for a period of time prior to returning to college to pursue advanced degrees, and all of them eventually went into teaching. The group consisted of Herb Klei and Mike Howard of UConn, George Knepple of William Patterson, and Pat Marino.

While at UConn, Angie was an instructor in chemical engineering and taught the unit operations laboratory. He did his research under Dr. L.F. Stutzman in the area of distillation dynamics and control.

After receiving his PhD, Angie joined the Department of Chemical Engineering and Chemistry at Newark College of Engineering in Newark, New Jersey, and he and I began what was to be a long cooperative effort. In the late 1960s we worked together on a five-story unit operations lab and a separate process dynamics and control lab, and in addition to designing about thirty experiments, we successfully wrote proposals and received funding from NSF, the State of New Jersey, and the industrial sector, amounting to approximately one-half million dollars. We developed a new teaching format that included a six-hour once-a-week lab with three different types of lab reports and oral student presen-

Continued on page 86

ChE at **UCLA**

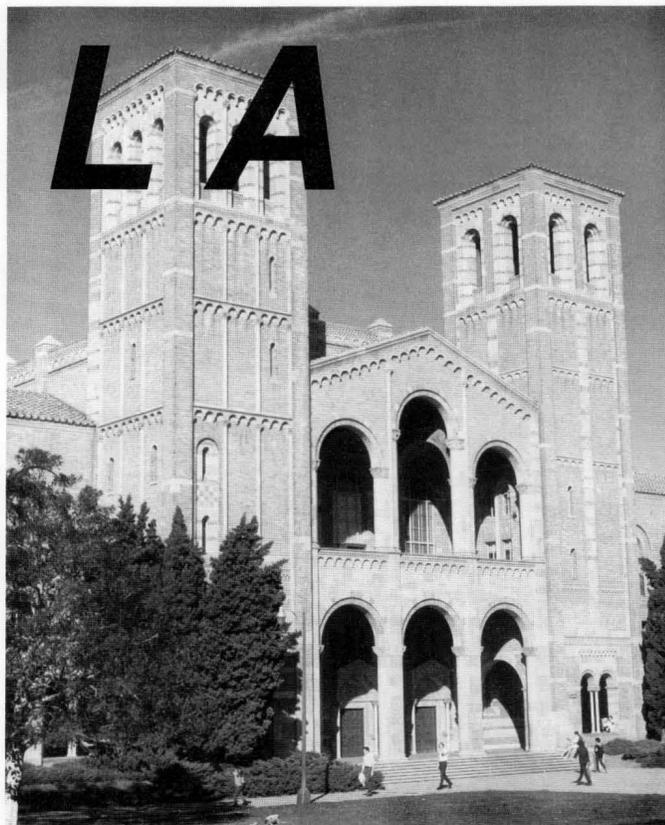
D.T. ALLEN, S.M. SENKAN
 University of California
 Los Angeles, CA 90024

The University of California at Los Angeles, founded in 1929, is located in rolling green hills just five miles from the ocean, in one of the most attractive areas of Southern California. It is bordered on the north by the residential community of Bel-Air and the Santa Monica mountains. Its southern boundary is Westwood Village, which serves as a shopping and entertainment center for Los Angeles. The attractive campus on 419 acres is the home of about 2000 faculty and 35,000 students.

The UCLA Department of Chemical Engineering is part of the School of Engineering and Applied Science, which was originally established as the College of Engineering in 1944. The school has grown steadily in stature and reputation and now ranks among the top ten schools of engineering nationwide and is among the top five schools of engineering at public universities. Chemical engineering is a relatively young department, officially established in 1983 and accredited by ABET shortly thereafter. Prior to 1983 the department was part of a unified undergraduate engineering program.

Since its establishment and accreditation in 1983, the department has undergone steady growth in stature and reputation. At present the department offers BS, MS, and PhD degrees in chemical engineering, and the current total enrollment is about 150 undergraduate and 50 full-time graduate students. The department offices and most of the research laboratories are housed in Boelter Hall, which is currently undergoing a major renovation that will double the available floor space.

At present the department offers BS, MS, and PhD degrees in chemical engineering, and the current total enrollment is about 150 undergraduate and 50 full-time graduate students. . . . the annual research budget is over 2 million dollars



Royce Hall, one of the four buildings that made up the original UCLA campus in Westwood

The number of faculty has also increased steadily, to a current level of twelve. This has led to a spectacular increase in graduate research activity; at present the annual research budget of the department is over 2 million dollars, placing it in the top fifteen in the nation in federal research funding. These funds support our fifty graduate students, numerous undergraduate research assistants, and post-doctoral research associates. The department typically admits about fifteen new graduate students each year, including both domestic and international scholars.

THE FACULTY AND THEIR RESEARCH

The design of clean, environmentally compatible technologies is a key challenge facing modern industry and the profession. The UCLA chemical engineering department is playing a leading international role in developing the research and design fundamentals needed for a rational approach. The department presently houses two highly-visible na-

tional research centers: the National Center for Intermedia Transport (sponsored by the US Environmental Protection Agency since 1981), directed by Yoram Cohen, and the National Science Foundation Engineering Research Center for Hazardous Substances Control (established in 1987), directed by Sheldon Friedlander. Although many of our faculty members participate in the activities of these centers, the research conducted in the department is diverse, as can be seen in the following paragraphs and in the Table 1 summary.

Reaction Engineering

Reaction engineering and kinetics is one of the major research areas in the department. The research programs undertaken by Professors Allen, Hicks, and Senkan seek a better understanding of the mechanisms of homogeneous and heterogeneous reactions at the molecular level. **David Allen's** research emphasizes the application reaction engineering principles to energy and environmental issues. His current interests include the molecular modeling of petroleum processing (particularly catalytic cracking) as well as gas-to-particle reaction pathways in urban atmospheres, and development of catalytic hydrodechlorination processes. In his research, **Robert Hicks** studies the catalytic oxidation of hydrocarbons using Pt and Pd as catalysts, with the objective of developing more efficient automobile catalytic converters that will lead to reduced pollutant emissions at cold-start conditions. **Selim Senkan's** research in reaction engineering is directed toward the development of detailed chemical kinetic mechanisms (DCKM) describing high-temperature processes such as hydrocarbon pyrolysis, oxidation, and combustion. DCKMs developed by Professor Senkan involve the participation of hundreds of species in thousands of elementary reac-

tions, and rely on the use of large-scale computing. The data needed in the development of DCKMs are derived from experiments conducted jointly with physical chemists and theoretically via the use of computational quantum mechanics.

Materials Processing

The research of **Yoram Cohen** involves the development of novel materials and resins using polymer adsorption, polymer grafting, and surface silylation processes. **Traugott Frederking's** research in thermodynamics and transport phenomena at low temperatures (*i.e.*, cryogenics) is paving the way for the development and better utilization of superconductors. **Sheldon Friedlander** is investigating the development of new technologies involving ultrafine particles, including the design of aerosol reactors and the engineering of submicron agglomerate structures composed of multicomponent aerosols. The deposition of semiconductor and metal thin films for microelectronic devices using organometallic chemical vapor deposition is an expanding area of research of **Robert Hicks**.

Combustion

At present, combustion and combustion-related activities are underway in the departments of chemical engineering, mechanical engineering, and chemistry. **Eldon Knuth** developed one of the first Molecular Beam Mass Spectrometer systems in the world to study flame structure. He is currently exploring relaxation processes in molecular beams and cluster formation in low-temperature freejets. **Selim Senkan** is investigating the effects of halogens in hydrocarbon combustion, and in particular their role in the formation of toxic combustion by-products. His research has important applications to hazardous waste incineration. In addition, his research empha-



*Students can enjoy swimming, skiing, and mountain climbing...
on the same day!*

sizes the use of combustion as a manufacturing process to synthesize useful chemicals from abundant natural resources by partial oxidation. **Owen Smith's** research in combustion emphasizes the development of non-intrusive optical diagnostics, such as particle image velocimetry and laser induced fluorescence. He recently developed a two-dimensional resonantly-stabilized dump combustor which promises to be particularly useful in waste incineration.

Transport Phenomena

Yoram Cohen and **Sheldon Friedlander** study the transport of pollutants in air, water, soil, and other environmental media, particularly through the National Center for Intermedia Transport. These studies are not confined merely to dispersion within single environmental media; rather, they focus on processes occurring at interfaces (particularly air-soil and air-water interfaces) and the incorporation of these intermedia transport processes into multimedia studies of pollutant impact on the environment. The application of transport phenomena at cryogenic temperatures is the specialty of **Traugott Freder-**

king. He is currently working on screen and perforated-plate compact cryocooler systems at liquid-helium temperatures, with the objective of developing a basic understanding of thermal boundary layer conditions at superconductor-liquid interfaces.

Electrochemistry

Fundamental and applied electrochemistry is the major research thrust of **Ken Nobe**. Typical industrial applications that are addressed in his laboratory include reduction of corrosion rates in marine environments, reduction of hydrogen embrittlement of high-strength steels, and improvement of the efficiency of electrochemical manufacturing operations like the electrodeposition of specialized metals like Invar. Along with the late Manuel Baizer, Professor Nobe and his group have also pioneered paired electroorganic syntheses in flow reactors. In a collaborative activity, **Vincent Vilker** and Nobe are exploring electroenzymology as a method for the synthesis of fine chemicals and for the development of biosensors.

TABLE 1
Chemical Engineering Faculty and Research Interests at UCLA

DAVID T. ALLEN

Environmental Reaction Engineering

Atmospheric Aerosol Chemistry • Processing of Heavy Fuels and Hazardous Waste • Molecular Models of Catalytic Cracking Chemistry

YORAM COHEN

Polymer Science and Transport Phenomena

Polymerization Reaction Engineering • Brownian Dynamics of Macromolecules • Polymer Grafting and Adsorption • Non-Newtonian Fluid Mechanics • Water Purification • Multimedia Transport of Toxic Chemicals and Exposure Analysis

TRAUGOTT H. K. FREDERKING

Cryogenics

Low Temperature Transport in Porous Media, Phase Separation, Thermo-mechanical Devices • Heat Transfer • Cryocooler Components, Super-conducting Devices and Related Transport Phenomena

SHELDON K. FRIEDLANDER

Aerosol Technology and Air Pollution

Formation and Behavior of Submicron Particles • Source Allocation and Receptor Modeling • Air Pollution Control • Mass Transfer and Diffusion • Particle/Surface Interactions

ROBERT F. HICKS

Surface and Interface Engineering

Catalysis • Reaction Engineering of Organometallic Vapor Deposition

ELDON L. KNUTH

Molecular Dynamics in Gas Flow

Vibrational, Rotational, Translational Relaxations • Condensation and Evaporation • Chemical Relaxations

VASILIOS MANOUSIOUTHAKIS

Process Design, Dynamics and Control

Linear and Nonlinear Control Systems Design • Integration of Design and Control • Process and Control Systems Design for Microelectronic Material Manufacturing • Waste Minimization Through Chemical Process Synthesis • Separation Network Synthesis

HAROLD G. MONBOUQUETTE

Biochemical Engineering

Biomimetic Membrane Systems • Culture of Microbes that Thrive at Extremes of Temperature, pH, and Salt Concentration • Biosystems for Heavy Metal Recovery • Immobilized-Cell Fermentations

KEN NOBE

Electrochemistry

Catalysis • Battery and Fuel Cells • Corrosion and Electrodeposition of Metals and Semiconductors • Bioelectrochemistry

SELIM M. SENKAN

High-Temperature Chemical Kinetics and Reaction Eng.

Combustion, Gas Kinetics, Flame Chemistry • Incineration of Hazardous Materials • Computational Quantum Mechanics • Synthesis of Useful Chemicals by Combustion

OWEN I. SMITH

Combustion

High-Temperature Chemical Kinetics • Reaction Mechanisms in Combustion, Incineration and Chemical Vapor Deposition • Optical Methods for Combustion Diagnostics

VINCENT L. VILKER

Biochemical Engineering

Colloid and Interfacial Phenomena • Proteins, Virus, and Bacteria • Bioelectrochemical Catalysis

Biochemical Engineering

Professors Monbouquette and Vilker form the chemical engineering component of a strong collaborative research program in biochemical engineering. Collaborating with faculty in pharmacology, biological chemistry, molecular biology, microbiology, public health, and civil engineering, they are working on problems related to the cleanup of groundwater contamination, chemical synthesis, and chemical sensors via the use of modern biochemical methods. **Vincent Vilker's** research is focused on biocatalysis of bacterial redox enzymes. He is developing processes to detoxify trace contaminants in water, to synthesize oxygenated hydrocarbons and fuel additives and is undertaking research to optimize the production of enzyme system proteins in natural or cloned host bacteria. **Harold Monbouquette** is pioneering the use of archaeobacteria (*i.e.*, bacteria that thrive under extreme conditions, such as temperatures in excess of 100 C and pH levels below 1 and above 10) to synthesize highly stable enzymes for use in the treatment of toxic wastes and for the synthesis of new biomaterials.

Process Design and Control

The design and control of chemical processes for minimal environmental impact is an underlying theme in much of **Vasilios Manousiouthakis'** work. He has developed the concept of mass-exchange networks, which is extremely important in chemical process industries. He has also developed approaches for estimating the waste minimization potential of chemical processes. His research in process control involves studies on the dynamic behavior and control of generalized linear and non-linear systems using algebra, topology, functional analysis, differential geometry, and optimization.

Separations

The overall goal of the separations program, guided by **Yoram Cohen** and **Harold Monbouquette**, is the development of novel separations processes, including highly selective membranes and sorbent media, through chemical tailoring of the phase interface. Current projects include the construction and study of new polymer-silica resins for selective sorption of organics and heavy metals and biomimetic membranes for metal recovery. They have recently initiated a collaborative project involving the creation and testing of novel ceramic-supported polymer membranes for applications in pervaporation and hyperfiltration.

As is evident from the foregoing discussion, research activities undertaken by chemical engineering faculty at UCLA span studies from the molecular level (characterized by length scales on the order of Angstroms) to the design and control of large-scale systems (characterized by length scales on the order of meters to kilometers). As indicated, many of the studies deal with environmental issues. An important outgrowth of these coupled activities is that the students not only receive training in the funda-

mentals and applications of science and technology, but they are also sensitized to the needs of society at a time when crucial questions are being asked on how to grow and innovate in an era of economic, environmental, and energy constraints.

The environmental theme in the department's research has also had a significant impact on undergraduate education. Specialized courses in pollution control technology, mass transfer of pollutants in the ambient environment, and combustion, energy, and the environment have been developed or are in the planning stages. An undergraduate course on toxic substances control (designed for non-engineers) has also been created.

In addition to the development of specialized courses, the department has focused on incorporating environmental issues into all parts of the curriculum. Examples include design of a waste-to-energy incinerator in the capstone design course and the development of chemical reactors with minimal by-product formation in the chemical reaction engineering course.

The department also offers a variety of additional specialty courses, reflecting the breadth of the research activities of the faculty. These courses are complemented by hundreds of science and engineering courses offered in other departments. Exposure to world-class researchers in chemistry, molecular biology, atmospheric sciences, and other disciplines provides exciting opportunities for the intellectual growth of our students.

LIFE IN SOUTHERN CALIFORNIA

The faculty and students of UCLA enjoy a wealth of cultural and recreational opportunities, both on campus and in greater Los Angeles. Mountain climbing and skiing, as well as surfing and sailing centers, are all easily accessible from campus and are available virtually at any time of the year. World renowned artists in dance, music, and the arts regularly perform both on campus and at the nearby Los Angeles Music Center. And of course, there is Hollywood, Universal Studios, Disneyland . . .

As LA has become one of the leading metropolitan areas on the Pacific Rim, the city has become a melting pot of many cultures. Los Angeles has a Chinatown, a Little Tokyo, a Koreatown and many other ethnic communities, together with an outstanding selection of restaurants. These communities offer students a window on the world which is available in few other cities. □

DEVELOPING A COURSE IN CHEMICAL ENGINEERING ETHICS

One Class' Experiences

JAMES C. WATTERS, DOMINIC A. ZOELLER

*University of Louisville
Louisville, KY 40292*

The 1988-89 ABET accreditation guidelines^[1] for engineering programs in the United States state, "An understanding of the **ethical**, social, economic, and safety considerations in engineering practice is essential for a successful engineering career." This tenet obliges engineering programs to incorporate a minimum amount of coursework on engineering ethics into what is already a tightly-packed curriculum.

The manner in which ethics are introduced into the curricula allows for a number of choices. One choice is to incorporate a discussion of ethics into the context of an existing course or courses; another choice is to develop a separate course that deals exclusively with ethical and other closely-related issues. Then the decision must be made as to what level in the curriculum to place the course. Finally, a curriculum must be developed which meets not only the requirements of ABET but also the needs of the students and the instructor.

INTEGRATION VS. STAND-ALONE APPROACH

The pros and cons of integrating "new" material into existing courses versus devising a stand-alone course to present the material, have long been debated. In recent years, with the emphasis on incorporating developing technologies into our curricula, there have been many champions of the integration approach. Integration has the obvious advantage of not adding any extra credits or courses to an already demanding courseload. However, we believe that for

A stand-alone course in ethics has advantages — an instructor . . . can be given free rein to develop the curriculum without being confined by the boundaries of a traditional theory or practice course.

James C. Watters is an associate professor of chemical engineering at the University of Louisville, and is currently the Acting Department Chair. He received his BE in chemical engineering from the National University of Ireland, University College (Dublin, Ireland) and his MS and PhD degrees from the University of Maryland. His research interests are in novel separation processes, membranes, polymer synthesis, and methods of teaching and learning.



Dominic A. Zoeller (photo unavailable) received the Master of Engineering degree in chemical engineering from the University of Louisville in 1989. He is currently a production engineer in the specialty monomers plant of the Dow Chemical Company in Midland, Michigan.

the integration approach to work, the topic must be included in more than one existing course and thus would probably be taught by more than one faculty member. It has been our experience (in several engineering disciplines) that many engineering faculty members are uncomfortable with the area of ethics as a subject to be included in their existing technical courses. This discomfort may stem from their own lack of knowledge or fear of ethical issues, or their disdain for "diluting" the traditional courses with "soft" topics. In any event, while the integration approach may look like a good idea at first blush, we contend that it is difficult to carry out in practice. As a result of such deliberations, at Louisville we instituted a two-credit course devoted to "Ethical Issues in Chemical Engineering."

A stand-alone course in ethics has advantages. From a teaching perspective, an instructor with a genuine interest in the topic can be given free rein to develop the curriculum without being confined by the boundaries of a traditional theory or practice course. Also, the student in such a course can dwell on the course topics without worrying that the "non-technical" issues are taking time from the

seemingly "more important" technical topics of an integrated course.

A disadvantage of the stand-alone course may be the inability of students to integrate ethical issues into technical coursework areas. Both students and educators tend to neatly segment learning into separate courses, with almost sacrosanct boundaries that are not to be crossed. However, this problem can be overcome by judicious placement of the course into the curriculum.

WHEN TO TEACH

Once we had decided to introduce a separate course in ethics, the next hurdle was to decide where it belonged in the curriculum. Should it be early (for example in the sophomore year), before the student has been exposed to many of the technical areas of the profession and is still "fresh" or "naive"? Or, should it be later (perhaps in the senior year) when the more knowledgeable and, presumably, more mature and "street-wise" student can better synthesize his or her experiences in the profession to decision-making?

The University of Louisville is unique among chemical engineering programs in the United States in that our accredited degree is the Master of Engineering, a five-year program with mandatory cooperative internship training. We included the "Ethical Issues in Chemical Engineering" course in the final semester of the fifth year, although it could easily fit into the final semester of the fourth year in a school with a more traditional program. We considered it most beneficial to approach ethical issues from the more mature viewpoint of a fourth- or fifth-

year student. This was particularly helpful for our students since they had all had co-op internships. Many had already experienced or witnessed the grey areas of real-world situations. In fact, many of them identified with some of the classic case studies we discussed and volunteered that they had experienced similar quandries in their internships.

We elected to offer a two-credit course, meeting once a week for one hour and forty-five minutes. This framework ensured that students would take the course seriously (since two credits were at stake), and it allowed for the inclusion of class exercises and films that would be difficult to use in a standard, fifty-minute, time slot. The course was taught by one of the authors (JCW), an Associate Professor in the chemical engineering department who has an interest in, and commitment to, teaching professional responsibility. The pros and cons of using engineering faculty to teach ethics have been debated,^[2,3] but in our case, financial considerations dictated that it be taught by one of our own faculty.

CONTENT AND FORMAT

The course, first taught in the spring of 1988, originally took a philosophical and historical perspective on ethics, an approach that the present author was uncomfortable with. He elected instead to use a case-study approach that was loosely based on a now discontinued, cross-disciplinary course called "Technology and Society" with which he had been involved in the early 1980s.^[4]

Table 1 lists the content of "Ethical Issues in Chemical Engineering" as presented in the spring of 1989. Class format included lectures, discussions,

TABLE 1
Course Outline: Ethics and Values in Engineering

The course will examine the foundations of our value systems and how these relate to our decisions as engineers. In this context we will examine codes of ethics as proposed by the various engineering societies, classic ethics case studies from the literature, whistle-blowing and beyond, and our rights and responsibilities as professionals. The format will include lectures, videotapes, discussions, and presentations by class members. Grading will be based on successfully completing assigned homework and on participation in class discussion.

SCHEDULE

- Introduction
- Why engineers should be concerned with ethics
- Film: *What You are Now is What You Were When*

- Class discussion: Origin of our value systems
- Class exercise: Where do you draw the line?
- Codes of ethics: Advantages and drawbacks
- Ethics case studies: UTexas film and discussion
- Ethics case studies: Discussion of assigned problems
- Ethics—The Law: Professional societies
- Classic ethics cases: Student presentations
- Classic ethics cases: Student presentations
- Film: "Do Scientists Cheat?" (NOVA)
- Whistle-blowing: What, When, How
- Films: "Enemy of the People" (60 Minutes)
- "Pomeroy File" (60 Minutes)
- Whistle-blowing: Support, discussion
- Responsibility: Film, *Toxic Trials*
- Summary and Conclusions -

Integration has the obvious advantage of not adding any extra credits or courses to an already demanding course load. However, we believe that for the integration approach to work, the topic must be included in more than one existing course and thus would probably be taught by more than one faculty member.

videotapes, and presentations by students. Class materials included texts, films, and experiential exercises. Appendix A presents a brief annotated bibliography of the materials used and referenced during the semester. Topics addressed included the foundation of our individual value systems, codes of ethics and their limitations, whistle-blowing and its consequences, and the whole concept of responsibility for one's actions. Grades were based on weekly homework assignments, participation in classroom discussions, and presentations of assigned materials. No examinations were given—the authors firmly believe that a topic such as ethics is best taught and best received by students in a non-threatening, semi-informal format.

The first weeks of the course are devoted to an examination of what each student believes on ethical and moral issues, where those beliefs came from, and why such issues should be of concern. The film *What You are Now is What You Were When* presents a perspective that relates one's moral philosophy to the major features of one's early upbringing. Students are encouraged to apply this model to people they know, such as parents, teachers, ministers, politicians, *etc.*, and to discuss how applicable it is to their own lives.

