



CAROL McCONICA

... of Colorado State University

• Award Lecture •

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Part 2: Mixtures

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CAROL McCONICA

of Colorado State University

SUSAN SKOG

Colorado State University
Fort Collins, CO 80523

THE VIRTUES of solitude have not been lost on Carol McConica. In many ways, her life has been shaped by them. In solitude, she has been free to speculate, to experiment, to innovate—and to buck traditional constraints.

At an early age, this Colorado State University chemical engineer grew to love the feeling of being alone, of forging a kinship with nature. The daughter of Colorado geologists, Carol and her sister spent many summers living out of a tent in rural settings throughout the West, isolated from the constraints and expectations of civilization.

"We had no TV, no media, no *Seventeen* magazine. We had no running water, no electricity. We had nothing. We had a natural environment for a playground. We grew up being in touch with nature, and my parents couldn't have cared less about societal roles," McConica remembers.

"That was wonderful. I think what happened was that I was molded by nature rather than by man. You become very creative, very independent and resilient."

Today, at 37, McConica has replaced the tent in the wilderness with a research lab, but the isolation from traditional limitations still allows her to search for knowledge in unconventional areas.

Continuing to relish creativity, McConica is one of only a handful of chemical engineers on the cutting-edge of integrated circuit processing. After securing funding for the sophisticated, ultra-clean equipment and facilities necessary for her research, McConica built one of the nation's pioneering academic programs in the deposition of tungsten as the conducting interconnect on silicon computer chips. She believes that tungsten (which, ironically, was mined by her grandfather in the Colorado mountains) may be the key to denser, faster, more powerful microchips.



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"In a lot of ways, I am leading my own solo ascent. It's like breaking a trail in a howling snowstorm, year after year. I am drawn to that, but it is overwhelming at times.

"You are out there breaking a new trail by yourself, raising money by yourself, being absolutely and totally isolated. On the other hand, without the constraints of a bureaucracy, I have a freedom of motion that no corporation can offer."

That freedom of motion allows McConica to travel between the academic world and the corporate environment, which she first entered in 1979 as a Hewlett-Packard Company engineer. A female manager with HP lured McConica to the computer company just as she was completing her graduate program at Stanford. McConica was the first American woman to receive a doctorate in chemical engineering from Stanford.

The integrated circuits industry, McConica soon discovered, was a good match for her curiosity and temperament. "I was attracted to it because it is such a high-paced industry, and I am a real driver-driver. I like to have an idea, test it out today, and see if it works tomorrow.

"In the oil industry it may take five years to design and