The next segment of the course deals with professionalism and the concept of ethics codes. Many codes, such as those of AIChE, IEEE, and NSPE, are examined for thoroughness, applicability, *etc.* Students quickly learn that some codes (such as AIChE's) are very vague, while others (such as NSPE's) are much more detailed. Yet even the detailed ones do not come close to addressing every situation and, in fact, some of the tenets are potentially contradictory. The student who is looking for a "quick fix" in the codes soon realizes that absolution of personal decision-making is rarely to be found.

The concept of taking responsibility for one's own actions also starts to develop at this point in the course. Students are asked to discuss the case studies presented by Kohn,^[5] with particular reference to the ethics codes, and they quickly realize that even some of the seemingly simpler situations involving ethical decision-making lack easy black-and-white answers. When the student responses are

compared with those of employed engineers (tabulated by Hughson and Kohn^[6]) the diverse opinions are readily apparent. The comparison also allowed us to see how opinions have changed over a period of ten years.

The culmination of this segment of the course was a discussion, based on Unger,^[7] of the interfaces between ethics and the law, and between ethics and professional societies. Students are struck by the widely different levels of support afforded by the various professional societies for engineers with ethical dilemmas.

The last segment of the course deals with whistle-blowing and its consequences. This topic actually weaves a thread through the whole course, since many of the case studies evolved from someone "blowing a whistle" or from someone having been the victim of such action. The excellent NOVA film, "Do Scientists Cheat?" demonstrates the consequences of not blowing a whistle as well as what happens when one does. The two *60 Minutes* segments, "Enemy of the People" and "The Pomeroy File," outline the histories of a whistle-blower and of one who "dared" to speak out in public on a controversial issue.

Each week students had to carry out a homework assignment that consisted primarily of discussion questions, many culled from *Ethics in Engineering*^[8]. Around mid-semester, the students (working in pairs) developed an in-depth study of a major ethics case. Topics included Bhopal, the Challenger, BART, the Corvair, the Pinto gas tank, Hooker Chemicals, *etc.* In addition to a written report, the teams presented their findings orally, either formally or in a role-playing format.

OBSERVATIONS OF A STUDENT (DAZ)

As a fifth-year student in engineering, I felt a great deal of apprehension in attending my first ethics class. It seemed strange that after spending five years honing my skills in making cold, calculating, right-or-wrong decisions, the administration now felt it necessary to train me in ethics. Unfortunately, this attitude was shared by most of my classmates. However, I found that several aspects of the course

enabled me to take the concepts and theories beyond the walls of the classroom.

The first tool was the textbook,^[7] which was clear-cut and easy to read. In some cases, the author admitted that there were no right answers, even with the aid of hindsight. This was refreshing. By using current and semi-current examples from the engineering field, the author was able to keep the interest of the reader. In many cases the incidents presented were already common knowledge, while other events had taken place prior to our collective memory. It was interesting to compare class reactions to these two different stimuli. In the first case, the class usually had preconceived notions about the case, but when the incident was unfamiliar they were at the mercy of the materials presented for making their conclusions. In most cases the class easily formed a consensus on ethical issues.

The second tool for generating interest in the class was the syllabus. Dr. Watters recognized that it would be impossible to alter the psychological constitution of the students and sought instead to raise our level of consciousness in the area of ethical questions. By working through several scenarios, reading the text and several handouts, watching some video presentations on ethical issues, and holding candid discussions, he hoped we might recognize our position in the ethical loop.

The effect of this candid approach to what could have been a boring do-the-right-thing course was profound. We began to view the class as a lively forum rather than a waste of time. As we prepared for each class through the reading assignments and our weekly reports, we were intrigued by the questions we could not answer. We explored the difficulty of enforcing a uniform code of ethics in a predominantly free-will society. We discovered the moral dilemma of self-preservation versus doing what is right, and we discussed legislative efforts to mandate morals. We discovered that being ostracized by your peers and associates is often the penalty of being ethical.

Dr. Watters realized that such a class does not lend itself to the general form of the engineering curriculum and that he could not simply spout platitudes to the class. Instead he allowed us to "discover" the ethical questions of which we were ignorant.

There was also an investigative assignment for the class to carry out. Transcripts of several ethical incidents were distributed to the class and were to

be researched by teams of two. The students were required to research their individual case and present to the class the ethical issues involved, the mistakes that were made, where the blame lay, and, if possible, where the players are now.

The selection of cases consisted of three major types. First was the historical case. The incident was usually common knowledge to all participants, the data were available from simple research, and a

We explored the difficulty of enforcing a uniform code of ethics in a predominantly free-will society. We discovered the moral dilemma of self-preservation versus doing what is right, and we discussed legislative efforts to mandate morals.

conclusion had in most cases been made. For such a case, the students were able to perform all of the tasks of the investigation unless some of the information had been lost in history.

The second form was a historical case which was not common knowledge. Like the previous example, there is a great deal of information available and a conclusion has probably been made. However, their lack of familiarity with the incident allows the students to arrive at their own conclusions. Care must be taken, however, that the students do not simply write a book report, but rather that they seek out sources for several viewpoints.

The third type of case was the current event, and it was the most difficult to research. Since ethics, or the lack thereof, is a popular subject in the press, there are usually several general examples from which to select. However, it may be difficult to get enough information to make legitimate decisions since in many cases the incidents are still under investigation. When that is the case, the scenario may better serve the class as a source of impromptu discussion.

From my perspective as a student, there are several effective ways to spark interest:

- Emphasize participation over a letter grade
- Promote open-ended discussions
- Moderate discussion in an unoffensive manner
- Use reading and AV materials as a starting point for dialogue, not as an end unto itself
- Keep all of the students involved in the discussions
- Use interactive exercises where possible
- Allow time for dialogue
- Instructors should be open-minded about students' opinions and, if need be, avoid subjects on which they have a strong personal bias

Some important concepts taken from the class

include the following:

- Personal convictions dictate the level of an individual's ethics.
- IEEE is a model for a professional organization's support of its members on ethical issues.
- Persistent and tactful communication is the most powerful weapon available to the subordinate engineer for the prevention of serious ethical blunders.
- In many cases ethical dilemmas are "lose-lose" situations: to be a whistle-blower can result in firing and/or blackballing, but allowing an unethical practice to persist poses personal problems as well as leads to the possibility of being fired, blackballed, or imprisoned.
- The most common and most difficult dilemma is faced when one must choose between survival and "doing the right thing."

MUSINGS OF AN INSTRUCTOR (JCW)

When I first volunteered to teach the ethics course I experienced some feelings of trepidation. After all, how was I going to have any impact on the ideas and ideals of a group of young adults, in their early- to mid-twenties, who had known me for several years socially as well as in the classroom? However, this uncertainty actually led me to the approach I took. Because we knew each other, I felt we could be honest with each other and refrain from judging each other by each other's opinions. We could be critical of those opinions and we could try to change or influence them, but we would not judge a classmate simply by his or her opinion on some topic. This approach led to some initial reticence, but everyone soon became comfortable with talking in our group, and some excellent discussions resulted.

A feature which aided the give-and-take of our discussions was the removal of the pressures of an examination. Class goals, objectives, and requirements were clearly spelled out from the beginning, and the students knew what they had to do to "make the grade." They came to look upon the ethics class not only as a break from the normal routine of theory and research, but also as something which would be important in their future.

Just how topical and current an ethics course can be was illustrated by an incident which happened during the course of the semester—the vessel, *Exxon Valdez*, hit a reef in Alaska. For several weeks the class followed this developing story, and we discussed the ethics of supertankers, drunk-driving piloting, complacency on safety issues, progress versus the environment, the rising price of gas at the pumps, etc. It was invaluable as a learning experience, it reinforced theory, and it illustrated that a well-designed ethics course should be flexible enough

to capitalize on current events.

Overall, the course was well received by the students. The discussions were lively and the effort they put into the assigned projects was excellent. To involve all the students in the discussion, class size should be small (preferably less than twenty students). This type of course requires that students be treated as adults, and students thus treated will generally respond favorably. The result is a satisfying and fulfilling experience for all concerned.

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APPENDIX

ANNOTATED BIBLIOGRAPHY

The following is a list of materials (books, films, articles, etc.) used or usable in an ethics course. It is by no means complete. The opinions expressed are those of the senior author (JCW) and are intended to aid an instructor formulating a new course in ethics.

• Books

Unger, Stephen H., *Controlling Technology: Ethics and the Responsible Engineer*, Holt, Rinehart, and Winston, New York (1982)

A concise survey of many aspects of the ethics question, including the codes of ethics, the role of engineering societies, ethics and the law, and how to avoid conflict. The author takes a down-to-earth approach to his topic and the text is liberally laced with case studies which illustrate the theory. The book is biased towards electrical engineering (reflecting the background of the author), so there is heavy emphasis on the IEEE code and EE case studies. The book was generally well received by the students in my class, though the value for money was questioned (\$20 for a 190-page paperback).*

Martin, M.W., and R. Schinzinger, *Ethics in Engineering*, McGraw-Hill, New York, NY (1983, 1989)

This book is subdivided into four sections: The Scope of

Chemical Engineering Education

Engineering Ethics; The Experimental Nature of Engineering; Engineers, Management and Organizations; and Career Choice and Future Issues. The approach is more philosophical in nature than Unger's, especially in the first section. However, the text is generally readable and has a broader scope than Unger's. It contains excellent discussion problems for homework or in-class analysis. There are some problems in the first edition which are omitted from the second, and the second edition includes some recent case studies such as Bhopal and Challenger, along with some new problems.

Flores, A., *Ethical Problems in Engineering, Vol. One: Readings*, Rensselaer Polytechnic Institute, Troy, NY (1980)

This volume consists of a series of essays by several authors on the general topics of professionalism, codes of ethics, competitive practice, employed professionals, and social responsibility. As with any series of papers, this one lacks the continuity of a monograph and the entries sometimes overlap. The resulting text tends to drag and makes very dry reading. However, a short, judiciously-chosen selection could enhance a lecture course.

Baum, R.J., *Ethical Problems in Engineering, 2nd ed., Vol. Two: Case Studies*, Rensselaer Polytechnic Institute, Troy, NY (1980)

This is the companion volume to the book by Flores. It presents analyses of, and essays on, many of the classic ethical cases from about 1960 to 1980. Included are the BART case, the Pinto gas tank, the Corvair, Hooker Chemicals, and many others, some of which are not so well known. They serve as excellent starting points for student research and classroom discussion. Some of the studies are quite brief, while others extend to twenty or more pages.

• Films

"What You are Now is What You Were When"

This film, about ninety minutes long, is a monologue by Dr. R. Massey, formerly of the University of Colorado-Boulder, which examines the origins of our value systems by looking at influences in our past lives, such as family, church, schools, peers, media, etc. His model is then applied to different generations to see how events in their teens and twenties influence their outlook and actions today. Massey is a dynamic presenter who talks "a mile a minute" with a strong Texas twang. Students either love him and find him hilarious, or loathe him and find him nauseous. My version of the film is somewhat dated (1976), but I understand there is a more recent edition available. The film contains some mild profanity, but nothing the students haven't heard in the movies, or indeed in the AIChE room!

"Do Scientists Cheat?" NOVA (1989)

This excellent film examines if and how practitioners of science cheat in presenting research results. The pressures put on young scientists to publish and win grants are cited as major causes for this errant behavior. Some classic and recent cases are examined in detail. The consequences for one scientist who "blew the whistle" on another's falsified data are discussed, leading to the seeming conclusion that neither of them escaped from the situation unscathed. The film makes a good jumping-off point for classroom discussion of whistle-blowing, ethics in academe, falsifying of data, etc. (lasts about one hour).

"Enemy of the People," 60 Minutes

An examination of the case of an employee of Lockheed Georgia who made an issue of cost overruns in government contracts. He was ostracized by his community (a one-company town), his church, and his employer. When he was finally reinstated in the company, it was in a "paper-pushing" position. The issue of whistle blowing as a lose-lose situation is very evident in this film (lasts about twenty minutes).

"The Pomeroy File," 60 Minutes

This film examines the case of a pilot for Continental Airlines who spoke up at a town meeting against a proposed nuclear power plant and later found out that a national security file had been compiled on him, citing him as a subversive. The issues of freedom of speech, national security files on individuals, "subversives," and the use of such files as leverage with an individual's employer, are discussed.

Ethics Case Studies, Chemical Engineering Department, University of Texas. Contact: D.M. Himmelblau

This film features role-playing of five of the cases presented by Kohn (1980), including analysis by a panel of "experts." While the acting leaves something to be desired and the dialogue and roles are highly sexist, it is helpful to see these case studies portrayed as "real life" situations (lasts about thirty minutes, about five to seven minutes per case).

The concept of responsibility within the chemical industries is highlighted in many recent *NOVA* and *Frontline* films. Some examples are "Toxic Trials" (concerning chemicals in the groundwater being linked to above-normal incidences of leukemia in Woburn, Massachusetts), "Who's Killing Calvert City?" (about pollution problems and local politics in Calvert City, Kentucky), and "Nuclear Legacy" (about the nuclear-waste disposal problem). Each film lasts about one hour.

• Simulations / Games

Where Do You Draw the Line? An Ethics Game (Simile II, Del Mar, CA 1977)

Five (or less) groups of participants make ethical judgments about the behavior of people described in a variety of situations. Each group makes decisions about different sets of situations and as the results are tabulated some interesting discussions occur. Once it is made apparent that each group was considering different situations, discussion can be directed towards discovering the assumptions which the groups used to make their judgments and the implications of those assumptions. The issues raised are stealing, income tax evasion, and withholding of information (takes about ninety minutes, including discussion time).

Whistle-blowing Case (Lindauer and Hagerty, 1983)

A young engineer is presented with an ethical dilemma and is forced to make a decision on blowing the whistle on his employer. A cast of ten to twelve characters, representing various interests in the case, provide him/her with support or harassment (takes about one hour to complete, with up to another hour for discussion). □

AN INTRODUCTION TO EQUILIBRIUM THERMODYNAMICS

A Rational Approach to Its Teaching

PART 1: Notation and Mathematics¹

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Traditionally, undergraduate students of thermodynamics have difficulty understanding the subject and its material. While we do not deny that there are conceptual difficulties to overcome, it seems to us that there are two factors in the usual approach that make a student's introduction to thermodynamics more difficult than is necessary.

First, there is the underlying mathematics of the state functions and the notation associated with it. This often seems to suggest that the "state functions" and their mathematics are different from the functions which the student has already met in his previous mathematical education. Second, the way in which the state functions (internal energy, entropy, and temperature) are introduced is not easily related to the students' previous background in physics.

In order to address these two problems, we developed an approach which has now been taught to third-year chemical engineering undergraduates for the last six to seven years. It has been our experience that the students have been able to relate the material to their previous work in mathematics and physics with relative ease, and that they have been able to assimilate the subject without undue difficulty. As a result, the general level of understanding—of both the students and the teachers—has been significantly improved.

Since the approach tackles the two factors mentioned above, which have applicability in quite dif-

¹ Part 2 of this paper, "Internal Energy, Entropy, and Temperature," will appear in the next issue of *CEE*.



Donald Williams has taught at the University of the Witwatersrand since 1967. He has a special interest in teaching chemical engineering to students at the junior end of the curriculum and has recently devised a new course to be taught to first-year students. His interest in improving the teaching of thermodynamics was first aroused while being taught by David Glasser in one of his earliest efforts.

David Glasser is a professor of chemical engineering at the University of the Witwatersrand. He holds degrees from the University of Cape Town and Imperial College (London). His main areas of interest are reaction engineering and mathematical modeling. He has been interested in teaching thermodynamics ever since he first became involved after being "made an offer" as the most-junior member of the academic staff.



ferent areas, it is convenient to divide our presentation into two parts. Part 1 will consider notation and the mathematical development, and Part 2 (which will appear in the next issue of *CEE*) will be concerned with the introduction of the state functions. The notation which we introduce was developed by Harris,^[1,2] and the axiomatic approach adopted in Part 2 is based on Callen,^[3] who suggested this method as long ago as 1960. We find it surprising that Callen's approach has not found more favor with educators. It is the purpose of this paper to show how these ideas can be combined to form a logical and consistent introduction to thermodynamics.

Notation and Mathematical Development

Thermodynamics traditionally employs a derivative notation which is rarely used elsewhere and which is not obviously consistent with the mathematics which students learn and use in other courses. Thus, the conceptual difficulties are compounded by the need to learn a sort of "thermodynamic mathe-

matics" which has special kinds of partial derivatives and non-exact differentials. The mere manipulation of the notation becomes such an arcane process that this ability is in itself regarded as "thermo," and purely mathematical results are confused with the results of thermodynamics.

These non-standard forms arise for historical reasons and from the problems which arise in using the same symbol to denote a value as well as a function. We will outline below an alternative method of presenting the material which is entirely consistent with the mathematics of functions to which students are accustomed.

We start by emphasizing that the development at this stage is purely algebraic, and no physical significance is intended to be attached to any of the variables we use. Everything could, in fact, be developed in terms of x , y , and z . However, we prefer to adopt a set of symbols in which the equations we develop will turn out (when at a later stage we do give significance to some of the symbols) to be directly useful.

Notation

Consider a variable H which may be expressed as a mathematical function (that is a rule for obtaining a value for a dependent variable from given values of a set of independent variables) of two other variables T and P . For example, we might write that

$$H = T^2 + 2T \log(P) \quad (1)$$

Now suppose that another variable V may also be expressed as a function of T and P ; suppose, for example, that $V = T/P$. Since we can solve this relationship to give $P = T/V$, we can substitute in Eq. (1) to express H as a function of T and V

$$H = T^2 + 2T \log(T / V) \quad (2)$$

We thus have two possible functions for H . The first gives us the rule for calculating a value of H from given values of T and P . The second is the rule for calculating a value of H from values of T and V . We might be tempted to indicate these two possible functions for H by some such notation as $H(T,P)$ and $H(T,V)$. However, this is contrary to all the rules for functions we have learned in mathematics, where if $H(T,P)$ is given by Eq. (1), then it follows that

$$H(T, V) = T^2 + 2T \log(V) \quad (3)$$

which is not the same as Eq. (1) and will *not* give the required value for H as Eq. (2) will when the state of the system is given by corresponding values of the variables P , V , and T . To keep to the mathematical

We find it surprising that Callen's approach has not found more favor with educators. It is the purpose of this paper to show how these ideas can be combined to form a logical and consistent introduction to thermodynamics.

formulation to which we are accustomed, we need to write something like

$$H = f(T, P)$$

for Eq. (1), and

$$H = g(T, V)$$

for Eq. (2), the corresponding relationship in terms of T and V , where we use f and g to indicate that *different* functions are involved. It is clear that we need to avoid confusion between the *value* of H at certain conditions and its functional form in terms of the chosen independent variables.

The difficulty in thermodynamics arises from two factors. First, the actual functional relationships are rarely known explicitly, and we are usually forced to work only with their derivatives and other properties. Second, given the large number of dependent variables of interest (H) and the even larger possible number of combinations of independent variables (P, T, V, \dots), there are not really enough function symbols (f, g, \dots) to go around. Even if there were enough, it would be very tricky to remember which function symbol represented which variable as a function of which independent variables.

We solve this problem by adopting a notation where f and g are replaced, respectively, by H^{TP} and H^{TV} . We may then write **equations** such as $H = H^{TP}(T, P)$ and $H = H^{TV}(T, V)$, where the superscripts remind us both that we are dealing with independent functional forms and of the independent variables with which we are concerned, while the terms in brackets tell us the values of these variables at which to evaluate the function. For the example above, we will now have the functions

$$H^{TP} = T^2 + 2T \log(P) \quad (4a)$$

and

$$H^{TV} = T^2 + 2T \log(T / V) \quad (4b)$$

Note also that values such as $H^{TP}(273,1)$ and $H^{TV}(273,22.4)$ are clear and unambiguous.

Derivatives

Of course, we usually find in thermodynamics that we are concerned not so much with the functions, that is f or g or H^{TP} (which indeed often turn out to be unknown), but with their derivatives. For

the function f of Eq. (1) there are two possible derivatives:

$$\frac{\partial f}{\partial T} \quad \text{and} \quad \frac{\partial f}{\partial P}$$

These derivatives are defined in the usual fashion. For example

$$\frac{\partial f}{\partial T} = \lim_{\Delta T \rightarrow 0} \left(\frac{f(T + \Delta T, P) - f(T, P)}{\Delta T} \right) \quad (5)$$

Using our superscript function notation, we may write the two derivatives of f as

$$\frac{\partial H^{TP}}{\partial T} \quad \text{and} \quad \frac{\partial H^{TP}}{\partial P}$$

This notation is found to be considerably less confusing for the student than the conventional one in which the first of the above derivatives is written as

$$\left(\frac{\partial H}{\partial T} \right)_P$$

where the P is usually read as "at constant P ." Beside being somewhat clumsy, this (as we all know) can lead the student into the confusion shown by many classic 'howlers,' such as denying the existence of this derivative at a point in a process in which P is not constant. In fact, of course, as the superscript notation emphasizes, P is *not* a constant, but is an independent variable of both H^{TP} and $\partial H^{TP}/\partial T$, of exactly the same status as T .

We stress the need to *understand* the usual notation, which the students will, of course, find in texts and other sources which they consult, even if (in the initial stages at least) this understanding is reached by translating into our own notation in order to clarify the functional dependencies. It is, in fact, interesting to note that students may frequently be observed using the superscript notation for this purpose when working with the differential equations of other courses, such as transport phenomena.

Differentials

Consider now the equation $y = f(x)$. We define dy and dx to be any two variables which satisfy the equation

$$dy = \frac{\partial f}{\partial x} dx \quad (6)$$

and we call dy and dx *differentials*. (We need to write the derivative with the symbol ∂ to avoid confusion with the differentials using the symbol d .) Note that dy and dx are *any* quantities which satisfy this equation; in particular, there are no implications about the "smallness" of these quantities. It is clear that dx and dy define a line which is tangent to the $f(x)$ curve at the point (x, y) .

Similarly, for our function H^{TP} we define the dif-

ferentials dT , dH , and dP as quantities which satisfy

$$dH = \frac{\partial H^{TP}}{\partial T} dT + \frac{\partial H^{TP}}{\partial P} dP \quad (7)$$

If we divide Eq. (7) by dT , we obtain

$$\frac{dH}{dT} = \frac{\partial H^{TP}}{\partial T} + \frac{\partial H^{TP}}{\partial P} \frac{dP}{dT} \quad (8)$$

where we emphasize that the first and last terms are merely the ratios of two differentials, *not* derivatives.

Notice that from Eq. (7), if dP is zero (which is perfectly acceptable since we have not divided through by dP at any stage), we obtain

$$\left. \frac{dH}{dT} \right|_{dP=0} = \frac{\partial H^{TP}}{\partial T} \quad (9)$$

Just as the differentials of Eq. (6) define a tangent line to the curve $y = f(x)$, the differentials of Eq. (7) represent movement on a plane which is the tangent plane at the point (P, T) to the $H = H^{TP}(P, T)$ surface.

The important point to note is that the left-hand side of Eq. (9) is an algebraic expression, *not* a limit as in Eq. (5). This is a direct consequence of the definition of Eq. (7) and the fact that the differentials are not necessarily small quantities. The important result is that all future manipulations will be algebraic; the limit process only occurs in the definition of the derivative in Eq. (5).

We need to note, however, that when we place a constraint such as $dP = 0$ on an expression such as the quotient on the left of Eq. (9), the values of dH and dT are no longer arbitrary, as we have constrained their variation.

Using these concepts (especially that of Eq. 9), the student may develop all of the familiar relationships using only simple and unambiguous algebra. For example, consider the two differentials dH and dT . It is clear that

$$\frac{dT}{dH} = 1 / \left(\frac{dH}{dT} \right) \quad (10)$$

where we emphasize that the two terms are ratios of differentials, *not* derivatives. Now, consider Eq. (10) when $dP = 0$. From Eq. (9) we obtain

$$\frac{\partial T^{HP}}{\partial H} = 1 / \left(\frac{\partial H^{TP}}{\partial T} \right) \quad (11)$$

If we consider the following ratios of differentials:

$$\frac{dH}{dT} = \frac{dH}{dV} \frac{dV}{dT} \quad (12)$$

we may, from the situation when $dP = 0$, obtain the well-known relation

$$\frac{\partial H^{TP}}{\partial T} = \frac{\partial H^{VP}}{\partial V} \frac{\partial V^{TP}}{\partial T} \quad (13)$$

Shorthand Notation for Derivatives

The notation which we have adopted for derivatives, although clear, makes for slightly tedious writing and somewhat more tedious typing or typesetting (although certainly no more so than the traditional notation). We may save some effort and space by adopting a shorthand in which

$$\frac{\partial H^{TP}}{\partial T} \text{ is replaced by } H^{T'P}$$

Although useful for simple statements and equations, this notation is somewhat more difficult for the novice to use in performing algebra. It may be preferable to use the expanded form, especially in handwriting, to perform manipulations such as those of Eqs. (10) to (13) above. This notation may easily be extended to higher derivatives, as the functions of thermodynamics are sufficiently "smooth" that the order of differentiation is not important. (Alternatively, if the order of differentiation is important, we may use notation such as $H^{T'P}$ and $H^{P'T}$ to indicate the difference.)

Integrals

We define an integral in the usual way as the limit of a sum. That is, over some path $V = V(S)$ from S_1 to S_2

$$\int_{S_1}^{S_2} T^{SV} dS = \lim_{N \rightarrow \infty} \left(\sum_{i=1}^N T^{SV} [S_i, V(S_i)] \Delta S_i \right)$$

where $N \Delta S_i = S_2 - S_1$. (There is no ambiguity about dS when used in conjunction with the integral sign.)

Canonical Variables

Consider a function U^{SV} . This function leads to differentials given by

$$dU = \frac{\partial U^{SV}}{\partial S} dS + \frac{\partial U^{SV}}{\partial V} dV \quad (14)$$

or, expressed more concisely in the shorthand notation explained above

$$dU = U^{S'V} dS + U^{SV'} dV \quad (15)$$

If we define the functions

$$T^{SV} = U^{S'V} \quad \text{and} \quad P^{SV} = -U^{SV'} \quad (16)$$

then obviously

$$dU = TdS - PdV \quad (17)$$

We may now regard this equation as being a differential relationship between U and four variables (T , P , V , and S), only two of which are independent.

As many readers will know, we can show that
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there is a "special" relationship between U and the pair of variables, S and V , which is not shared by the other variables, T and P . The reasoning is outlined as follows.

Consider the (known) relation

$$T = U^{S'V} = T^{SV} \quad (18)$$

Assume that from the function T^{SV} we may uniquely solve for S ; that is

$$S = S^{TV} \quad (19)$$

We may substituted $S = S^{TV}$ into $U = U^{SV}$ to get

$$U = U^{SV} (S^{TV}, V) = U^{TV} \quad (20)$$

By similar arguments, we may obtain U^{SP} , U^{PV} , U^{TS} and all the other various combinations of independent variables.

We now note, however, that the *reverse* processes are *not* possible. If we have U^{TV} we cannot uniquely obtain U^{SV} . This is because in the process of differentiating U^{SV} to obtain T or P we lose information. Suppose, for example, that the functional form of U^{SV} is such that

$$U^{SV} = K + A^S + B^V + C^{SV} \quad (21)$$

Then in the process of differentiating U with respect to S in order to obtain T^{SV} as defined by Eq. (18), we lose all information about K and the function B^V . It is therefore not possible to reconstruct U^{SV} from U^{TV} , since the integration process which reverses the differentiation involves the addition of arbitrary "constants" (they may be functions of V) about which we have no information from U^{TV} .

This special nature of U^{SV} is expressed by saying that S and V are the *canonical variables* of U .

The question obviously arises: Is this behavior peculiar to U^{SV} , or are there other functions which have different canonical variables? It turns out that there are such functions. If we invent a new function $A = U - TS$, then A can be shown (by a similar argument to the one above) to have canonical variables T and V . By a similar process, if we let $H = U + PV$ and $G = U - TS + PV$, then H has as its canonical variables S and P , while G has T and P . These new functions H^{SP} , G^{TP} , and A^{TV} are the only new ones we can define with these properties among the four variables T , P , S , and V , and so they have a special significance. (For students with suitable mathematical backgrounds, one may of course obtain H , G , and A directly by Legendre transforms; for others, the argument above may suffice.)

Useful Relations

We may notice from the definition of H above

that the quantity T , which we defined by $T = U^{SV}$, will also be equal to H^{SP} . We may thus obtain the familiar relationships for T , P , S , and V , such as

$$T = U^{S'V} = H^{S'P} \quad (22)$$

Maxwell Relations

These relationships may be obtained as shown in the following example, where we have set the derivatives out in full for clarity. Since

$$T^{SV} = \frac{\partial U^{SV}}{\partial S} \quad (23)$$

then, provided the functions are twice continuously differentiable, it follows that

$$\frac{\partial T^{SV}}{\partial V} = \frac{\partial^2 U^{SV}}{\partial V \partial S} = \frac{\partial^2 U^{SV}}{\partial S \partial V} \quad (24)$$

$$= \frac{\partial}{\partial S} \left(\frac{\partial U^{SV}}{\partial V} \right) \quad (25)$$

$$= - \frac{\partial P^{SV}}{\partial S} \quad (26)$$

This result may be written more succinctly as $T^{SV} = -P^{SV}$. By similar methods, we may obtain the usual other results, known as *Maxwell Relations*, or *Cross-Differentiation Identities*.

Path-Dependent Functions

Consider the difference ΔU between the values U_1 and U_2 of the function U^{SV} at two points (S_1, V_1) and (S_2, V_2) . This is given by

$$\Delta U = U_2 - U_1 \quad (27a)$$

where

$$U_1 = U^{SV}(S_1, V_1) \quad (27b)$$

and

$$U_2 = U^{SV}(S_2, V_2) \quad (27c)$$

We may also calculate ΔU from $dU = TdS - PdV$ as

$$\Delta U = \int_1^2 dU = \int_1^2 TdS - \int_1^2 PdV = \int_1^2 U^{SV} dS - \int_1^2 U^{SV'} dV \quad (28)$$

We see that the term TdS is a function of S and V , and will in general therefore have different values at different points on the (S, V) plane. The $\int TdS$ term is a line integral whose value will depend upon the *path* from (S_1, V_1) to (S_2, V_2) along which we evaluate it. The same applies to the term $\int PdV$.

The student might see this more clearly if it is explained in the following fashion. At every point on the (S, V) plane, there is a value of P , since we may write $P = P^{SV}$. We may therefore draw the path on

the (P, V) plane corresponding to the path on the (S, V) plane along which we are integrating from point 1 to point 2. On the (P, V) plane, the term $\int PdV$ is simply the area under the curve, which obviously depends upon the P - V path we are considering.

For future convenience we shall define these two path-dependent integrals as

$$Q = \int TdS \quad (29)$$

and

$$W = - \int PdV \quad (30)$$

so that Eq. (28) becomes

$$\Delta U = Q + W \quad (31)$$

We note that while the value of ΔU depends only on the initial and final states (S_1, V_1) and (S_2, V_2) , the values of Q and W depend on the path between those two states along which we evaluate their defining integrals.

Functions of More Variables

All the functions which we have considered above have been functions of two variables. The reasoning may be extended in a straightforward fashion to functions of a larger number of variables. Although there is nothing radically new here, experience suggests that in the classroom situation it is better to start, as we have done above, with only two independent variables. Once the concepts are grasped for these functions, students have no trouble understanding the similar results for functions of more variables.

Let us then consider n further independent variables. We shall give these the symbols $N_1, N_2, \dots, N_i, \dots, N_n$. The symbolism $[N_i]$ represents this whole set of variables. We shall also need the set of $n-1$ variables $[N_{j \neq i}]$ that is $N_1, N_2, \dots, N_{i-1}, N_{i+1}, \dots, N_n$ excluding N_i .

We may then consider the function

$$U = U^{SV[N_j]} \quad (32)$$

from which we may write the differential

$$dU = U^{S'V[N_j]} dS + U^{SV'[N_j]} dV + \sum_i U^{SVN'_i[N_{j \neq i}]} dN_i \quad (33)$$

We may then define

$$T = U^{S'V[N_j]} \quad (34)$$

$$P = -U^{SV'[N_j]} \quad (35)$$

$$\mu_i = U^{SVN'_i[N_{j \neq i}]} \quad (36)$$

Substituting these definitions into Eq. (33), we obtain

REQUEST FOR FALL ISSUE PAPERS

Each year *Chemical Engineering Education* publishes a special fall issue devoted to graduate education. It consists of 1) articles on graduate courses and research, written by professors at various universities, and 2) ads placed by chemical engineering departments describing their graduate programs. Anyone interested in contributing to the editorial content of the 1991 fall issue should write to the editor, indicating the subject of the contribution and the tentative date it will be submitted.

Deadline is June 1, 1991.

$$dU = TdS - PdV + \sum_i \mu_i dN_i \quad (37)$$

The above definitions of T and P are no different to those we have used previously. We may define the functions A, H, and G as we have done before. Thus

$$A = U - TS = A^{TV\{N_j\}}$$

and H and G are defined in an analogous fashion.

There are also many new functions we could define with canonical variables involving one or more of our new variables $[N_j]$. For instance

$$B = U - \mu_1 N_1 = B^{SV\mu_1\{N_{j \neq 1}\}} \quad (38)$$

but these in general do not turn out to be useful functions, so we shall not explore this avenue further.

We may also obtain, as we did above, a set of Maxwell relations. For example, from the second derivatives of U, we may obtain

$$T^{SV\{N_j\}} = -P^{S^V\{N_j\}} \quad (39)$$

while from A we may obtain

$$S^{TV\{N_j\}} = P^{T^V\{N_j\}} \quad (40)$$

Many other relationships are of course possible. For example

$$\mu_j^{TPN'_j\{N_{k \neq j}\}} = \mu_i^{TPN'_i\{N_{k \neq i}\}} \quad (41)$$

It perhaps needs to be stressed again at this point that all the above development is purely mathematical. All the relations we have developed follow from the properties of functions and their derivatives and from our (arbitrary) definition of the symbols P and T in terms of the derivatives of U^{SV} . We have not yet done any "thermodynamics"!

The development that may be referred to as "thermo" (including the identification of our symbols T and P with their usual meaning) will form the subject of Part 2 of this paper.

We may also note that in this approach the mathematics we use is entirely consistent with that which a student has learned in the standard mathematics course. In particular, we have no need for any special kinds of derivatives. We have found in our teaching that students readily assimilate this material

and do not appear to have the same problems of understanding that the authors did when they were undergraduates.

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ChE book review

A GUIDE TO CHEMICAL ENGINEERING PROCESS DESIGN AND ECONOMICS

by Gael D. Ulrich

John Wiley & Sons; 472 pages, \$33.95 (1984)

Reviewed by

Andrew N. Hrymak

McMaster University

This book is intended as a reference text for a course using case studies such as those from the AIChE design competition. Topics covered in the book fall into three main categories: process design, economics, and technical report writing. Extensive references to well-known chemical engineering texts and handbooks are found throughout the book.

The first section is entitled "Process Design." The chapters within this half of the book cover the design process, process conception, flowsheets, and the specification and design of individual pieces of equipment. In Chapter 2, the reader is introduced to the importance of understanding the process and obtaining typical flowsheets from the literature and Chapter 3 summarizes flowsheet preparation and common symbols.

Chapter 4 is a lengthy chapter devoted to the specification and design of individual pieces of process equipment. Separate sections cover different classes of units (such as heat exchangers, pumps, reactors, etc.). Each section gives a brief overview of

Continued on page 95.

WE HOLD THESE TRUTHS TO BE SELF-EVIDENT

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Being engineering professors, we all know about the need to make assumptions . . . and we also know that if the assumptions are invalid, the results can be worthless. We learn early in our careers to check our results (*Does the model fit the data? Does the algorithm converge? Does the product meet quality specifications?*) and if they are not satisfactory, to question our assumptions (*Is the solution ideal? Is the reactor isothermal? Is flow laminar?*), and we try to develop the same critical, questioning mentality in our students.

When it comes to education, however, our mentality changes. We generally do whatever it is we do without much critical evaluation of how well or how poorly it is working, and we accept without question what Armando Rugarcia^[2] calls *academic myths*—assumptions that have never been shown to have any basis in reality and often defy common sense. Here are some of them.

MYTHS ABOUT . . . FACULTY RECRUITMENT

- *People who (1) don't have Ph.D.'s, or (2) have spent their careers in industry and have no research publications, are not qualified to be engineering professors.*
- *When filling faculty vacancies, an engineering department benefits most by selecting the candidates in the hottest and currently most fundable research areas. How much grant money they attract in the next five years is more important than whether they know enough engineering to teach the core courses and to change research areas if their present one goes out of fashion.*
- *The best way to handle required courses that*

no one wants to teach, such as the unit operations laboratory or the capstone design course, is to rotate them among the faculty so that no one gets stuck with them too often. An inferior solution is to fill a vacant faculty position with someone who has the desire to teach these courses and the expertise to teach them well.

- *When selecting a department head, the faculty benefits most by choosing the candidate with the strongest research record, regardless of administrative experience or ability. How he or she runs the department in the next five to ten years is less important than what he or she does in research after that.*

MYTHS ABOUT . . . RESEARCH AND TEACHING

- *Excellence in research and excellence in teaching are highly correlated.*
- *Requiring EVERY faculty member to build up a strong research program as a condition for promotion and tenure is in the students' (professors', department's) best interests.*
- *Excusing new professors from teaching responsibilities so they can write proposals is a good thing to do. Excusing them from research responsibilities so they can develop a couple of good courses makes no sense.*
- *Professors who are excellent at research and mediocre-to-adequate at teaching deserve ten-*



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ure. Professors who are excellent at teaching and mediocre-to-adequate at research don't.

MYTHS ABOUT . . . CURRICULUM DESIGN AND PEDAGOGY

- Our graduates routinely say they never use 90% of what we taught them. Since we're engineering professors, 90% of what they're doing must not be engineering.
- It makes sense educationally to teach students a generalized theory (e.g., transport theory) before teaching them anything about the specific phenomena and devices that the theory was invented to describe (e.g., unit operations).
- Tensor calculus, quantum chemistry, and statistical mechanics should be taught to every chemical engineering undergraduate; statistical process control, project management, and technical writing they can pick up on their own—there's no room for those subjects in our crowded curriculum.
- The best thing to do with ethics, safety, environmental science, and all those other important things ABET says we have to teach, is stick them all in the capstone design course.
- I accomplish something useful when I spend fifty minutes in class writing detailed derivations on the chalkboard for the students to copy.
- We can't teach students to think critically or creatively—either they can do it or they can't.
- Students who complain that our lectures have nothing to do with the real world don't know anything about the real world—and we do.
- If I have covered the syllabus, I have done my job successfully.

MYTHS ABOUT . . . EVALUATION OF STUDENTS (GRADING)

- How well our students will do as engineers correlates highly with (a) their undergraduate GPA; (b) their ability to solve problems with unfamiliar twists on 50-minute exams; (c) anything else that we typically use to evaluate them.
- An average score of 40 on my final exam proves (a) I set high standards; (b) they didn't understand the material. There is no possi-

bility that it proves (c) the test was lousy.

- An average score of 85 on your final exam proves (a) it was a trivial test; (b) you're a soft grader; (c) there was widespread cheating. There is no possibility that the result proves (d) they learned the material.
- Performance on the written Ph.D. qualifying examination correlates with anything except performance in courses on the same material.

MYTHS ABOUT . . . EVALUATION OF TEACHING

- All methods of evaluating teaching are unreliable, and student evaluations are the most unreliable of all.
- If you get consistently outstanding student evaluations, it must be because you are (a) an easy grader; (b) an "entertainer." It is certainly not because you are (c) an outstanding teacher.
- If I get consistently rotten student evaluations, it is because (a) the students are ignorant and lazy; (b) I don't water down the material for them; (c) they don't understand what I am doing for them now but in later years they'll come back and thank me. It is **definitely** not because (d) I am doing a rotten teaching job.

I could go on, but you get the idea.

When I classify these points as myths I am not saying there's nothing to them; it's just that as far as I know they've never been scientifically or even empirically validated. (Mentioning someone who is great at both teaching and research, for instance, doesn't quite do it.) If you can justify one or another of these assumptions, let me know and I'll set the record straight.¹ If, on the other hand, you conclude that the assumptions might be faulty, then how about considering whether some alternative assumptions might lead to better ways of doing things? Couldn't hurt. □

¹ Before you attempt it, though, you might want to check out the literature: McKeachie^[1] provides invaluable summaries of the research on most of the topics in question, and Rugarcia^[2] makes some interesting points specifically on the research/teaching dichotomy.

1. McKeachie, W.J., *Teaching Tips: A Guidebook for the Beginning College Teacher*, 8th ed., Toronto, D.C. Heath & Co. (1986)
2. Rugarcia, A., "The Link Between Teaching and Research: Myth or Possibility?" *Engineering Ed.*, **81**, 20 (1991)

A COURSE IN IMMOBILIZED ENZYME AND CELL TECHNOLOGY

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Courses addressing topics in biotechnology are becoming more common in the chemical engineering curriculum. Many departments offer a senior- or first-year graduate course in biochemical engineering fundamentals, often following the curriculum developed by Bailey and Ollis.^{11,21} Tavlarides¹³¹ also describes a course in enzyme and biochemical engineering for graduate students. However, the text of Baily and Ollis, now in its second edition,¹⁴¹ appears to be the book of choice, due to the fact that its orientation is towards chemical engineering while most other books are aimed at biochemists or biotechnologists. The only exception to this might be the text of Aiba, *et al.*,¹⁵¹ which is (unfortunately) out of print. There has been an increase in the number of potential texts during the last few years, such as the text by Bu'lock and Kristiansen.¹⁶¹

Basic enzyme technology is often addressed in such an introductory course, and it usually includes enzyme kinetics in some detail along with some reference to immobilized enzymes. More advanced courses in enzyme kinetics are quite often handled by chemistry departments at the graduate level. However, selected advanced enzyme technology concepts within chemical engineering are frequently included as special topics in courses such as advanced

kinetics and reactor design. In most of these cases, the topic of immobilized cells is given only passing reference at best. One application example that is sometimes addressed relates to biofilms which immobilize microbes that form on the walls of fermentation vessels, including the aeration tanks in wastewater treatment. Biosensors may also be discussed. Otherwise, applications are often only briefly covered, if at all.

The technology of immobilized enzymes and cells has grown tremendously over the last decade. Chemical engineers are involved in the immobilization processes themselves in addition to the ultimate utilization in some bioreactor configuration. The description of the kinetics and mass transfer aspects of immobilized systems depends on a good foundation in chemical engineering transport phenomena and reaction engineering. Many enzyme applications involve the enzyme in an immobilized form due to a number of advantages (versus the free form) such as ease of recovery, maintenance of the active form at higher levels for longer times, more freedom in reactor operation, and less potential product contamination problems.¹⁷¹

Economic considerations often favor the immobilized system¹⁸¹ for the same reasons stated above in addition to the higher throughput rates (relative to the free form) that can often be realized. However, a detailed economic analysis must consider the costs of the immobilization process itself since preparation for the more sophisticated techniques may be expensive.

Immobilized cells enjoy many of the same benefits as immobilized enzymes. In the case of mammalian cells, immobilization is often the only way



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Immobilization technology has found its way into a variety of applications, including organic chemical production, food processing, pharmaceutical production, environmental engineering, and (recently) biomedical situations. . . . This article describes a course in chemical engineering which addresses, in some detail, the technology of immobilized enzymes and cells.

that cells can be used in most reactor systems, due in most cases to their fragility. For example, mammalian cells may not be able to tolerate even the gentlest of mechanical agitation.

Immobilization technology has found its way into a variety of applications, including organic chemical production, food processing, pharmaceutical production, environmental engineering, and (recently) biomedical situations. Increased employment of this technology will probably parallel the continuing successes of molecular biology. Immobilized enzymes and cells are also important in the biosensor area, where very specific probes are now possible as a result of this technology.

This article describes a course in chemical engineering which addresses, in some detail, the technology of immobilized enzymes and cells. It is meant to be an elective course for advanced seniors or graduate students in chemical engineering or some other technical discipline. The course has been offered twice at this writing, and will be offered in the future as part of a series of chemical engineering electives in the biotechnology area.

COURSE OUTLINE

Table 1 presents the course outline. As can be seen, the one-semester course (3 semester credits) covers a variety of topics, including the basic immobilization methods, transport phenomena and kinetics of immobilized systems, reactor configurations, and applications. An important application area which received special attention involved biosensors. The topic of basic microbe physiology and the impact of immobilization procedures on viable organisms was also addressed.

Two texts were required for the course. *Process Engineering Aspects of Immobilized Cell Systems*, by Webb, *et al.*,^[9] was used along with *Immobilized Microbial Systems: Principles, Techniques, and Industrial Applications*, by Kolot.^[10] In addition, a number of journal articles and other readings (see Table 2, next page) were utilized.

Each class meeting typically started with the presentation of an application example, either by one of the students or by the instructor. The presentation and following discussion were limited to ten

TABLE 1
Course Outline

1. Introduction to immobilized enzyme and cell technology	B. Effect of immobilization on cell physiology
2. Immobilization methods	C. Activity of immobilized cell particles, including mass transfer and control of cell growth and metabolism
A. Entrapment	
• gels	
• fibers	
• microencapsulation	
• other methods	
B. Binding	4. Immobilized system kinetics
• Carrier binding	A. External mass transfer resistances
- physical adsorption onto surfaces (including physical aspects of various carriers)	B. Intraparticle diffusion and chemical reaction
- ionic binding	C. Simultaneous internal and external resistances
- chelation or metal binding	
- covalent binding	5. Reactor design considerations
C. Cross-linking	A. Basic enzyme kinetics
D. Analytical methods used to study the effectiveness of immobilization	B. Reactor configurations used for immobilized biocatalysts
	C. Miscellaneous topics
	• biofilm formation
	• mixing and agitation approaches
	• oxygen supply
	• control schemes
3. Immobilized cell physiology	6. Biosensors
A. Importance of cell physiology prior to immobilization	A. Types of sensors and underlying principles
	B. Applications

minutes. The two texts included a number of application discussions and were eventually addressed as part of this series. Additional examples, beyond those in the texts, were presented by the instructor during the course and are listed in Table 3.

There were also a few supplementary exercises. In the first exercise, students were instructed to contact an industrial supplier of immobilized enzymes and, if the supplier was cooperative, to obtain a sample of the product along with any descriptive literature. The samples thus obtained were displayed in one session for all to see. We also viewed some of the samples under a scanning electron microscope.

The second exercise involved the analysis of US Patents involving immobilized systems, specifically "Process for Preparing Biomass Attached to a Carrier" (Patent No. 4,560,479) and "Immobilization of Microorganisms on a Plastic Carrier" (Patent No. 4,696,901).

For the final exercise, students presented three in-class presentations on the following topics:

- **A method of physical adsorption of an enzyme or cell onto a surface, including the underlying physical principles**
- **An analytical procedure which could be used to determine the extent of success of an immobilization procedure**
- **An application example**

Students were told that the presentations should last ten to fifteen minutes. The general class was allowed to direct questions to the presenter following the presentation.

The students also did simple experiments involving the immobilization process itself. They formed alginate gels (no enzyme or microbe involvement) starting with sodium alginate solutions,^[11] and they formed K-carrageenan gels by dissolving the material in physiological saline, warming, and contacting with a gel-inducing agent.^[10]

DISCUSSION

The two texts used in the course were good selections. Their technical depth is satisfactory, and they are reasonably priced (the combined price is less than \$70). Neither book addresses immobilization methods in any depth. Also, analytical procedures to establish the success (or lack thereof) of an immobilization procedure are not cited. As a result, both of these important topics were addressed via outside

sources (see Table 2). Additionally, the topic of biosensors is not considered in either text, so outside supplementation in that area was also necessary (noted in Table 2). The discussion on biosensors stressed the underlying enzymatic principles involved and did not emphasize any associated electronics or probe hardware aspects. Finally, the texts do not consider engineering economic analysis at all, but this was easily handled by additional materials.

Application examples were presented throughout the course, some by the students themselves but most of them by the instructor. I found that mixing in the applications with the technical material was effective, and it helped the students to focus on the concept that there are many *real* applications, *i.e.*, that the topic is not just theoretical in nature. The students also found the discussion on the patents to be interesting, both as to the technical content and as to the nature of the patent and patenting process

TABLE 2
Selected Additional References

General Materials

- Enzyme Engineering Case Study: Immobilized Lactase^[14]
- Industrial Applications of Immobilized Enzymes: A commercial Overview^[8]
- Immobilized Enzymes: A Survey^[15]

Immobilization Methods

- Preparation and Properties of Gel Entrapped Enzymes^[16]
- Microbial Adhesion in Perspective^[17]
- Adherence of Marine Micro-Organisms to Smooth Surfaces^[18]
- Mechanisms involved in Sorption of Microorganisms to Solid Surfaces^[19]
- Microcarrier-Bound Mammalian Cells^[20]
- A Range of Ceramic Biosupports^[21]
- Carriers for Immobilized Biologically Active Systems^[22]
- Immobilization of Enzymes by Adsorption^[23]
- Covalent Linkage III: Immobilization of Enzymes by Intermolecular Cross-Linking^[24]
- Some Techniques Involved in Study of Adsorption of Microorganisms to Surfaces^[25]

Mass Transfer and Kinetics

- Mass Transfer in Immobilized Cells^[26]
- Oxygenation of Processes Involving Immobilized Cells^[27]
- Diffusion and Kinetics with Immobilized Enzymes^[28]

Reactor Technology

- Design and Operation of Immobilized Enzyme Reactors^[29]
- Reaction Engineering Parameters for Immobilized Biocatalysts^[30]

Biosensors

- Biosensors^[31]
- Membrane Systems: Analysis and Design^[32]
- Immobilized Enzymes for Clinical Analysis^[33]

itself—something most of the students knew little about.

Most students who selected this course had previously taken the senior chemical engineering class titled "Theory and Design of Bioprocesses," a course which uses the text of Bailey and Ollis. However, there are always some students who have not—typically, students in the environmental engineering sequence of civil engineering. Their participation in the course required several lectures on basic enzyme kinetics. Also, the section on intraparticle transport phenomena and kinetics required a presentation of some preliminary background (Bailey and Ollis give a good elementary treatment) in order to bring all the students up to speed.

The weakest area of the course involved the laboratories. Ideally, several experiments should be done (at least as demonstrations) which cover a variety of immobilization methods. A minimal series could include an example of gel entrapment, covalent cross-linking, microencapsulation, and physical absorption. These should be supported by SEM or some other appropriate analytical inspection procedure. Several recipes are presented by Trevan^[12] and by Rosevear.^[13] Another good experiment could involve a comparison of free and immobilized enzymes in a simple reaction experiment. I intend to improve the laboratory aspect of the course in future offerings.

Finally, the in-class presentations were effective for two reasons: it made students more aware of the available sources of information on the subject, and it gave students good practice in organizing and orally presenting a technical topic, something in which most of them did not have much experience.

TABLE 3
Selected Application Examples
(in addition to examples in the texts)

- Antibody Production^[34]
- Separation of L-Amino Acids from Mixtures of the L- and D-Amino Acids^[35,36]
- Hybridoma and Monoclonal Antibody Production^[37]
- Drug Production from Immobilized Plant Cells^[38]
- Hydrolysis of Lactose^[39]
- Encapsulation of Vaccines and Hormones^[40]
- High-Fructose Corn Syrup Production^[41]
- Bioconversion of Lipophilic Compounds^[42]
- Effect of Biofilm Presence on Reactor Performance^[4]

In summary, the course effectively presents a variety of new information regarding immobilized enzyme and cell technology. All the students claim to have received new knowledge, and all could see the potential and demonstrated significance of the technology. While this is a good stand-alone elective, it is especially effective when the students have previously taken an introductory course in biochemical engineering.

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EDUCATOR: Perna

Continued from page 63

tations for the two-semester senior course. For twenty years now we have continuously worked on upgrading the laboratory experiments and its format.

During these years, together with colleagues in the civil engineering department, Angie also initiated cooperative efforts at the graduate level in environmental engineering. The first joint effort was to secure an interdisciplinary water-pollution training grant for graduate civil and chemical engineers, funded by the Federal Water Pollution Control Administration. This then led to the development of an interdisciplinary program in environmental engineering. Angie developed courses in unit operations of water treatment processes and in solid waste management processes.

Angie and John Liskowitz developed other highly successful joint research and programs that eventually led to numerous EPA research grants as well as

an Exxon grant that funded an environmental toxicology option under the direction of Dick Trattner. Out of all these efforts came the impetus for the Institute for Hazardous and Toxic Waste Management and the NSF-initiated Haz-Tox Center.

While Angie's research efforts have been in the main environmentally oriented, his research interests span the spectrum from ultrasonic-aided mass transfer to characterization of leachate from MSW incinerator ash. His current interest is in MSW incinerator residue, which he has been working on jointly with Don Sundstrom and Herb Klei (University of Connecticut). This research is an outgrowth of a two-year (1988-90) stint as a visiting professor of chemical engineering and a research fellow at the Environmental Research Institute at UConn.

A fellow of AIChE and ASEE, he is the recipient of numerous citation certificates and awards, including the ASEE/MidAtlantic Western Electric Award, the DELOS Distinguished Service Award, and the ODK Award of Merit.

His AIChE activities include service on ten institute committees, Technical Program Vice-Chairman of the 1977 NYC Annual Meeting, and Chairman of both the Student Chapters Committee and the Educational Projects Committee. He has also served as a Director of the New York City AIChE local section.

In ASEE he has served on numerous committees over the years, including Chairman of the 3M and DELOS Award Committees, in addition to holding ten elective offices, including Chairmanships of CHED, DELOS, and the Instrumentation Division.

In addition to the above professional activities, he has also served as Chairman of the ACS Mobay Committee, and as National President of Omega Chi Epsilon (the chemical engineering honor society), and President of the Association of College Honor Societies. He is also the author of approximately thirty-five papers, numerous presentations, coauthor of a book, and coeditor of three proceedings.

Angie's role in Omega Chi Epsilon deserves special attention. When Angie came to our department as a young assistant professor in 1967, I was Faculty Advisor of Omega Chi Epsilon, an honorary society with relatively few members at the time. I seized the opportunity to pass this advisorship on to our new young faculty member—I had more seniority and was being called upon with increasing frequency for other faculty business. Little did I realize what an impact this decision would have on the future of Omega Chi Epsilon. When he became advisor to our chapter in 1968, there were less than twenty national chapters in existence. After working intensively with our chapter, he became National Vice President of the organization in 1974 and then National President in 1978. When he completed his tenure as president he had expanded membership organization in Omega Chi Epsilon to forty chapters. He continued to work for the organization in his capacity as past president, and there are now forty-nine chapters nationwide.

His role as a national leader in Omega Chi Epsilon also led to the office of President of the Association of College Honor Societies, an umbrella group for the nation's more than sixty different honor societies.

These activities epitomize Angie's devotion to the profession. His volunteer involvement has always been intense, and he has given his time and talents happily and without thought of reward—his real reward has been his own satisfaction in having participated.

The multitude of people in our professional societies that Angie knows continually amazes me—and he always remembers their names! He and I have attended these meetings together for years, and although we were at the same sessions, he somehow always managed to meet many more colleagues than I, or anyone else, did. He never tires of meeting old, and new, friends and engaging in lengthy bull-sessions with them at meeting after meeting. His enthusiasm permeates the air at check-in and lasts long after everyone else is tired and ready to go home.

In addition to service on numerous department and institute committees at NJIT, Angie has been Chairman of the Faculty Council and President of the Professional Staff Association. He has also been a reviewer for NSF, EPA, AIChE, *CEE*, *I&EC*, *Engineering Education*, and the IACT, jr. He has been a consultant to the municipal and industrial sector, and during the summer of 1989 he served as a consultant and senior development officer to UNIDO in Vienna, Austria.

Angie's activities in the department include a stint as Acting Department Chairman (covering for me while I was on sabbatical leave) and as industrial fund raiser. During the 1970s his activities in fund raising led to a tripling of funds donated to the department and to the development of a Chemical Engineering Department Merit Award Program with its own endowment fund. At the present time he devotes his energies to teaching and the development of a Center for Municipal Solid Waste Studies.

When I was first contacted by *CEE* about the possibility of writing this article, I asked Angie for his permission and cooperation. He agreed with the one condition that he would be permitted to write the concluding paragraph for the article. It follows.

You know, I consider myself extremely fortunate in having had a department and an institute administration that has supported my activities at a number of professional society meetings, and I am appreciative of the large number of colleagues I have had the opportunity to interact with through the years. In many cases, these associations developed into strong friendships that I have grown to treasure. To all of these individuals and their families I would like to take this moment to express my sincere appreciation for their support and for the opportunity to have served with them, but mostly for their friendship over the years. I've got to say—I'm a very lucky fellow who has had a rewarding career. □

A SECOND-YEAR UNDERGRADUATE COURSE IN APPLIED DIFFERENTIAL EQUATIONS

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Conventional wisdom holds that lower-year courses in mathematics for engineers should be taught by mathematicians, who can supply the necessary depth and rigor that engineering instructors, however adept in applying the subject, may lack. Reality, however, tells us otherwise. Excessive insistence upon uniqueness, existence properties and proof of theorems, and unfamiliarity with engineering-flavored problems, coupled with a reluctance to blend lectures with practical examples, is counterproductive in lower-year courses. A large proportion of the students lose interest in the subject; their indifference, often mingled with hostility toward anything mathematical, can make the instruction of higher-year engineering mathematics and process control a difficult task.

There is much to be said, as a consequence, for the teaching of mathematics to undergraduate engineering students by engineering instructors who possess the required mathematical background *and* motivation. Having taught third-year (compulsory) and fourth-year (elective) courses (including process control) over the years, I have often been frustrated by the varying and unpredictable mathematics background of chemical engineering students entering their third year. Depending on the whim of the mathematician who taught the second-year course in ap-



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Excessive insistence upon uniqueness, existence properties and proof of theorems, and unfamiliarity with engineering-flavored problems, . . . is counterproductive in lower-year courses.

plied differential equations, one stream of students may have been given a healthy dose of certain topics (notably Laplace transformation) while the next group would have received little or no instruction in the same subject. Recently, when an opportunity of putting my thoughts of what this course should contain into practice, I seized it with alacrity.

The framework and "infrastructure" was given to me: 1) the course was to be administered by the mathematics faculty (including the assignment of a teaching assistant), 2) the traditionally-used text^[1] was designated, and 3) the course designation code and title was assigned. All this suited me fine. I was eager to set about my goal of putting a strong emphasis on the solution of chemical engineering problems via ordinary differential equations (ODE) which could be handled in the second year. The strategy was to discuss the theory behind each technique in a concise manner but without a formal proof (except where the procedure was short and straightforward) and to supply a goodly number of numerical illustrations.

Homework assignments, normally consisting of four to six non-elementary problems per set, were to be handed out and graded every week. A two-hour open-book midterm and a three-hour open-book final examination would serve as formal measures of student performance.

COURSE FRAMEWORK

The course structure is summarized in Table 1. The seven major topics follow a similar sequence in the textbook.^[1] In Part 1, the definitions, the gen-

eral, particular, and singular solutions, and the question of uniqueness are briefly covered, followed by a more-detailed discussion of direction fields and isoclines (in anticipation of nonlinear analysis in future years). In Part 2 the separable-variables technique, transformation methods, homogeneous equations, exact differential equations, the integrating-factor method, and Clairaut-type equations are treated. This portion of the course is heavily dosed with (elementary) numerical examples taken from chemical kinetics, reaction engineering, applied biochemistry, and heat-transfer theory.

Particular attention is paid to linear equations in Part 3, where Laplace transformation techniques are introduced and treated by anticipating later use in fourth-year process control courses in terms of transfer functions. Since the transfer function is the bridge in transform space between the input and output function in a linear system, its concept is introduced early to emphasize its usefulness in solving differential equations. The basic tools for handling transform inversion (*e.g.*, reduction to simpler forms via partial fractioning, convolution theorem, transform tables) are treated in detail, but contour integration is omitted due to the students' lack of knowledge of complex calculus in the second year.

The treatment of series solutions deviates from the conventional approach in that various classical methods (*e.g.*, the method of Frobenius) are covered briefly—but sufficiently for the introduction of Bessel

functions as an important technique for solving a class of second-order linear differential equations of practical importance. Due to time limitations, only the Bessel equation of the first kind is discussed, with appropriate applications; emphasis is laid particularly on the handling of the zeroes of Bessel functions in view of physical considerations (see Example 1).

In the next section, on orthogonal functions and Sturm-Liouville theory, the motivation for the orthogonality concept is emphasized and the general technique for the expansion of functions into orthogonal series is briefly shown (the discussion of Fourier series in solving partial differential equations in a subsequent third-year course is an extension of this topic).

Part 6 concerns a subject of growing importance at lower-year levels but which is not traditionally taught in this course: numerical techniques. I am convinced that the numerical handling of all mathematical problems of engineering importance should be introduced as early as possible and that an undue weighting of analytical techniques is outdated. The obsolete philosophy of neglecting numerical solutions at a lower-year level is also manifested in the textbook, which deals only with the Euler techniques and the Runge-Kutta method (in a surprisingly short chapter). To remedy this, I added the handling of second-order ODE's with two-point boundary value problems (see Example 2) and initial value problems

TABLE 1
Structure of Second-Year Course in Applied Differential Equations

SUBJECT	# OF ONE-HOUR LECTURES	ILLUSTRATIVE EXAMPLES OF THE NATURE
1. General concepts and philosophy of ODE's	3	None
2. First-order and simple ODE's	8	First-order irreversible batch reactors; mixing in a well-stirred tank at equal and unequal inflow and outflow rates; second-order irreversible batch reactions; radial heat conduction in a cylindrical solid; flow through containers of various geometries; growth and decay in simple biochemical reaction systems; production of isotopes in a nuclear reactor
3. Linear differential equations and Laplace transformation	12	Countercurrent heater-cooler problems; second-order underdamped control systems; two-element mixer cascades; elementary transfer function analysis
4. Series solutions and Bessel functions	3	Flux distribution in a cylindrical nuclear reactor; radial temperature distribution in a cylindrical conductor; buckling of a vertical column (in an ecumenical spirit!)
5. Orthogonal functions and Sturm-Liouville theory	2	None
6. The numerical solution of ODE's	4	None
7. System of ODE's and linear ODE's. Linearized systems	6	Consecutive irreversible first-order batch reactions; mixer cascades; flow through mixers equipped with valves

as a step in (what I conceive to be) the right direction. (I would be happy to see a strong component of numerical approaches in earlier calculus courses.)

Finally, Part 7 puts emphasis on the structural properties of linear systems, *e.g.*, eigenvalues and eigenvectors. It introduces the state-variable and state transition matrix concept, the decoupling of state variables via canonical transformation, and the solution of nonlinear systems for small excursions about their steady states via linearization (see Example 3). For obvious reasons, first- and second-order systems only serve for the purpose of illustration.

TYPICAL CLASS ILLUSTRATION EXAMPLES

EXAMPLE 1

Physical Importance of the Zeroes of Bessel Functions

The energy flux distribution in an upright cylindrical nuclear reactor of radius R is given by the ODE^[2]

$$r^2 \frac{d^2\phi}{dr^2} + r \frac{d\phi}{dr} + \gamma^2 r^2 \phi = 0 \quad (1)$$

where γ is a known physical parameter. At $r = R$, the flux ϕ is zero and the maximum energy flux, called the design power level of the reactor, exists at the axis: $\phi_{\max} = \phi(0)$. Since ϕ_{\max} is finite, the Y_0 -function (Bessel function of the second kind order zero) term must be suppressed in the general solution. Hence

$$\phi(r) = \phi_{\max} J_0(\gamma r) \quad (2)$$

where J_0 is the Bessel function of the first kind order zero. It follows that

$$J_0(\gamma R) = 0 \quad (3)$$

There are, in principle, an infinite number of roots which satisfy Eq. (3), but which one should be taken here?

This is where the physics of the problem must be considered. We know that the flux decreases from its maximum value at $r = 0$ to zero at $r = R$: so does $J_0(\gamma r)$ on $[0, \alpha_1]$, α_1 being the first zero of $J_0(x)$. Since $J_0(x)$ is negative between α_1 and the second zero α_2 , and negative energy flux is physically meaningless, the correct solution of Eq. (3) is

$$\gamma R = \alpha_1 = 2.4048$$

and the final solution to the problem is given by

$$\phi(r) = A J_0(2.4048 r / R) \quad (4)$$

The suppression of successive roots of Bessel functions past the first one due to physical constraints is an often-encountered requirement. Another instructive example, albeit not in chemical

engineering, is the stability of a vertical wire problem^[3] involving a fractional Bessel function of the first kind (good for a homework problem?).

EXAMPLE 2

A Simple Two-Point Boundary Value Problem

Given the linear ODE

$$\frac{d^2 y}{dx^2} = -\exp(-y^{1/2}) \quad (5)$$

with boundary conditions $x = 0, y = 1$, and $x = 2, y = 1$, the problem is to estimate the values of y in the interior of the $[0, 2]$ domain. Using the conventional central difference approximation for the second-order derivative, a grid structure with elements

$$y_{n+1} - 2y_n + y_{n-1} = -h^2 \exp(-y_n^{1/2}) \quad (6)$$

can be constructed, where n is an arbitrary node (or mesh point) position in the grid. This is a very good problem for illustrating at the same time the usefulness of linear algebra as well as finite-difference calculus and iteration strategies. In the simplest case we take a single interior point at $x = 1$, and thus $n = 0$ and $n = 2$ become boundary points. Consequently, Eq. (2) reduces to the finding of y_1 via the iteration scheme

$$y_1^{(k+1)} = 1 + (1/2) \exp\left(-\sqrt{y_1^{(k)}}\right) \quad (7)$$

starting with an arbitrary estimate $y_1^{(0)}$. If we choose $y_1^{(0)} = 1$, then $y_1^{(4)} = 1.16954$ and $y_1^{(5)} = 1.16955$ are obtained; with $y_1^{(0)} = 1$, $y_1^{(4)} = 1.16955$. If we choose two interval nodes $2/3$ units apart, we obtain the 2×2 matrix \mathbf{A} with elements $a_{11} = a_{22} = 2/3$ and $a_{12} = a_{21} = 1/3$, connecting the vector with elements $y_1^{(k+1)}, y_2^{(k+1)}$ to the vector with elements $1 + (2/3)^2 \exp(-y_1^{(k)}); 1 + (2/3)^2 \exp(-y_2^{(k)})$. Iteration quickly yields the values of $y_1 = y_2 = 1.15193$. Smaller grid sizes can be assigned for a homework problem, calling upon the students' computer skills. The approach is an adaptation of Hamming's treatment of two-point boundary value problems.^[4]

EXAMPLE 3

Linearization of Flow Through a Tank With a Valve in the Effluent Line

This problem is often discussed in process control texts^[5] and in the author's opinion it serves as an excellent and simple example to illustrate the concept of linearization and the usefulness of deviation variables in lower-level courses. The starting point is the mass balance.

$$A \frac{dh}{dt} = Q_i - k\sqrt{h} \quad (8)$$

where A is the uniform cross-sectional area of the tank, h is the instantaneous liquid level in the tank, Q_i is the liquid inflow rate, and k is the valve constant. At steady-state conditions

$$Q_i^* = k\sqrt{h^*}$$

Hence, in terms of deviation variables $y \equiv h - h^*$ and $x \equiv Q_i - Q_i^*$, Eq. (8) is rewritten as

$$A \frac{dy}{dt} = X(t) = k(\sqrt{h} - \sqrt{h^*}) \quad (9)$$

For sufficiently small magnitudes of x , the nonlinearity is removed by the truncated Taylor expansion

$$\sqrt{h} - \sqrt{h^*} \cong \frac{1}{2\sqrt{h^*}} y$$

and the linear approximation

$$A \frac{dy}{dt} + \frac{k}{2\sqrt{h^*}} y = x(t) \quad (10)$$

is obtained. The constraints on the validity of linearization are illustrated numerically under a specific set of conditions as shown in Table 2. Having discussed this problem in class, we then take up flow through two tanks in series and solve by elimination or elementary state variable theory, emphasizing the stability of the linearized system with negative real eigenvalues

$$-k_1 / 2A_1\sqrt{h_1^*} \quad \text{and} \quad -k_2 / 2A_2\sqrt{h_2^*}$$

STUDENT RESPONSE

By and large, student response was what could be expected in any course in engineering mathematics; those with a grasp of fundamental mathematical principles were receptive to the application flavor,

while those with a weak mathematical background were too bogged down in operational details to worry about the physical nature of the topics and problems discussed. There was, at any rate, not a single complaint about the application side of the course, and one of the two written comments supplied with a computerized course evaluation by students states, "Nice having some semi-real chemical engineering problems."

On a scale of ten, 42 responding students in a class of 69 gave 6.6 to the course and 7.5 to me (second-year course critiques often give overall scores below 5.0). Some students recognized their weakness in linear algebra (in spite of a two-term course taught in the first year) as a serious impediment in following Section 7 (Table 1). Orthogonal functions and Sturm-Liouville theory (Section 5) also proved to be a "baptism of fire" for many, and numerical techniques (Subject 6) made even the sleeping come temporarily alive—a sure sign of the ubiquitousness and appreciation of computers.

AFTERTHOUGHTS

The real challenge in teaching this course was in finding an appropriate balance between mathematical theory and engineering applications when students had little knowledge of either. The course content may thus have been a bit too ambitious. It may be more useful in the future to expand the numerical techniques portion at the expense of ODE systems, allotting at least as many formal lectures to the former as to the latter. Recently-written books, tuned more closely to the eighties, may also enhance the course.^[6]

The course was a source of great enjoyment for me, and I look forward to teaching it periodically. I hope that some of the students will subsequently explore the wonders of applied mathematics on their own.

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TABLE 2

**Comparison of True and Approximate Solutions
in Example 3**

for Step Inputs $X(t) = X_0 H(t)$ [$H(t)$: unit step function]

$A = 0.28 \text{ m}^2$; $Q_i^* = 0.39 \text{ m}^3/\text{min}$; $k = 0.408 \text{ m}^3/\text{min} \cdot \text{m}^{1/2}$

time (min)	h (m)			
	$x_0 = 0.01$ (m^3/min)		$x_0 = 0.1$ (m^3/min)	
	Eq. 9*	Eq. 10	Eq. 9*	Eq. 10
0.1	0.9174	0.9174	0.9483	0.9484
0.5	0.9288	0.9288	1.0632	1.0626
1.0	0.9390	0.9390	1.1678	1.1641
2.0	0.9508	0.9507	1.2963	1.2808
3.0	0.9564	0.9561	1.3638	1.3353
5.0	0.9603	0.9599	1.4195	1.3726
10.0	0.9614	0.9609	1.4416	1.3828
∞	0.9614	0.9610	1.4423	1.3830

* Solved by an arbitrary numerical technique, covered in Section 6 (Table 1)

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and T. C. Papanastasiou, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109.

REMOVAL OF CHLORINE FROM THE CHLORINE-NITROGEN MIXTURE IN A FILM OF LIQUID WATER

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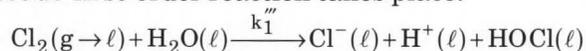
In industry there are many examples of absorption of a gas with or without chemical reaction in the liquid phase. In physical absorption, a particular gaseous component is removed from a gas mixture due to its larger solubility in the liquid phase solvent. The removal of butane and pentane from a refinery gas mixture by a heavy oil in the liquid phase is an example of physical absorption. In absorption with chemical reaction, the gaseous component to be removed transfers across the gas-liquid interface due to a difference in the bulk chemical potentials or concentrations in the two phases. The transferred gas then reacts with a liquid-phase component while simultaneously diffusing in the liquid phase mixture. The gas purification processes, such as removal of chlorine from nitrogen or air by means of water, removal of carbon dioxide from synthesis gas by means of aqueous solutions of hot potassium carbonate or monoethanolamine, and removal of H_2S and CO_2 from hydrocarbon cracking gas by means of ethanolamine or sodium hydroxide, are some examples of absorption with chemical reaction.



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PROBLEM STATEMENT

Chlorine is to be removed from a mixture of chlorine and nitrogen by absorption and reaction of chlorine with water in a falling liquid film, where a pseudo-first-order reaction takes place:



- Develop mathematical expressions describing two-dimensional concentration profiles of $Cl_2(A)$ in the liquid film, the total chlorine removal rate for the entire length of the film, and the mass transfer enhancement factor defined as the ratio of the actual rate of chlorine removal to the rate of chlorine removal in the absence of chemical reaction.
- Evaluate the two-dimensional chlorine concentration profile, the total chlorine removal rate, and the mass transfer enhancement factor for the following data:^[2]
 - System temperature: 24.5 °C
 - Chlorine concentration in the liquid film at the gas-liquid interface: $C_{A0} = 0.1746 \times 10^{-5}$ mole cm^{-3}
 - Width of the liquid film: $w = 1.0$ cm
 - Thickness of the liquid film: $\delta = 0.008$ cm
 - Height of the falling liquid film: $L = 1.0$ cm
 - Pseudo-first-order reaction rate constant: $k_1''' = 13.6$ s^{-1}
 - Molecular diffusivity of chlorine (A) in the liquid solution: $D_A = 1.477 \times 10^{-5}$ cm^2 s^{-1}

The chlorine removal process is to be carried out under isothermal and steady-state conditions by gently stirring the chlorine/nitrogen mixture as depicted in Figure 1.

PROBLEM SOLUTION

A sketch of the process is shown in Figure 1. Continuously flowing chlorine-nitrogen mixture is stirred and a film of liquid water falling along the vertical nonreactive plane wall is in contact with the gas phase. The gas mixture is at temperature, T , and pressure, P . The liquid phase concentration of chlorine at the gas-liquid interface can be determined for the evaluation of the numerical data using the methods given in References 3 and 4.

The solution^[1] to the momentum equation for the steady-state fully developed laminar flow gives an expression for the velocity, v_z , profile as

$$v_z(x) = v_m \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \quad (1)$$

where

$$v_m = \frac{\rho g \delta^2}{2\mu} \quad (2)$$

and v_m = maximum velocity of liquid at the liquid-film surface

g = gravitational acceleration

ρ = liquid density

μ = absolute viscosity

To set up the differential model describing transport and consumption of the species A (Cl_2) in the liquid phase region, we follow the generally accepted approach given in Reference 1. The origin of the cartesian coordinate system x, y, z is located at the surface of the liquid film at its top end (see Figure 1). Species A is assumed to be transported in the x and z directions only. The concentration of the species A, C_A , is a function of both x and z coordinates. A mole balance for component A is applied over the spatial element in the liquid region shown in Figure 1. The

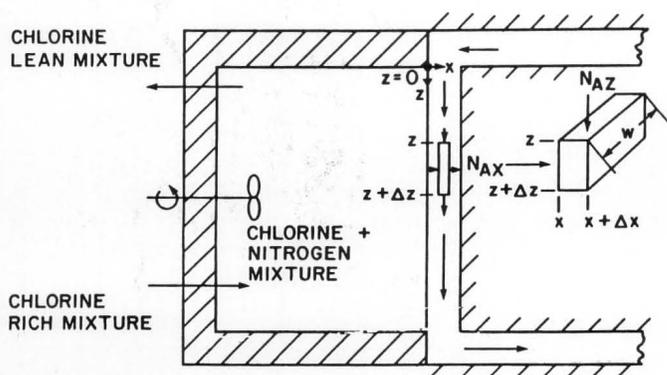


Figure 1. Sketch of the chlorine removal process by absorption and chemical reaction in the falling film of liquid water (not to scale).

resulting differential equation is

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Az}}{\partial z} + k_1''' C_A = 0 \quad (3)$$

Under the assumption of negligible transport of species A by diffusion in the z direction relative to its transport by the liquid bulk flow, and no bulk flow in the x direction, N_{Az} and N_{Ax} are approximated by

$$N_{Az} = C_A v_z(x) \quad (4)$$

$$N_{Ax} = -D_A \frac{\partial C_A}{\partial x} \quad (5)$$

N_{Az} and N_{Ax} represent the molar fluxes of species A in the z and x directions, respectively.

Equations (1), (3), (4), and (5) are combined to result in

$$-D_A \frac{\partial^2 C_A}{\partial x^2} + v_m \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \frac{\partial C_A}{\partial z} + k_1''' C_A = 0 \quad (6)$$

The required boundary conditions are:

$$\text{at } z=0 \quad C_A = 0 \quad \text{for } 0 < x \leq \delta \quad (7a)$$

$$\text{at } x=0 \quad C_A = C_{A0} \quad \text{for } 0 < z \leq L \quad (7b)$$

$$\text{at } x=\delta \quad \frac{\partial C_A}{\partial x} = 0 \quad \text{for } 0 < z \leq L \quad (7c)$$

If the region of the liquid film in the direction of the x coordinate, where molecules of the species A prevail, is thin relative to the liquid film thickness, then the liquid velocity in the downward direction in that region can be assumed to be close to the maximum velocity, v_m . This approximation results in the simplification of Eq. (6), making it suitable for obtaining an analytical solution. The simplified version of Eq. (6) is

$$-D_A \frac{\partial^2 C_A}{\partial x^2} + v_m \frac{\partial C_A}{\partial z} + k_1''' C_A = 0 \quad (8)$$

The boundary condition, Eq. (7c), is reduced to

$$x \rightarrow \infty, \quad C_A = 0 \quad \text{for } 0 \leq z \leq L \quad (9)$$

The assumption of constant velocity in Eq. (8) holds under the condition that chlorine is rapidly removed via chemical reaction in the liquid phase relative to its diffusion perpendicular to the gas-liquid interface.

Using the Laplace transform procedure,^[5,6] Eq. (8) is solved to obtain the following result:

$$\frac{C_A}{C_{A0}} = \frac{1}{2} \left[e^{-\sqrt{\beta} z} \operatorname{erfc} \left\{ \frac{1}{2} \sqrt{\frac{\alpha}{z}} - \sqrt{\frac{\beta}{\alpha}} z \right\} + e^{\sqrt{\beta} z} \operatorname{erfc} \left\{ \frac{1}{2} \sqrt{\frac{\alpha}{z}} + \sqrt{\frac{\beta}{\alpha}} z \right\} \right] \quad (10)$$

where

$$\alpha = \frac{v_m x^2}{D_A} \quad (11a)$$

$$\beta = \frac{k_1''' x^2}{D_A} \quad (11b)$$

Equation (10) describes the dimensionless concentration profile, C_A/C_{A0} , as a function of both x and z . Under the limit of $z \rightarrow \infty$ (i.e., sufficiently large z) so that erfc in the first term becomes $\text{erfc}(-\infty)$ and in the second term becomes $\text{erfc}(\infty)$, then Eq. (10) reduces to

$$\frac{C_A}{C_{A0}} = \exp(-\sqrt{\beta}) \quad (12)$$

The molar flux of species A into the liquid film at a z location is given by

$$N_{Ax} \Big|_{x=0} = -D_A \left(\frac{\partial C_A}{\partial x} \Big|_{x=0} \right) \quad (13)$$

The total removal rate of species A (i.e., of Cl_2) from the gas mixture is given by

$$W_A = w \int_{z=0}^{z=L} \left(N_{Ax} \Big|_{x=0} \right) dz$$

$$= w C_{A0} v_m \sqrt{\frac{D_A}{k_1'''}} \left[\left(\frac{1}{2} + u \right) \text{erf}(\sqrt{u}) + \sqrt{\frac{u}{\pi}} e^{-u} \right] \quad (14)$$

where

$$u = \frac{k_1''' L}{v_m} \quad (14a)$$

The expression for the removal rate of species A by its absorption in the absence of chemical reaction is obtained by substituting $k_1''' = 0$ in Eq. (14) and then applying the L'Hopital's rule to determine the resulting indeterminate limit. The result is given by

$$W_{A0} = w C_{A0} v_m \sqrt{D_A} \lim_{k_1''' \rightarrow 0} \frac{\left(\frac{d}{dk_1'''} \left\{ \left(\frac{1}{2} + u \right) \text{erf}(\sqrt{u}) + \sqrt{\frac{u}{\pi}} e^{-u} \right\} \right)}{\left(\frac{d}{dk_1'''} \left\{ k_1'''^{1/2} \right\} \right)}$$

$$= w C_{A0} L \sqrt{\frac{4 D_A v_m}{\pi L}} \quad (15)$$

Finally, the mass transfer enhancement factor is given by

$$E_{mts} = \frac{W_A}{W_{A0}} = \left(\frac{\sqrt{\pi}}{2} \right) \left[\frac{\left(\frac{1}{2} + u \right) \text{erf} \sqrt{u} + \sqrt{\frac{u}{\pi}} e^{-u}}{\sqrt{u}} \right] \quad (16)$$

The second part of the problem is answered by obtaining the numerical data by means of a Fortran program that solves the above theoretical equations.

Error and complementary error functions were computed using the approximation technique from Reference 7. It is noted that $\text{erfc}(x) = 1 - \text{erf}(x)$. The resulting two-dimensional dimensionless concentration profiles of chlorine in the liquid film are shown in Figure 2. The calculated total chlorine removal rate is $W_A = 0.278 \times 10^{-7} \text{ mol s}^{-1}$, and the resulting mass transfer enhancement factor is $E_{mts} = 1.982$.

Validity of the assumption of constant velocity in Eq. (8) was verified by solving Eq. (6) numerically. Analytical solution of Eq. (8) and the numerical solution of Eq. (6) are compared in Figure 3 for two (z/L) locations.

DISCUSSION OF RESULTS

Figure 2 shows the profiles of the dimensionless concentration, C_A/C_{A0} , of chlorine as a function of the dimensionless penetration distance, x/δ , at a num-

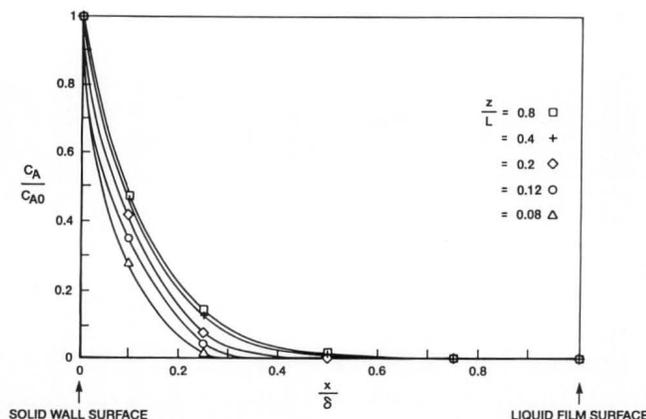


Figure 2. Two-dimensional concentration profiles of chlorine in the falling film of liquid water

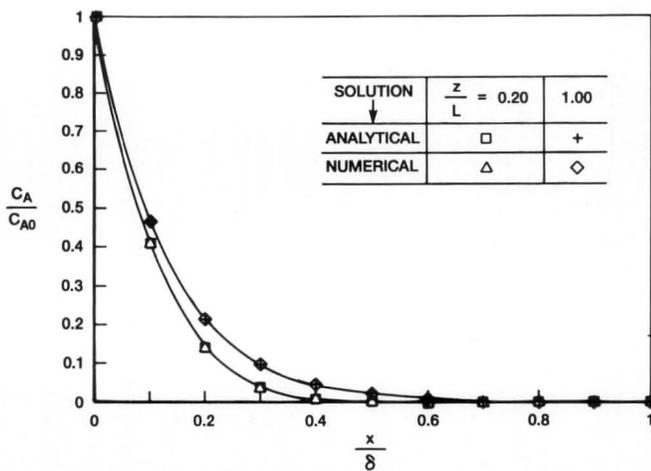


Figure 3. Comparison of the analytical solution of Eq. (8) with the numerical solution of Eq. (6).

ber of dimensionless depths, z/L . A rapid decrease in the chlorine concentration is interpreted in terms of its fast consumption via chemical reaction relative to its diffusion in the liquid phase. Agreement between the analytical solution of Eq. (8) and the numerical solution of Eq. (6) as seen in Figure 3 justifies the assumption of constant velocity in Eq. (8). The mass transfer enhancement factor value of 1.98 is indicative of about double the chlorine removal rate via its absorption without chemical reaction. The model predictions suggest that the continuously flowing liquid films can, indeed, be used for purification of gas mixtures, e.g., chlorine/nitrogen or air mixture, by absorption of trace species, e.g., chlorine, with chemical reaction in the liquid phase.

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REVIEW: Process Design

Continued from page 79.

the major types of equipment in the class, the basic operating principle, literature references, and sketches or photographs of the units. Short-cut sizing techniques and rules-of-thumb are used throughout the chapter for rough sizing. The major feature of the chapter is a set of tables which provide criteria for the preliminary specification of units within each equipment class. The selection tables are organized by principle of operation, applicable capacity range, important data to that class of equipment (i.e., particle size for crushing equipment), material compatibility, type of service, and any other criteria useful for differentiating alternatives within the class of equipment. Qualitative ranking of the units is provided when numerical comparisons are not appropriate for comparing equipment, such as past experience in the suitability of the unit for a particular

problem application. I tried to use the tables by selecting some units that I was particularly familiar with and found that they (and the text) provided enough basic information to describe the unit and give a size range. There is enough information to select a unit given the feed characteristics, but not enough information to do any analysis of the operation of the unit or detailed sizing.

The second section of the book (approximately one hundred and fifty pages) covers "Economic Analysis." Chapters cover capital and manufacturing cost estimation, economic optimization, and cash-flow analysis. The cost estimation techniques presented are adequate for a preliminary estimate. Figures provide capital cost estimates for different types of units, but there is no information about the error or spread of data used to create the figures. The chapter on cash-flow analysis (time value of money) is brief, and the coverage on the treatment of alternative investments could use more examples and discussion.

The final, brief, section is a single chapter on "Technical Reporting." There are many anecdotes to encourage the student to write effectively. It would have been useful to provide example outlines for different types of engineering design reports to give the student an idea of what information is expected, depending on the type of study being done.

After I finished reading the book, there were a number of things that troubled me. The *design process* is not emphasized as an iterative process that requires preliminary sizing and costing and then more detailed study and operations analysis (which may force changes in the original process concept). Little reference is made to modern computer packages that can do both the short-cut and the rigorous mass and energy balances (and sometimes the economics), and which allow the student to do a second pass at the design. The overall plant design is a set of chemical operations for which one must make decisions about unit alternatives as well as the process configuration itself. Process units interact through recycles so that design decisions in one unit can affect the operation, size, and economics of the rest of the plant. Some material and detailed examples on process configuration alternatives (process synthesis) would be useful for the student to see that different process concepts are possible.

If the instructor has a design course that is based on a well-defined case study, then the book provides reference material that would be useful for preliminary unit design and economic analysis. □

UNDERGRADUATE EDUCATION

Where Do We Go From Here?

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Chemical engineering undergraduate education has undergone many changes and transformations over the years. It has moved from a curriculum best described as industrial chemistry through the unit-operations approach, to an emphasis on engineering sciences (*i.e.*, transport phenomena) with greatly increased mathematical sophistication, and ultimately to a heavy infusion of computer-based methods and techniques.

The nature and background of the faculty has also changed. Initially, the typical professor was oriented toward practice and to what some called a handbook-approach to teaching. Later, however, as the unit operations approach took hold, faculty (while still oriented to practice) began to involve themselves in research that was designed to provide an understanding of complex phenomena. The next permutation saw faculty becoming both more mathematically and more scientifically oriented. Further, while engineering research had been mainly experimental in nature, it now began to take on a more theoretical slant. Finally, the "computer revolution" produced a new breed of professors, with many of them geared almost exclusively to a computer approach.

In addition to the above, the relationship of the faculty to industrial practice has also greatly changed. Where it was once common to encounter faculty with industrial experience, there are now far fewer such individuals, particularly among junior profes-

sors. It is not uncommon at some institutions to find many, if not all, of the departmental core courses taught by faculty whose experiences are wholly confined to academia.

The changing curriculum and changing faculty have obviously had a great impact on chemical engineering education (in particular, on undergraduate education). There is no question that today's baccalaureate graduates are considerably different from their predecessors of twenty, ten, or even five years ago. Today's chemical engineering graduates are sharp, they are highly-sophisticated mathematically, and they are quite proficient with respect to the computer.

All would seem to be well. However, when engineers in industry (including new hires) are asked to evaluate today's undergraduate chemical engineering education, they raise a number of questions. For example, newly-minted engineers complain about a lack of "practical information" in their training. The serious thing about this charge is that it even comes from students who have graduated from institutions which strongly emphasize practice rather than theory. Complaints of older engineers range from an inability of new hires to carry out well-known procedures to their lack of even a rudimentary understanding of equipment.

At this point, a number of different opinions would be elicited. One type of response would be that there is no problem and that all is well. Others, however, would probably recommend a massive reorganization of chemical engineering education in order to cure any and all perceived problems.

Actually, both camps are correct in their evaluation. Massive changes in curriculum, courses, *etc.*, are not needed; what *is* needed is a change in the way the material is presented. We must move from an over-balance and dependence on theory, mathe-



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One type of response would be that there is no problem and that all is well. Others, however, would probably recommend a massive reorganization of chemical engineering education . . .

matics, and the computer, to a new approach that not only recognizes and maintains those gains but also clearly links them to engineering practice.

How do we do this? We do it by changing the style and philosophy of teaching our undergraduate courses. At the risk of oversimplification, the following points should be considered:

- Continue to teach fundamentals, but emphasize the first principles even more strongly.
- Make the greatest possible use of phenomenological approaches.
- Clearly delineate the progression, use, and relationships between theoretical, semi-empirical, and empirical approaches.
- Emphasize practice by continually interlinking theory to actual or real situations. Do this quantitatively; if unable to do so, use qualitative and/or anecdotal examples.
- Build on first principles by using homework or examination problems that emphasize applications in different, new, or novel areas or applications (*i.e.*, enable the graduate to move into new areas of technology).
- Put mathematics into its proper perspective (*i.e.*, useful and important, but not the be-all or end-all).
- Use the computer, but emphasize that it is a means, not an end, and that garbage in gives garbage out.
- Work into each course the concepts of process and equipment.
- Emphasize innovation, creativity, and ingenuity, remembering that an engineer is a "person who carries through an enterprise by skillful or artful contrivance."

A response to the preceding might be that we already do these things in academia, so why bother? It should be evident that even if we are doing them, as academics we are falling short and must therefore emphasize them even more strongly.

Another comment might be that these are admittedly worthwhile objectives, but how can they be implemented? A possible scheme for implementation in chemical engineering departments would be to:

- Commit to a teaching philosophy that emphasizes the preceding points as well as others that accomplish the same goals.

- Take advantage of the valuable resource of faculty with industrial experience to track the undergraduate core courses so that theory and practice can be effectively interlinked.

- Utilize, as well, those faculty members who specialize in experimental research so that the aspects of equipment and processes can be emphasized.

- Develop good rapport with industry so that examples, guest lecturers, *etc.*, can be used to enrich core courses.

- Build on science and mathematics, but clearly emphasize the fact that engineering is different.

- Evaluate all of the preceding by contacts and discussions with recent graduates and more mature practicing engineers.

- Keep the undergraduate curriculum dynamic, recognizing that static situations produce deterioration.

Hopefully, this paper will stimulate discussion and more detailed consideration of undergraduate education in chemical engineering. This in itself would be a rewarding and beneficial exercise. □

ChE book review

VISCOUS FLOWS: THE PRACTICAL USE OF THEORY

by *Stuart Churchill*

Butterworths, 80 Montvale Avenue, Stoneham, MA 02180; \$52.95, 602 pages (1988)

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Professor Churchill has produced a textbook aimed at the student with prior background in fluid dynamics, although he states that it has been used with "surprising success" as a first course for undergraduates when the material is presented at a slower pace and with some deletion of detail. My own impression is that this book could indeed be used in a junior-level fluids course, but that its success would depend to a great degree on the skill of the teacher in choosing the topics to be included, and in supplementing the material of the text with ample classroom discussion so as to provide a broader context in which fluid dynamics is seen as an essential element of chemical process engineering. In the hands of a teacher whose main focus would be on the derivation of solutions to various fluid dynamics problems, the use of this text would be less successful in providing

Continued on page 111.

PURDUE-INDUSTRY COMPUTER SIMULATION MODULES

The Amoco Resid Hydrotreater Process

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The senior chemical engineering laboratory is a required part of most accredited chemical engineering programs and is considered a "capstone" course, drawing as it does on students' previous technical work. Furthermore, the senior laboratory typically requires the students to use their written and oral communication skills and, since lab projects are often group efforts, their interpersonal skills as well.

In Purdue's laboratory course students work together in groups of three, consisting of a group leader, an experimentalist, and a design engineer. Each group works on three month-long projects chosen from a list of about a dozen experiments which involve processes such as extraction, filtration, distillation, gas- and liquid-phase reaction, ion exchange, heat transfer, fluid flow, mixing, and diffusion.

In our view, the ideal laboratory experiment should duplicate a real industrial process. The students would use modern equipment to investigate a complex problem, and would do so under realistic time and budget constraints. Since universities can hardly afford to construct or operate industrial-scale plants, the next best alternative is to devise experiments which closely *simulate* the operation of industrial processes. With this in mind, we are developing a series of computer simulations intended for use in undergraduate chemical engineering laboratories. These simulations model actual industrial chemical processes and are being produced with the assis-

In our view, the ideal laboratory experiment should duplicate a real industrial process. The students would use modern equipment to investigate a complex problem . . .

¹ Amoco Corporation; ² Northwestern University

TABLE 1
Process Simulations and Industrial Sponsors

Company	Process
Amoco	Hydrodesulfurization
Mobil	Catalytic Reforming
Dow Chemical	Latex Emulsion Polymerization
Tennessee Eastman	Methyl Acetate from Coal
Air Products	Process Heat Transfer

tance of various corporate sponsors. The first five are listed in Table 1.

AMOCO RESID HYDROTREATER

The first simulation that we have completed models a hydrodesulfurization pilot plant (see Figure 1) built by Amoco in its Naperville, Illinois, research facility. The hydrotreater takes a mixture of heavy, high-sulfur hydrocarbons (called "resid oil") and upgrades it by

- breaking the long carbon chains to form smaller chains
- adding hydrogen to increase the saturation
- removing sulfur in the form of H₂S gas

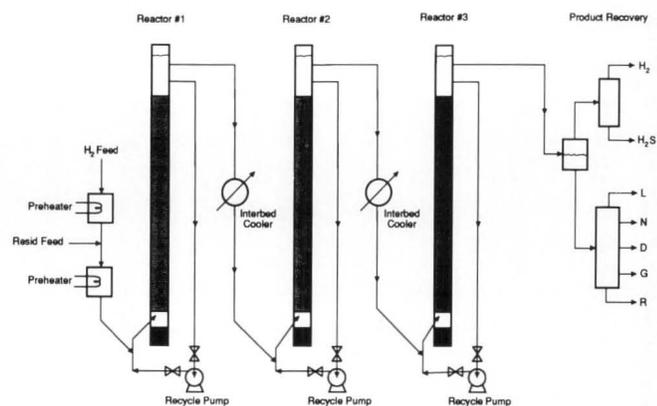
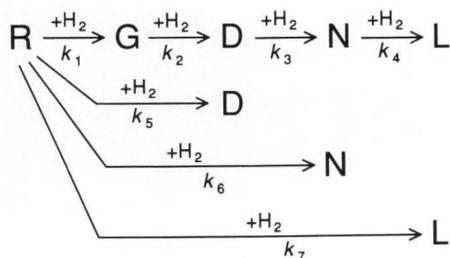


Figure 1. Amoco hydrodesulfurization pilot plant. The three ebullated-bed columns are well mixed by the recycle streams.

Non-Catalytic Reactions



Catalytic Reaction

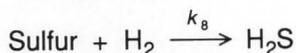


Figure 2. Hydrodesulfurization reaction scheme. Each of the components R, G, D, N, and L is a mixture of many different compounds, lumped together by boiling point.

The reaction scheme is shown in Figure 2. Each of the components R, G, D, N, and L is a complicated mixture of many different chemical species, the actual composition of which would be very difficult to specify exactly. R, G, D, N, and L are characterized by their average boiling points and their sulfur content (see Table 2).

The hydrogenation reactions (reactions 1 through 7) are modeled as a set of sequential and parallel first-order reactions. The net generation rates are given by

$$\begin{aligned}
 r_R &= -(k_1 + k_5 + k_6 + k_7)R \\
 r_G &= -k_2G + C_{RG}k_1R \\
 r_D &= -k_3D + C_{RD}k_5R + C_{GD}k_2G \\
 r_N &= -k_4N + C_{RN}k_6R + C_{DN}k_3D \\
 r_L &= C_{NL}k_4N + C_{RL}k_7R
 \end{aligned}$$

where R, G, D, N, and L are the weight fractions of the sulfur-free components; k_1, k_2, \dots , are rate constants, and $C_{RG}, C_{RD}, \dots, C_{RL}$ are stoichiometric coefficients.

The desulfurization reaction (reaction 8) is catalytic. It is first order in hydrogen, second order in sulfur, and inhibited by resid:

$$-r_s = \frac{Ak_8\pi S^2}{1 + K_9R}$$

Here A is a catalyst deactivation factor ($A = 1$ for fresh catalyst), π is the partial pressure of hydrogen, k_8 is a kinetic rate constant, and K_9 is an equilibrium constant.

The rate constants for reactions 1 through 8 are given by Arrhenius-type relations

$$k_i = a_i \exp(-E_i / RT), \quad i = 1, \dots, 8$$

where a_i is the pre-exponential factor and E_i is the activation energy for the i^{th} reaction.

The reactions are carried out in well mixed, ebullated-bed reactors, which are modeled as continuous stirred-tank reactors (CSTRs). Under some conditions, the simultaneous solution of the mass and energy balances for a CSTR may exhibit multiple steady states (see Figure 3). The reactors usually operate at the intermediate steady state, which is unstable with respect to temperature; at the lower steady state the conversion is too low and at the upper steady state the temperature is too high.

THE COMPUTER PROGRAM

The program consists of more than 10,000 lines of FORTRAN and C code. It can simulate the steady-state behavior of one, two, or three reactors in series,

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TABLE 2
Reactants

Component	Average B.P. (°F)	Sulfur (wt. %)
Resid (R)	>1200	5.0
Gas Oil (G)	827	2.0
Distillate (D)	514	1.0
Naphthas (N)	280	0.5
Light Gas (L)	<200	0.0

or the dynamic behavior of a single reactor. The program currently runs on the Sun 3/60 workstation, although it can be readily modified to run on any machine that supports the X Window System.

A graphical user interface makes the program easy to use, even for students having minimal experience with Sun computers. The user employs a mouse to select from options presented on "pull-down" menus. Should the user get lost or forget what to do, he or she can get help from the program itself.

USE OF THE MODULES AT PURDUE

Eight three-hour lab periods are allotted to each project. In preparation for the first scheduled lab period, the students are asked to study a written description of the process and to view a short videotaped "plant tour" supplied by the corporate sponsor. They also attend an orientation meeting with the instructor, where general questions about the process, the simulation, and the lab are answered.

THE INITIAL ASSIGNMENT

In keeping with our attempt to provide realism in the project, the students are given their assignment on official Amoco stationery. They are required to do the following things:

- Determine the values of the pre-exponential factors for the hydrogenations
- Check activation energy for one of the hydrogenations
- Determine the pre-exponential factor a_8 and activation energy E_8 for the desulfurization
- Check the form of the catalyst deactivation equation and measure the catalyst deactivation rate

The assignment letter authorizes the students to run the Naperville pilot plant and two small laboratory reactors.

BUDGETARY LIMITATIONS

Contributing to the sense of realism in this module is a requirement that the students work within a budget. Initially they are given \$150,000 (simulated money, of course!) with which to work. Table 3 lists the time and money required for various tasks involving the pilot plant and laboratory reactor. Note that the students are charged a fee each time they seek help from the "consultant" (*i.e.*, the instructor).

THE PLANNING CONFERENCE

The students spend the first two lab periods preparing a plan of attack, which they must present to the instructor in a planning conference before the

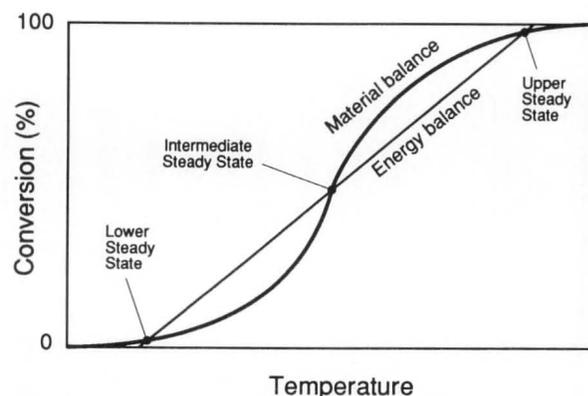


Figure 3. Multiple steady states in a CSTR. The system usually operates at the intermediate steady time.

third period. In this conference the instructor asks the students to describe, in order, the experiments they intend to carry out. At each step they must justify their plans. The instructor asks questions and gives hints where necessary, but is careful not to reveal too much about the solution to the problem.

The students are faced with a number of choices regarding the type and number of reactors, the catalyst age, the feed composition, and the reactor temperature. In making these choices, they have to keep in mind a number of constraints:

- It takes five days¹ and \$75,000 (half the budget) to clean and prepare the pilot plant.
- It costs another three days¹ and \$50,000 to replace the catalyst in the pilot plant; obviously, the students cannot afford to change their minds on the catalyst selection.
- Each pilot plant run takes twenty-four hours.¹
- The pre-exponential factors a_1, \dots, a_7 must be measured in the pilot plant.
- Other constants can be obtained from the lab reactor, but their values must be checked in the pilot plant.

It makes sense to use the lab reactors as much as possible, since they are considerably cheaper to operate than the pilot plant. Furthermore, the lab reactors are easily refilled with catalyst, permitting the students to take data related to catalyst age. However, all constants that are determined from laboratory data *must* be checked in the pilot plant. (By "checked" we mean that four or five points over a reasonable range should agree with the previously determined values.)

STEADY-STATE SIMULATION

Once the students have demonstrated to the instructor's satisfaction that they have a good grasp of the problem, they are shown how to operate the computer program in the steady-state mode. This enables them to simulate the operation of the labo-

¹ Simulated time

ratory reactors and the pilot plant, from which they can obtain the required kinetic constants.

The students are permitted to take data from the third through the sixth lab period. During the sixth period the group leader is required to give a fifteen-minute oral progress report, which is videotaped and critiqued in private with the speaker.

DYNAMIC SIMULATION

After the group leader's progress report, the instructor shows the students how to run the simulator in the dynamic mode. The students are then given a second assignment letter informing them that they have been selected to act as consultants during the start-up of a resid hydrotreater at Amoco's Texas City refinery. They are asked to simulate the start-up of a single reactor, controlling the operating conditions manually to reach steady state. Then they are to cease controlling the system and to note the time that elapses before automatic shutdown occurs.

The start-up problem is especially challenging because the operating conditions within the reactor can only be controlled indirectly, by setting the temperature, flow rate, and composition of the feed stream. Furthermore, instantaneous changes in these variables are not permitted; the students must wait fifteen minutes between changes in the feed settings, and they are limited to changing feed temperature by no more than 100 F at a time. Finding a suitable control strategy is typically a trial-and-error process. (Dynamic simulation runs are not charged against the students' budgets.)

Two lab periods are allotted for the start-up problem. The students then have one week to produce a full written report, including the results of their

TABLE 3
Expenses

Initial preparation and start-up of pilot plant (includes cost of initial charge of catalyst)	5 days	\$75,000
Replacement of catalyst in pilot plant	3 days	\$50,000
One pilot plant run (includes labor, materials, analysis, etc.)		
Three reactors in series	24 hours	\$4,500 ¹
Two reactors in series	24 hours	\$4,000 ¹
One reactor	24 hours	\$3,500 ¹
One laboratory reactor run (includes catalyst replacement)	24 hours	\$500 ¹
Consultation	?	\$500

¹Multiply by 1.5 for Saturday runs; by 2.0 for Sunday runs

steady-state experiments and an outline of their recommended start-up procedure.

ROLE OF THE INSTRUCTOR

The instructor has four important parts to play in a simulation project:

1. *Mother Nature*—sets the mean values and random variability of all parameters used in the simulation
2. *Boss*—receives the oral and written reports from the group
3. *Consultant*—helps with specific technical questions, but charges a fee that must be paid from the budget.
4. *Instructor*—assigns the grades, of course.

COMPUTER SIMULATIONS FOR EDUCATION

Although it would be possible to design a senior laboratory made up entirely of computer-simulated experiments, we believe that students should also gain "hands-on" experience by working with real laboratory equipment. For this reason, we allow only one of the three required experiments to be a computer project.

We have used the Amoco module here at Purdue for five semesters, with great success. As an alternative to traditional lab experiments, computer simulation offers a number of significant advantages:

- Processes that are too large, complex, or hazardous for the university lab can be readily simulated on the computer.
- Realistic time and budget constraints can be built into the simulation, giving the students a taste of "real world" engineering problems.
- The emphasis of the laboratory can be shifted from the details of operating a particular piece of laboratory equipment (which may not be representative of current industrial practice) to more general considerations of proper experimental design and data analysis.
- Computer simulation is relatively inexpensive compared to the cost of building and maintaining experimental equipment.
- Simulated experiments take up no laboratory space and are able to serve large classes because the same computer can run many different simulations.

AVAILABILITY OF THE MODULES

Anyone interested in obtaining more information on the Purdue-Industry ChE Simulation Modules should contact Professor Squires. An NSF-sponsored workshop on the modules will be held at Purdue on July 26-28, 1991.

ACKNOWLEDGMENTS

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CRYSTALLIZATION

An Interesting Experience in the ChE Laboratory

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The economy of Chile is strongly based on metallic mining activity. However, large reserves of salt and brines available in northern Chile have led to a significant increase in the amount of research effort expended on non-metallic mining exploitation and processing. Wealthy reserves of lithium, potassium, nitrates, sulphates, boron, etc., including varied crystalline forms, are found there.

The Universidad de Antofagasta has played an important role in the development of these non-metallic mining research projects. Crystallization has been one of the chosen subjects and has been taught during the last three terms in the department of chemical engineering.

Crystallization is offered as a four semester-hour course, including lecture and laboratory work which consists of four experiments. The one described in this paper is aimed at the study of sodium-sulphate crystallization in a MSMPR continuously-agitated crystallizer tank. It is intended for the study of crystallization kinetics of decahydrated sodium sulphate.

The nucleation growth rate kinetics were evaluated by measuring the crystal size distribution (CSD) and using the mass, energy, and population balances.

CRYSTALLIZATION KINETICS

Industrial crystallization is defined as a technique aimed at producing crystals with specific characteristics of purity and size distribution. Crystallization is an extremely complex process which is affected by a number of variables, such as supersaturation level, temperature, agitation, impurities, mechanical effects, etc. Important advances related to analytical description and process understanding

have been achieved since the 1960s.

The population-balance approach to the description of crystal size distribution is the most widely accepted approach, and it has proved to be the most fertile in germinating new developments for describing and modeling crystallizers.

The population-balance equations were first formalized by Randolph and Larson.^[1] They allowed us to get the nucleation and crystalline growth kinetics. Two phenomena are involved in the crystallization process: the formation of new particles by nucleation processes and crystal growth processes. They both depend on supersaturation, but in different manners.

During nucleation, small regions are formed within the homogeneous phase that consist of variable numbers of ordered atoms or molecules, called clusters or embryos. Some of these are in equilibrium with the mother liquor. This cluster, termed a critical nucleus, is converted during further growth into a macrospecies which forms the new phase.

Kinetics data on crystallization processes are of basic importance for the design of industrial crystallization equipment. These data determine the size of the crystallizer and the crystal size of the product.



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POPULATION BALANCE

A population balance general relationship valid in a crystal size range L_1 to L_2 (ΔL) and in the period of time Δt , is the starting point in the analysis.

N of crystals entering the reactor with size ΔL + N of crystals entering range ΔL because of growth = N of crystals exiting the reactor with size ΔL + Crystals exiting the range ΔL because of growth

- a) The number of crystal seeds entering the crystallizer having a size range ($L_1, L_1 + \Delta L$) during Δt interval, is given by

$$Q_1 \cdot n_s \cdot \Delta L \cdot \Delta t \quad (1)$$

where n_s is the population density at the inflow, $n_s \Delta L$ represents the fraction of crystals with size ΔL , and Q_1 is the volumetric inflow.

- b) The number of crystals entering to ΔL range in the Δt interval due to G_1 growth is given by

$$V \cdot G_1 \cdot n_1 \cdot \Delta t \quad (2)$$

where V is the volume of the crystallizer. The growth function of G_1 crystals is represented as a supersaturation and crystal size function.

$$G = G(L, \Delta C) \quad (3)$$

$$G = G_c(C) \cdot \phi(L) \quad (4)$$

- c) The number of crystals having a size range ($L_1, L_1 + \Delta L$) which are removed from the reactor during Δt interval are given by

$$Q_2 \cdot n \cdot \Delta L \cdot \Delta t \quad (5)$$

where n is the population density at the exit and Q_2 is the volumetric exit flow.

- d) The number of crystals growing outside the size range ($L_1, L_1 + \Delta L$) at Δt interval is

$$V \cdot G_2 \cdot n \cdot \Delta t \quad (6)$$

Then the population balance [using Eqs. (2) to (5) in the size range ($L_1, L_1 + \Delta L$)] is

$$V G_1 n_1 \Delta t + Q_1 n_s \Delta L \Delta t = V G_2 n \Delta t + Q_2 n \Delta L \Delta t \quad (7)$$

Carrying out the appropriate arrangements in Eq. (7) and considering that there are no crystals in the feeding, yields

$$-\frac{d(Gn)}{dL} = \frac{Q_2}{V} n \quad (8)$$

Defining the half-time residence as

$$\tau = \frac{V}{Q} \quad (9)$$

The population-balance equations were first formalized by Randolph and Larson. They allowed us to get the nucleation and crystalline growth kinetics. Two phenomena are involved in the crystallization process: the formation of new particles by nucleation processes and crystal growth processes.

and assuming steady state

$$\frac{d(Gn)}{dL} + \frac{n}{\tau} = 0 \quad (10)$$

Integrating Eq. 10, by separation of variables when $G \neq G(L)$, yields

$$n = n_0 \exp(-L / G\tau) \quad (11)$$

in which n_0 is the nuclei population density.

Therefore Eq. (7) represents the crystal size distribution (CSD) of the process, where the distribution function n represents the number of particles having a certain size range per unit volume and a characteristic size.

$$n(L) = \frac{\text{Number of particles with size between } L \text{ and } (L + \Delta L)}{(\text{Volume})(\Delta L)} \quad (12)$$

This size distribution function can be directly obtained by determining the number of particles associated to each size range, as

$$\Delta N = \frac{\text{Mass of crystals retained in a sieve} / \rho_c}{(\text{average size particle volume})(\text{volume})} \quad (13)$$

where ρ_c is the crystal density. Using an average size

$$L = \frac{L_1 + L_2}{2} \quad (14)$$

and defining the particle volume as

$$V_p = k_v L^3 \quad (15)$$

in which k_v is the crystal shape factor

Also

$$\Delta L = L_2 - L_1 \quad (16)$$

where L_1 is the lower mesh opening (through which the particles enter) and L_2 is the retaining mesh opening of the sieve. Therefore

$$n = \frac{\Delta N}{\Delta L} \quad (17)$$

$$n = \frac{W}{\rho_c k_v L^3 \Delta L V_s} \quad (18)$$

where V_s is the volume occupied by the solution. Then it is possible to interpret the population

density of zero particle size, or nuclei number density, n^0 , as

$$n^0 = B/G \quad (19)$$

resulting in Eq. (11)

$$\ln(n) = \ln \frac{B}{G} - \frac{1}{G\tau} L \quad (20)$$

This equation is very important, since by using experimental distribution functions (obtained through screening tests) it is possible to find the adequate system kinetic model. Representing graphically $\ln(n)$ versus L we obtain a straight line of slope $-1/G\tau$ and intercept B/G from which the growth velocity G can be determined at specific values of τ . In addition, it is possible to obtain the value of nucleation velocity B .

EXPERIMENT

The experimental equipment used in this study (see Figure 1) was a translucent acrylic MSMPR crystallizer, cylindrical in shape and 15.2 cm diameter by 39 cm height. Inside the tank there were three baffles and a 10 cm diameter by 15.2 cm height concentric tube, located at 6.5 cm distance from the bottom of the tank. The overflow volume is 3.250 ml. The system was provided with agitation similar to a perfect mixed crystallizer proposed by Randolph.^[3]

Due to the significant decrease in solubility exhibited by decahydrated sulphate sodium solution with decreasing temperature, the crystallization was carried out by cooling. The feeding solution was pumped from a storage container provided with a heater (25 ± 0.1 C) to the crystallizer (using a double-head peristaltic pump in order to obtain a perfectly regulated flow). The crystallizer was maintained at 18 C inside a 20 l thermostatic bath, obtaining the supersaturation by cooling. The feeding flow was monitored with a Gilmont rotameter provided with a precision valve.

One of the experiments was carried out at 500 rpm for a residence time of 0.62 hours. The solution flow for this experiment was established measuring the solution density in order to reach the steady state. After steady state was reached, the outlet flow was vacuum-filtered and the product was washed with acetone to eliminate residual water and avoid agglomeration of crystals. After the drying stage the crystals were screened in a Rotap provided with standard Tyler sieves with mesh of 16, 18, 20, 30, 40, 50, 70, 100, and 140, by which the crystal size distribution was obtained.

RESULTS

Table 1 shows the experimental steady-state data for an experiment at 500 rpm with a residence time of 0.62 hours and the conditions mentioned in the previous section.

Equations (13) to (18) were used in order to obtain the values of the crystal size distribution function. The former results were plugged into the population balance from which the experimental results, plotted in Figure 2, were obtained.

To determine the crystal shape factor under the conditions used in this work, small samples of known crystal size were counted and weighted, determining the shape factor by the relation

$$k_v = \frac{W}{\rho_c(L)^3 \Delta N} \quad (21)$$

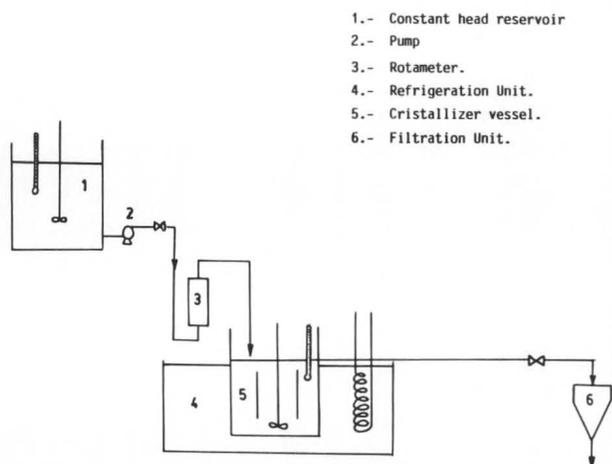


Figure 1. Experimental equipment

TABLE 1
Experimental Data

VOLUMETRIC FLOW Q_A (cc/min)	CRYSTAL DENSITY ρ_c (g/cc)	OPERATION TIME top (min)
102	1.464	15
Mesh	Sieve Opening L (mm)	Sieve Mass (g)
16	1.180	9.12
18	1.000	32.12
20	0.850	39.82
30	0.600	235.42
40	0.425	89.14
50	0.300	54.42
70	0.212	22.02
100	0.150	7.22
140	0.106	1.22
BED	-	0.50

Sample Mass M_c (g) = 490.99

where ΔN is the number of crystals in the sample of mass W . An average shape factor of 0.553 was obtained.

From the data plotted in Figure 2, we obtain the slope and interception values by applying a linear regression method to Eq. (20), obtaining

$$\frac{1}{G\tau} = 4.9951 (1/\text{mm})$$

$$B/G = 2.7154 \times 10^7 (\text{crist./1 mm})$$

with a correlation factor = 0.979.

Clearing the equation, we obtain the growth and nucleation velocity

$$G = 0.3216 (\text{mm/h})$$

$$B = 1.04451 \times 10^7 (\text{crist./1 h})$$

CONCLUSIONS

The laboratory experiment described above allows a good understanding of the crystallization process. The key factors affecting this process (*i.e.*, agitation, size distribution, nucleation) are better grasped by the student when theoretical equations are worked out together with real-life processes.

Even though this work presented only one set of experimental data, the experiment itself is very flexible since it is possible to work out various situations under different conditions (temperature, concentra-

tion, spatial time, agitation velocity, etc.). For instance, the parameters affecting the B and G values can be determined by testing B and G under different operating conditions. Thus the students can find a kinetic equation of the studied system, through $B = k(G)^b$. Furthermore, it also allows the student to understand the influence that each variable has in the crystallization process, *i.e.*, agitation velocity. In industrial processing this has great importance since a homogeneous crystal size distribution is required by connecting processes such as centrifugation, among other things.

Due to its simple phase diagram, the $\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ system is a good example for experimental study and teaching purposes. In fact, this system exhibits direct and reverse solubility between 0 and 60 C with formation of different hydrates. For the reason stated below, the experiment allows a good versatility in crystallization products when working under different operating conditions.

The graphical representation of the equilibrium phases as well as the distribution of crystal size is an effective way to understand the phenomenon from a physical point of view. Also, the solubility diagram allows the student to calculate theoretical output by means of simple material balances.

By analyzing the experimental data (presented in Table 1) the crystal mass turned out to be 490.95 g, and the predicted value was expected to be 500 g. This result means a 2% accuracy when the crystal performance is considered. The resulting difference may be due to the fact that some of the crystals produced remain attached to the crystallizer walls and to the losses in the drying and filtration processes.

Since in the former graph a linear relationship was obtained, it can be stated that the experiment was performed under the basic assumptions of crystal growth independent of its size and steady-state conditions.

ACKNOWLEDGEMENT

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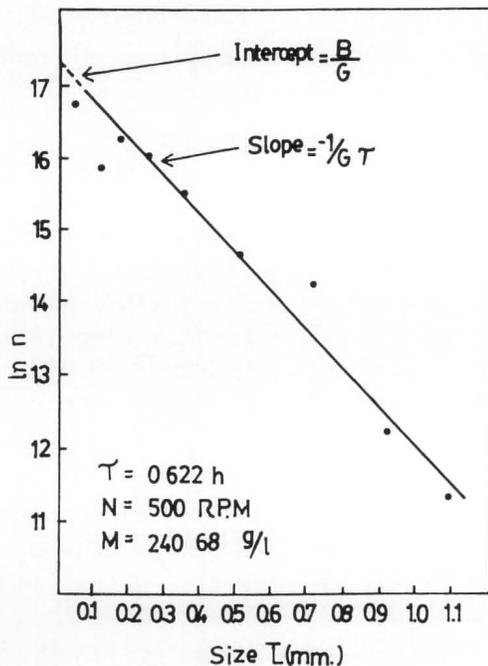


Figure 2. Crystal size distribution obtained from a laboratory-scale MSMCR crystallizer

PRINCIPLES OF STAGewise SEPARATION PROCESS CALCULATIONS

A Simple Algebraic Approach Using Solvent Extraction

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Traditionally, graphical techniques such as the McCabe-Thiele and Ponchon-Savarit methods have been used to introduce undergraduate chemical engineering students to the design and analysis of multistage separation processes. While the students have quickly grasped the concepts of simultaneously solving the material balances and phase equilibrium relationships, their understanding of transforming such principles into graphical methods has often been slow to develop. A strong emphasis on the use of computers from the beginning of the first-year course at Bath has resulted in students who find it increasingly difficult to adapt their minds to solving complex problems by graphical methods.

Building on the mathematical expertise of freshmen, a simple liquid-liquid equilibrium (LLE) system has been used to demonstrate most of the essential features of multistage contacting, whether cross- or counter-current. Solutions to the material balances and phase equilibria are all algebraic and simple to derive and only an elementary knowledge of series summation is required to derive the solution for minimum solvent-to-feed ratio. The simple LLE system can then be used to introduce students to the graphical techniques which are necessary for complex equilibria.



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BACKGROUND

At the University of Bath, lecture programs in separation processes are given in each of the three taught years in the BEng Honours degree courses in chemical engineering and chemical and bio-process engineering. Most students elect to spend their third year on industrial placement, working effectively as graduate engineers with leading process engineering companies. Thus it is important that all the core material in separation processes is given in the first two years of the BEng courses.

In the first year, students are expected to gain an understanding of the fundamental principles of phase equilibria and their application (with material and energy balances) to the design and operation of common separation processes. Examples are drawn especially from binary distillation, solvent extraction, batch adsorption, batch crystallization, *etc.*

In the second year, the principles of continuous-phase contacting are presented, using examples drawn especially from gas absorption, stripping, distillation, and solvent extraction. The selection and sequencing of separation processes, together with the principles and practices of multicomponent separations, adsorption, membrane processes, and other highly-selective separations are reserved for the final year lecture course.

Modern textbooks in chemical engineering continue to adopt the use of graphical techniques to explain stagewise separation process calculations. The main advantage of using such techniques at the outset is realized by the lecturer, who can easily create visual aids to explain concepts such as cross-current multistaging, countercurrent multistaging, minimum solvent flowrate, minimum reflux ratio, total reflux, *etc.*

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However, while some students readily understand that graphical methods are based on the fundamental material balances and phase relationships, there are many students who find the use of hypothetical pole points or difference streams to be mysterious techniques. In addition, with the advent of modern, powerful computers and supporting software, the use of graphical methods (with their inherent inaccuracies) should be discouraged for all except check calculations or for systems with complex equilibria which are difficult to model thermodynamically.

Most freshmen already appreciate the basic concepts of partitioning a solute between a solvent and a diluent. They are also mathematically competent. With these points in mind, the first-year course in separation processes now commences with a totally algebraic approach to stagewise contacting, using a simple liquid-liquid equilibrium system to illustrate a number of important aspects of stagewise contacting. For solvent extraction, these are

- the equilibrium stage model
- simultaneous solution of single-stage material balances and phase equilibria
- multistage cross-current contacting
- efficient use of solvent in multistage cross-current contacting
- multistage counter-current contacting
- advantage of counter-current contacting over cross-current contacting
- minimum solvent-to-feed ratio

The use of solvent extraction to explain important facets of stagewise contacting is particularly apt since this process is one of five which have been identified by the UK Science and Engineering Research Council as requiring special research attention under its Separation Processes Initiative. Others include membrane processes, selective adsorption, highly-selective separations, and the opportunities for exploiting centrifugal fields.

SIMPLE LIQUID-LIQUID EQUILIBRIUM

The algebraic analyses are restricted to the simplest case of extraction of a solute from a diluent by means of a solvent which is immiscible with the diluent even in the presence of the solute. The distribution coefficient K for the solute is constant and is given by

$$K = \frac{Y}{X} = \frac{\text{mass of solute per unit mass of solvent in extract}}{\text{mass of solute per unit mass of diluent in raffinate}}$$

In the first year, students are expected to gain an understanding of the fundamental principles of phase equilibria and their application (with material and energy balances) to the design and operation of common separation processes.

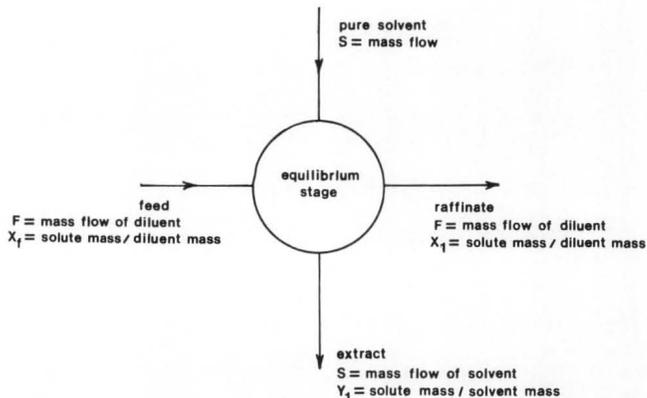


FIGURE 1. Single equilibrium stage with pure solvent.

The use of mass ratios in place of mass fractions is readily understood by the students. The simple conversions are given later in this article.

SINGLE EQUILIBRIUM STAGE

Students are encouraged to read about discrete stage solvent extraction equipment such as the mixer-settler. A single equilibrium stage is shown schematically in Figure 1. To keep the problem as simple as possible, a feedstock containing only solute and diluent is contacted with a pure solvent. The performance of the unit is calculated as a function of the following parameters:

S = mass flow of solvent

F = mass flow of diluent in feedstock

X_f = mass of solute per unit mass of diluent in feedstock

X_1 = mass of solute per unit mass of diluent in raffinate

The material balances for diluent and solvent are trivial because these two components are immiscible. The solute material balance is

$$X_f F = X_1 F + Y_1 S \quad (1)$$

The assumption that the stage behaves as an equilibrium stage means that the phases leaving are in equilibrium, *i.e.*,

$$Y_1 = KX_1 \quad (2)$$

Hence the performance of the single stage is given

by the simultaneous solution of Eqs. (1) and (2)

$$\frac{X_1}{X_f} = \frac{1}{(r+1)} \quad (3)$$

where

$$r = KS / F \quad (4)$$

It is readily seen from Eq. (3) that the amount of solute extracted can be improved by one or a combination of the following:

- increasing the solvent-to-feed ratio
- increasing K either by changing the temperature or by using another solvent
- passing the raffinate as the feedstock to second and further equilibrium stages, *i.e.*, cross-current extraction shown schematically in Figure 2.

MULTISTAGE CROSS-CURRENT EXTRACTION

Provided that an equal flowrate of pure solvent S is fed to each stage, the solute balance for the general stage n is

$$X_{n-1}F = X_nF + Y_nS \quad (5)$$

Applying the equilibrium relationship yields

$$\frac{X_n}{X_{n-1}} = \frac{1}{(r+1)} \quad (6)$$

Hence for a battery of N equilibrium stages

$$\frac{X_N}{X_f} = \frac{1}{(r+1)^N} \quad (7)$$

From Eq. (7) it can be seen that X_N/X_f tends to zero as N tends to infinity.

EFFICIENT USE OF SOLVENT

Equation (7) can be used to show that a greater extraction of solute can be obtained if the total flow of solvent is split between a number of equilibrium stages rather than all the solvent being used in a single equilibrium stage. This general result is most easily demonstrated by the example of splitting the solvent equally between two equilibrium stages. For

this case

$$\frac{X_2}{X_f} = \frac{1}{\left\{\frac{r}{2} + 1\right\}^2} = \frac{1}{\left\{\frac{r}{2}\right\}^2 + r + 1} \quad (8)$$

Comparison of Eq. (8) with Eq. (3) confirms the improvement in the extraction of solute, but at the additional expense of providing an extra equilibrium stage. The general result for splitting a total flow of solvent S equally into N stages is

$$\frac{X_N}{X_f} = \frac{1}{\left\{\frac{r}{N} + 1\right\}^N} \quad (9)$$

MULTISTAGE COUNTER-CURRENT EXTRACTION

The counter-current extraction scheme is shown in Figure 3. A solute balance across stage 1 gives

$$X_fF + Y_2S = X_1F + Y_1S \quad (10)$$

but

$$Y_1 = KX_1 \quad \text{and} \quad Y_2 = KX_2$$

Hence

$$X_1 - X_f = r(X_2 - X_1) \quad (11)$$

Applying solute balances across each stage in turn yields

$$X_2 - X_1 = r(X_3 - X_2) \quad (12)$$

$$X_n - X_{n-1} = r(X_{n+1} - X_n) \quad (13)$$

$$X_N - X_{N-1} = r(X_{N+1} - X_N) \quad (14)$$

Eliminating X_1 from Eqs. (11) and (12) gives

$$X_2 - X_f = \{r + r^2\}(X_3 - X_2) \quad (15)$$

With further eliminations of intermediate raffinate compositions, it can be shown that

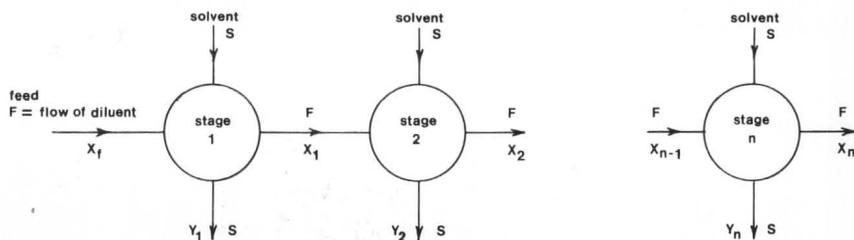


FIGURE 2. Multistage cross-current extraction with pure solvent.

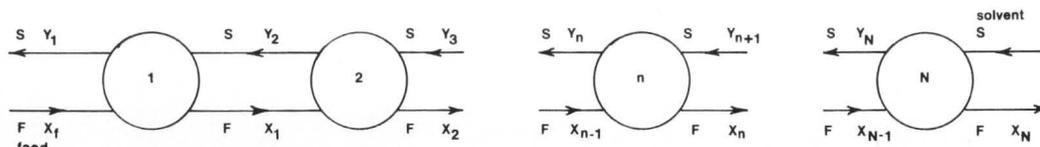


FIGURE 3. Multistage counter-current extraction with pure solvent.

$$X_n - X_f = \{r + r^2 + r^3 + \dots + r^n\}(X_{n+1} - X_n) \quad (16)$$

i.e.,

$$X_n - X_f = \{X_{n+1} - X_n\} \sum_{i=1}^n r^i \quad (17)$$

and hence

$$X_N - X_f = \{X_{N+1} - X_N\} \sum_{i=1}^N r^i \quad (18)$$

Since X_{N+1} would be nominally in equilibrium with a pure solvent stream S,

$$X_{N+1} = 0 \quad (19)$$

Hence from Eq. (18)

$$\frac{X_N}{X_f} = \frac{1}{1 + \sum_{i=1}^N r^i} = \frac{1}{\sum_{i=0}^N r^i} \quad (20)$$

The performance of a battery of counter-current extractors (Eq. 20) is compared with that of a battery of cross-current extractors in which the solvent is split equally between all N stages (Eq. 9) in Figure 4. It should be noted that for the same total solvent flowrate S and the same number of stages, the performance of the counter-current battery is always superior to that of the cross-current battery. Figure 4 can be used to demonstrate that the amount of separation that can be achieved on each successive stage decreases as the number of stages increases.

MINIMUM SOLVENT FLOWRATE

For the counter-current system, Eq. (20) may be simplified by summation of the series to give

$$\frac{X_N}{X_f} = \frac{1-r}{1-r^{N+1}} \quad \text{for } r \neq 1 \quad (21)$$

When KS/F is greater than unity, the term r^{N+1} tends

to infinity as N tends to infinity, and therefore X_N/X_f tends to zero. Thus complete extraction of the solute is possible with an infinite number of stages. This is clearly shown in Figure 4.

Reducing the solvent flowrate reduces the value of KS/F. When KS/F becomes less than unity, r^{N+1} tends to zero as N tends to infinity, and hence Eq. (21) becomes

$$\frac{X_N}{X_f} = 1 - r \quad (22)$$

It is clear from Eq. (22) that complete extraction of the solute is not possible (even with an infinite number of stages) when KS/F is less than one. The limiting performance is given by Eq. (22), and this result is also clearly shown in Figure 4. The highest flowrate, at which the limiting performance expressed by Eq. (22) occurs, is given by

$$r = 1 \quad (23)$$

i.e., by

$$S = \frac{F}{K} \quad (24)$$

Solvent flowrates in excess of this value would allow X_N/X_f to tend to zero as N tends to infinity. The concept of minimum solvent-to-feed ratio for a given specification, *i.e.*, to reduce a solute concentration from X_f to X_N , is thus clearly demonstrated by the simple LLE system.

USE OF THE SIMPLE SYSTEM AS AN INTRODUCTION TO GRAPHICAL METHODS

The above algebraic analyses enable the principal features of multistage contacting to be demonstrated quickly, although the liquid-liquid equilibrium system is hypothetical. The equilibria for real systems are more complex, particularly when the solute concentrations are high. The above LLE system can be used to introduce students to the graphical solution methods. For convenience, the solute ratios Y and X should be converted to mass fractions. Thus, since the solvent and all extracts contain no diluent, the mass fraction of solute is given by

$$y = \frac{Y}{1+Y} \quad (25)$$

Similarly, since the feed and all raffinates contain no solvent, the mass fraction of solute is given by

$$x = \frac{X}{1+X} \quad (26)$$

The locus of extracts (solute and solvent only) is clearly the hypotenuse of the right-angled diagram shown in Figure 5, while the locus of raffinates (solute and diluent) is clearly the abscissa.

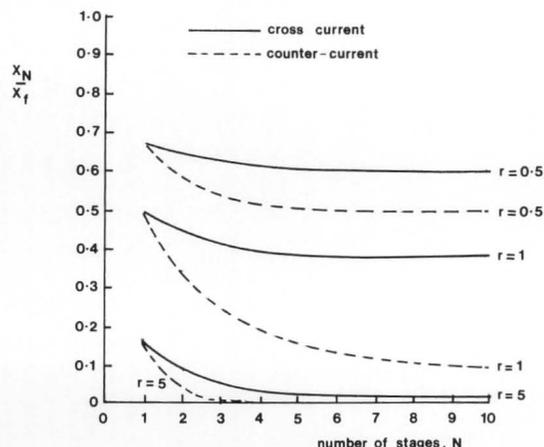


FIGURE 4. Comparison of multistage cross- and counter-current extraction.

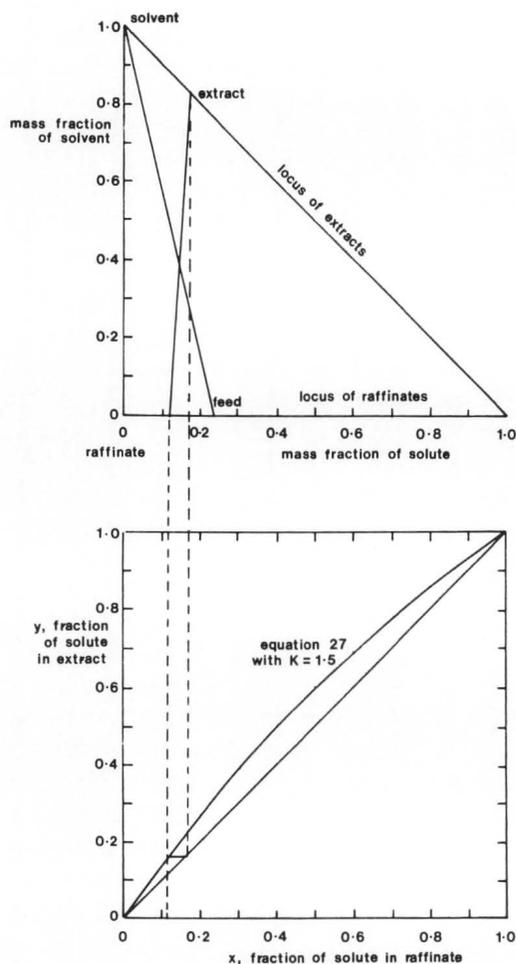


FIGURE 5. Single stage extraction with simple LLE system.

A single stage calculation of the extraction by a pure solvent of a solute from a mixture with only the diluent is shown in Figure 5. The value of the partition coefficient used in this example is $K = 1.5$. When written in terms of mass fractions rather than solute ratios, the equilibrium relationship is no longer in linear form. Substituting Eqs. (25) and (26) in the equilibrium relationship $Y = KX$ gives the revised form of the equation

$$\left\{ \frac{y}{1-y} \right\} = K \left\{ \frac{x}{1-x} \right\} \quad (27)$$

Students are encouraged to derive the inverse lever arm rule from the material balances and to apply the rule to the single stage calculation. Analyses of cross- and counter-current extractions, including minimum solvent-to-feed ratio, can also be studied using the system shown in Figure 5. However, at this point in the first-year course, students would be expected to be using real chemical systems in which either one pair or two pairs of the three components are partially miscible, and the corresponding graphs

would show the extract and raffinate loci not to be the sides of the triangle.

CONCLUSION

A simple liquid-liquid equilibrium system involving a constant partition coefficient, which is based on solute ratios, is used to develop an understanding of multistage contacting in the first-year separation processes course of BEng degrees at Bath. The algebraic solutions are used to demonstrate the advantage of counter-current operation over cross-current operation, to demonstrate the effectiveness of splitting the solvent in cross-current operation, and to demonstrate the problem of minimum solvent-to-feed flow ratio in counter-current operation.

NOTATION

- F = mass flowrate of diluent in feedstock
- K = distribution or partition coefficient expressed in mass ratio units
- N = number of stages in solvent extraction battery
- r = parameter defined by Eq. (4)
- S = mass flowrate of pure solvent
- x = mass fraction of solute (in feed or raffinate)
- X = mass of solute per unit mass of diluent
- y = mass fraction of solute (in extract)
- Y = mass of solute per unit mass of solvent

Subscripts

- f = feed
- n = phase leaving stage n
- N = phase leaving stage N
- 1 = phase leaving stage 1
- 2 = phase leaving stage 2 □

ChE books received

Organic Reactions: Volume 38, edited by Beak et al.; John Wiley & Sons, 1 Wiley Dr., Somerset, NJ 08875-1272; 805 pages, \$89.95 (1990)

CAE: Computer Modeling for Polymer Processing, by Charles L. Tucker, III; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 623 pages, \$99 (1990)

Biotechnology Focus 2, by R. K. Finn and P. Prave; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 543 pages, \$79 (1990)

Fermentation: A Practical Approach, edited by McNeil and Harvey; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 226 pages, \$65.00 (1990)

Polymer Characterization, by Schröder, Müller, Arndt; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 344 pages, \$47.50 (1989)

REVIEW: Viscous Flows

Continued from page 97

an appropriate background in fluid dynamics. Since there are those among us who do bring this focus into our undergraduate classes, some thought must be given to the selection of this book for a first undergraduate course.

Professor Churchill has laid out the book in a logical and attractive manner. It begins with several chapters on one-dimensional laminar flows. These flow fields are physically appealing and mathematically tractable for the undergraduate, and they provide a foundation for some of the later material. As is the case with most fluids texts, the flows illustrated are almost entirely newtonian (though there is a short chapter on non-newtonian flow through channels) and flows in which surface tension plays a dominant role are barely mentioned. This is a choice an author must make in order to keep the size of the text manageable, and it is a defensible choice. Extensive referencing makes it possible for the introduction of additional material by the teacher or by the self-motivated independent student.

Following this introductory material there is a presentation of the Navier-Stokes equations and a discussion of the special cases of creeping flow and inviscid flow. Several subsequent chapters treat boundary layer flows in great detail, with special attention given to a comparison of experimental results with the mathematical models for these flows. Similarly, flows over solid cylinders and spheres are discussed with extensive comparison of theory to observations on the structure of the flow (wakes, eddies, *etc.*) and on drag coefficients for these bodies. A long chapter on bubbles and drops, illustrating the role of the deformable interface (here, of course, surface tension enters) is presented. There is almost too much material here—I found myself bogged down in the seeming repetitive presentations of data on terminal velocity of rising bubbles.

On the whole, I think this text is a viable option for introduction into the undergraduate curriculum, with the reservations regarding the importance of the instructor that I have indicated above. It would be an excellent choice as the basis for a second course in fluid dynamics.

One criticism of this textbook arises first upon reading Chapter 10, which presents a long (seventy pages) description of various flow fields that are exact solutions of the Navier-Stokes equations. Here the author has an opportunity to introduce a number of practical applications of theory (note the sub-
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title of the book) but this is not done either through worked examples within the chapter or through the introduction of problems at the end of the chapter. Of the 105 problems that follow Chapter 10, most are of the form of "reduce the equations," and "derive an expression." Only four of the problems are stated in a form that implies a clear practical use of the theory presented in the chapter. I am disappointed that in a text with this prominent sub-title there is so little illustration of the practical use of theory.

If the feature of the text which I have just criticized were only a matter of author's choice and style, one could accept the text as it stands since there is so much of it to applaud. Unfortunately, the failure to give more attention to practical applications, in favor of derivations of solutions, leads on occasion to comments that are at least confusing and which are potentially misleading.

For example, a derivation is presented on pages 182 and 183 for the radially outward flow field generated by pressure within a porous cylindrical reservoir of fluid. This is an *extensional* flow field, and extensional flows are important and are often neglected in typical fluid dynamics texts. The solution for the radial distribution of pressure is derived and the statement is made that the pressure is independent of viscosity because there are no shear stresses. To most students this would imply that extensional flows do not exhibit viscous effects, which is clearly at odds with experience and intuition. The introduction of an example at this point, showing how to calculate the pressure required to drive this flow at a specified volumetric flowrate, would serve to clarify this point, with the bonus that the student would be introduced to the concept of balancing the *total* radial stress (which includes the radial *viscous* normal stress) at the boundary of the flow. This would permit the student to learn and appreciate the distinction between shear stresses and normal stresses.

Practical applications of the theories presented, as well as of the empirical correlations of data described so extensively in many chapters, do appear in several chapters more than in others. For example, in Chapters 19 and 20 the topics of flow through porous media and sedimentation and fluidization are covered in considerable detail, and a number of problems at the end of each chapter provide an opportunity for the reader to explore the use of the material in several practical contexts. Thus, this text is not devoid of practical applications. I just would have hoped for more of them in view of the implication of the subtitle of the text. □

COMPUTATION OF MULTIPLE REACTION EQUILIBRIA

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Chemical equilibrium problems with simultaneous reactions can be solved by direct minimization of the Gibbs free energy or by algebraic methods.^[1] Direct minimization using optimization techniques such as steepest descent is slower but has the advantage that the minimization can be carried out adiabatically as well as isothermally.^[2] Algebraic calculations are very fast but require elaborate programming to ensure convergence.^[3]

Whatever solution method is used, *chemical reactions are not required as input data*. The input to the program consists of temperature, pressure, and a list of chemical compounds expected to be present at equilibrium with their initial amounts.

The Turbo Pascal (MS DOS) program used to solve the examples in this paper by algebraic methods may be obtained by mailing a 3.5-inch diskette with a self-addressed, stamped return envelope to the author, or by E-mail (myers@cheme.seas.upenn.edu). A minimization program running under Microsoft Windows is available from O'Brien.^[2]

The Pascal program uses matrix algebra for the atom balance. The list of chemical compounds is converted to an atomic matrix **A** (see the Appendix) by a subroutine that parses the chemical formulae of compounds in terms of the number of atoms of each



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element. The amount of each compound is expressed as a vector **n**. The atom balance is

$$\mathbf{m} = \mathbf{A}\mathbf{n} \quad (1)$$

where **m** is determined by the starting concentration **n**.

The stoichiometric matrix **N** for the set of chemical reactions is obtained from the atomic matrix **A** by solving the equation

$$\mathbf{A}\mathbf{N}^T = 0 \quad (2)$$

for **N** (see the Appendix). An element of **N** is v_{ij} , the stoichiometric coefficient of compound *j* in reaction *i*.

For *C* chemical compounds containing *E* elements, the number of independent chemical reactions is $R = C - \rho$, where ρ is the rank of **A**. The amount n_j of compound *j* at equilibrium is expressed in the terms of its starting amount n_j^0 ;

$$n_j = n_j^0 + \sum_i v_{ij} \xi_i \quad (3)$$

where ξ_i is the extent of the *i*th reaction. The Newton-Raphson method is used to solve the *R* nonlinear algebraic equations:

$$\ln K_i = -\sum_j v_{ij} \left(\frac{G_j}{RT} \right) = \left(\sum_j v_{ij} \right) \ln \left(\frac{P}{P_0} \right) + \sum_j v_{ij} \ln \left(\frac{n_j}{\sum_j n_j} \right) \quad (4)$$

for the unknown extent of each reaction ξ_i . K_i is the equilibrium constant of the *i*th reaction. Possible divergence of Newton's method is avoided by dividing the compounds into two groups: primary and secondary. Each secondary compound appears as a product in one and only one reaction (see the Appendix). The algorithm sequentially examines all possible combinations of primary and secondary compounds to find a set of reactions with equilibrium constants less than unity. Then the starting concentration is recalculated from Eq. (1) in terms of the selected set of primary compounds. Convergence is assured be-

cause each reaction must proceed to the right to form a finite amount of secondary compound, but not too far to the right because the equilibrium constant $K_i < 1$. The search for the convergent set of reactions is accelerated by selecting the most stable compounds as primary, and the least stable (highest values of Gibbs free energy) as secondary compounds.

This program is limited to reactions of perfect gases. Condensed phases (liquid or solid) may be present if they are at unit activity. Under these limitations, it is legitimate to view the software as a black box to which the input is thermochemical data, composition of feed, and state variables. The output is the equilibrium composition. The details of the algorithm are less important to the user than the program's speed and the conditions under which it fails, such as high pressure or simultaneous phase and chemical equilibria. Computer output can always be checked by substituting the equilibrium mole fractions into the chemical equilibrium constants.

COAL METHANATION

We will illustrate the procedure for coal methanation using steam and hydrogen. Coal is simulated by graphite. Gases present at equilibrium are H_2 , H_2O , CO , CO_2 , and CH_4 . In addition to the amount of each compound and its state (solid, liquid, gas), the program calls for the pressure, feed composition, and dimensionless Gibbs free energy (G/RT) at the temperature of interest. The feed is entered as the amount of each compound, but the equilibrium composition depends only upon the atomic composition (C,H,O) of the feed. In this example there are six compounds and three elements, so the number of chemical reactions $R = C - \rho = 3$. The program prints a set of independent chemical reactions with their associated equilibrium constants to facilitate check-

ing the results.

The thermochemical data may be calculated either by thermodynamics or by statistical mechanics. The thermodynamic expression for the dimensionless Gibbs free energy obtained by integrating the Gibbs-Helmholtz equation is

$$\left(\frac{G}{RT}\right) = \left(\frac{G_0}{RT_0}\right) - \left(\frac{H_0 - I(T_0)}{R}\right) \left(\frac{1}{T_0} - \frac{1}{T}\right) - \int_{T_0}^T \frac{I(T)}{RT^2} dT \quad (5)$$

where G_0 and H_0 are values of the molar Gibbs free energy and molar enthalpy of formation at the reference temperature T_0 and reference pressure P_0 , and $I(T)$ is the indefinite integral of the molar heat capacity of the compound at the standard pressure P_0 :

$$I(T) = \int C_p(T) dT \quad (6)$$

For example, for the commonly used polynomial^[4]

$$C_p = A + BT + CT^2 + DT^3 + ET^4 \quad (7)$$

we have

$$I(T) = AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4 - \frac{E}{T} \quad (8)$$

and

$$\int_{T_0}^T \frac{I(T)}{RT^2} dT = \frac{A}{R} \ln \frac{T}{T_0} + \frac{B}{2R}(T - T_0) + \frac{C}{6R}(T^2 - T_0^2) + \frac{D}{12R}(T^3 - T_0^3) + \frac{E}{2R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (9)$$

Heat capacity data^[4] for the compounds under consideration are listed in Table 1.

The dimensionless free energies of formation tabulated in Table 2 were calculated using Eq. (5). The feed contains hydrogen and water in the ratio $H_2/H_2O = 2$ with excess carbon.

TABLE 1

Free energies (G_0) and enthalpies (H_0) of formation at $T_0 = 298.15$ K; heat capacity coefficients (A,B,C,D,E) for Eq. (7).

Compound	State	G_0 kJ/mol	H_0 kJ/mol	A J/mol-K	B J/mol-K ²	C J/mol-K ³	D J/mol-K ⁴	E J-K/mol
CO ₂	(g)	-394.65	-393.77	19.795	7.344E-2	-5.602E-5	1.715E-8	0.0
H ₂ O	(g)	-228.77	-242.00	32.242	1.924E-3	1.055E-5	-3.596E-9	0.0
CO	(g)	-137.37	-110.62	30.869	-1.285E-2	2.789E-5	-1.272E-8	0.0
CH ₄	(g)	-50.87	-74.90	19.251	5.212E-2	1.197E-5	-1.132E-8	0.0
H ₂	(g)	0.0	0.0	27.143	9.274E-3	-1.381E-5	7.645E-9	0.0
C	(s)	0.0	0.0	16.873	4.773E-3	0.0	0.0	-8.541E5

TABLE 2

Input to computer program for finding equilibrium of coal methanation reactions at 800K.

Compound	State	G_i/RT	n_i° , mol
CO ₂	(g)	-61.3410	0.0
H ₂ O	(g)	-32.5318	1.0
CO	(g)	-28.6855	0.0
CH ₄	(g)	-3.4398	0.0
H ₂	(g)	-1.2607	2.0
C	(s)	-0.5925	2.0

Additional data supplied to the program are the pressure ($P = 0.5$ MPa) and the number of moles of inert gas (zero in this case). Table 3 gives the equilibrium state computed for the feed composition in Table 2. Computation time for the equilibrium point in Table 3 is 0.5 second on an 80386/80387 personal computer rated at 0.075 MFLOPS (mega floating-point operations per second). This includes the time for reading and writing to a file. Therefore, enough points for a graph can be generated in less than a minute. For example, Figure 1 shows the effect of the H_2/H_2O feed ratio upon the equilibrium yield, expressed as moles of methane per mole of carbon consumed.

The program's output includes the chemical reactions with their equilibrium constants in Table 4.

Results of chemical equilibrium calculations for coal methanation are given by Sandler^[5] for the case of no hydrogen in the feed stream. Helfferich^[6] solved for the amount of hydrogen feed required to produce 0.9 mole of methane per mole of carbon consumed.

Ethane can be added to the list of compounds in Table 2 to find out if it is present in detectable amounts at equilibrium (it is not). Or, iron and iron oxide can be added to the list to find out if the process conditions favor oxidation of the reactor according to the reaction $Fe + H_2O = FeO + H_2$ (the result is no FeO at equilibrium).

COMBUSTION OF HYDRAZINE

Chemical equilibrium problems that require

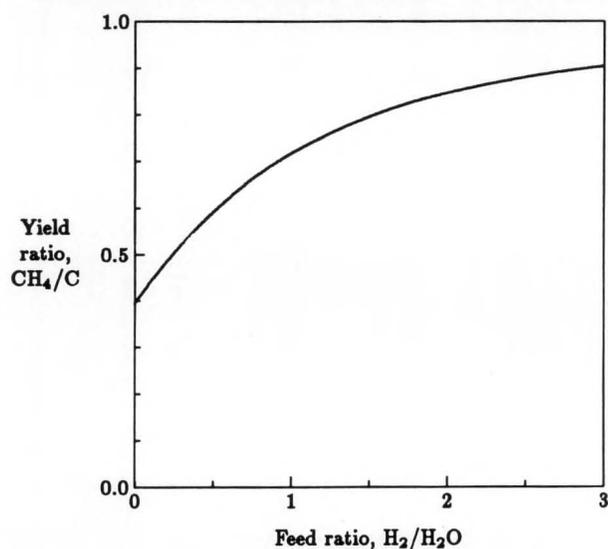


Figure 1. Equilibrium yield of CH_4 per unit amount of carbon consumed as a function of ratio H_2/H_2O in feed.
 $T = 800$ K, $P = 0.5$ MPa

computers for their solution arise in high-temperature chemistry. For example, combustion of hydrazine ($NH_2NH_2 + O_2 \rightarrow N_2 + 2 H_2O$) generates OH, NH, NO, H_2 , O_2 , N, H, and O as well as the principle products N_2 and H_2O . For this problem it is convenient to use the formulae of statistical mechanics. For

TABLE 3

Chemical equilibrium for coal methanation reactions at 800 K, 0.5 MPa.
No inert gases; amount in feed, n_i^o ; amount at equilibrium, n_i ; mole fraction in gas phase at equilibrium, y_i .

Compound	n_i^o , mol	n_i , mol	y_i
CO_2	0.0	0.13258	0.05808
H_2O	1.0	0.70954	0.31080
CO	0.0	0.02530	0.01108
CH_4	0.0	0.87494	0.38325
H_2	2.0	0.54058	0.23679
C	2.0	0.96718	0.0
Total	5.0	3.25012	1.0

TABLE 4

Chemical equilibrium constants at 800 K

Reaction	K
$C(s) + CO_2 \rightleftharpoons 2 CO$	0.01043
$2 C(s) + 2 H_2O \rightleftharpoons CO_2 + CH_4$	0.23041
$C(s) + 2 H_2O \rightleftharpoons CO_2 + 2 H_2$	0.16635

TABLE 5

Molecular constants

Molecule	MW, g/mol	θ_r , K	θ_v , K	D_0/k , K	σ	ω_0
H_2	2.016	87.55	6332	51,970	2	1
O_2	31.999	2.07	2274	59,360	2	3
N_2	28.013	2.88	3374	113,350	2	1
NO	30.006	2.41	2740	75,390	1	2
NH	15.015	24.03	4722	39,460	1	3
OH	17.007	27.21	5378	50,970	1	2
H_2O	18.015	13.40	2295	110,360	2	1
		20.90	5254			
		40.10	5404			
N	14.007	-	-	0	-	4
H	1.008	-	-	0	-	2
O	15.999	-	-	0	-	5

a diatomic molecule modeled as a rigid rotor, harmonic oscillator in its electronic ground state, the dimensionless Gibbs free energy is

$$\frac{G}{NkT} = \underbrace{-\ln\left(\frac{kT}{P_0\Lambda^3}\right)}_{\uparrow \text{Translation}} - \underbrace{\ln\left(\frac{T}{\sigma\theta_r}\right)}_{\uparrow \text{Rotation}} + \underbrace{\ln(1 - e^{-x})}_{\uparrow \text{Vibration}} - \underbrace{\frac{D_0}{kT}}_{\uparrow \text{Electronic}} - \ln\omega_e \quad (10)$$

where Λ is the deBroglie wavelength of the molecule

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} \quad (11)$$

and $x = \theta_v/T = hv/kT$. The rotational symmetry number is σ and the degeneracy of the electronic ground state is ω_e . The energy of the molecule in its electronic and vibrational ground states relative to the isolated atoms at $T = 0$ is D_0 , and the characteristic temperature for rotation is $\theta_r = h^2/8\pi^2Ik$.

Monatomic species (N, H, O) have no rotational or vibrational terms. For nonlinear, polyatomic molecules (H_2O), there is a separate term for each vibrational mode and the rotational term is replaced by

$$\left[\frac{G}{NkT}\right]_{\text{rot}} = -\ln\left[\frac{\pi T^3}{\sigma^2\theta_a\theta_b\theta_c}\right]^{0.5} \quad (12)$$

For NO another term must be added to account for excitation from the ground electronic state (1) to the first excited state (2)

$$\left[\frac{G}{NkT}\right]_{\text{elec}} = -\ln\left[1 + \frac{\omega_{e2}}{\omega_{e1}} e^{-(\epsilon_2 - \epsilon_1)/kT}\right] \quad (13)$$

where $\omega_{e1} = \omega_{e2} = 2$ and $(\epsilon_2 - \epsilon_1)/k = 172$ K. Constants extracted from Herzberg⁽⁷⁾ and NBS⁽⁸⁾ are given in Table 5.

Computation time for the equilibrium state reported in Table 6 was 1.5 seconds on a computer rated at 0.075 MFLOPS. The results are that the equilibrium concentrations of N and NH are low enough to be neglected under these conditions.

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NOTATION

- A = atomic matrix
 C = number of chemical compounds present
 C_p = heat capacity
 D_0 = electronic energy
 E = number of elements present
 G = Gibbs free energy at P_0
 H = enthalpy at P_0
 h = Planck constant
 I = function of heat capacity, Eq. (5); rotational moment of inertia

TABLE 6
Chemical equilibrium for combustion of hydrazine at 3500 K, 1 MPa. Input to program, n_i^0 ; amount at equilibrium, n_i ; mole fraction, y_i

Compound	G/NkT	n_i^0 , mol	n_i , mol	y_i
H ₂ O	-61.2859	2.0	1.40718	0.40850
N ₂	-60.9791	1.0	0.96259	0.27944
NO	-52.6323	0.0	0.07465	0.02167
O ₂	-47.4720	0.0	0.14014	0.04068
OH	-41.3420	0.0	0.17333	0.05032
NH	-38.4545	0.0	2.95E-5	8.57E-6
H ₂	-35.8107	0.0	0.39011	0.11325
O	-22.5047	0.0	0.06456	0.01874
N	-22.0821	0.0	1.29E-4	3.76E-5
H	-17.4415	0.0	0.23205	0.06736
Total		3.0	3.44478	1.00000

TABLE 7
Chemical equilibrium constants at 3500 K and standard pressure $P_0 = 1$ atm.

Reaction	K
0.5 H ₂ O + 0.25 O ₂ ⇌ OH	0.31069
0.5 O ₂ ⇌ O	0.29191
0.5 H ₂ O ⇌ 0.25 O ₂ + H	0.26357
0.5 N ₂ + 0.5 O ₂ ⇌ NO	0.20326
H ₂ O ⇌ 0.5 O ₂ + H ₂	0.17566
0.5 N ₂ ⇌ N	2.23E-4
0.5 H ₂ O + 0.5 N ₂ ⇌ 0.25 O ₂ + NH	2.02E-5

- k = Boltzmann constant
- K = chemical equilibrium constant
- m** = element vector
- N = number of molecules
- n** = compound vector
- n = amount, mol
- P = pressure
- P_o = reference pressure
- R = gas constant
- T = absolute temperature
- x = dimensionless frequency of vibration = hv/kT
- y = mole fraction in gas phase

Greek Letters

- θ_r = characteristic temperature of rotation
- θ_v = characteristic temperature of vibration
- Λ = deBroglie wavelength, Eq. (11)
- ν - frequency of vibration
- ξ - extent of reaction
- ρ - rank of **A**
- σ - rotational symmetry number (integer)
- ω_e - degeneracy of electronic ground state (integer)

Superscript

- o - refers to feed composition (initial state)

Subscript

- o - refers to standard state at 298.15 K, 1 atm.
- i - refers to ith reaction
- j - refers to jth compound

APPENDIX

Matrix operations are illustrated for a reaction system consisting of nine compounds (C = 9) and four elements (E = 4). The E-by-C atomic matrix is:

$$\mathbf{A} = \begin{matrix} & \text{CO}_2 & \text{SO}_2 & \text{H}_2\text{O} & \text{S}_2 & \text{CO} & \text{COS} & \text{CS}_2 & \text{H}_2\text{S} & \text{H}_2 \\ \begin{matrix} \text{C} \\ \text{O} \\ \text{S} \\ \text{H} \end{matrix} & \left(\begin{array}{ccccccccc} 1 & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 \\ 2 & 2 & 1 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 2 & 0 & 1 & 2 & 1 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 2 & 2 \end{array} \right) \end{matrix}$$

The rank of **A** is ρ = 4, so there are C - ρ = R = 5 independent chemical reactions. A particular set is found by dividing the C compounds into ρ primary compounds and R secondary compounds. The stoichiometric matrix **N** is obtained from Eq. (2) as follows: The atomic matrix is written with the ρ primary compounds in the first ρ columns of **A** so that the E-by-ρ atomic matrix **A_p** for the primary compounds is

at the left and the remainder of the **A** matrix contains the E-by-R matrix for the secondary compounds

$$\mathbf{A} = \left[\mathbf{A}_p, \mathbf{A}_s \right]$$

For **A** as written above, the secondary compounds are CO, COS, CS₂, H₂S, and H₂. After selecting the secondary compounds, a unit matrix as large as possible is formed in the upper left-hand corner of **A** using elementary row operations, so that a new matrix **A** is generated with the following reduced row echelon form

$$\mathbf{A} = \left[\begin{array}{cc} \mathbf{I}_\rho & \mathbf{B} \\ 0 & 0 \end{array} \right]$$

where **I_p** is a ρ-by-ρ identity matrix and **B** is a ρ-by-R matrix. The number of rows of zeros is E - ρ. Zeros are present when the rank of **A** is less than the number of elements E. In this example E = ρ.

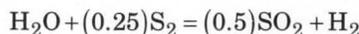
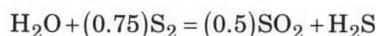
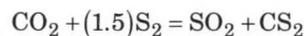
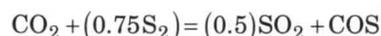
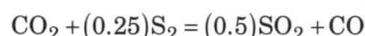
The stoichiometric matrix **N** is constructed by appending an R-by-R identity matrix **I_s** to the R-by-ρ negative transpose of **B**

$$\mathbf{N} = \left[-\mathbf{B}^T, \mathbf{I}_s \right]$$

The result from **A** as written above is

$$\mathbf{N} = \begin{matrix} & \text{CO}_2 & \text{SO}_2 & \text{H}_2\text{O} & \text{S}_2 & \text{CO} & \text{COS} & \text{CS}_2 & \text{H}_2\text{S} & \text{H}_2 \\ \left(\begin{array}{cccccccccc} -1 & 0.5 & 0 & -0.25 & 1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0.5 & 0 & -0.75 & 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & -1.5 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0.5 & -1 & -0.75 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0.5 & -1 & -0.25 & 0 & 0 & 0 & 0 & 1 & 0 \end{array} \right) \end{matrix}$$

The rows of **N** are the chemical reactions



The secondary compounds (CO, COS, CS₂, H₂S, H₂) appear in one and only one reaction. There are

$$\frac{C!}{R!(C-R)!}$$

sets of reactions, each containing a different combination of R secondary compounds. In this example the number of reaction sets is

$$\frac{9!}{5! 4!} = 126$$

□

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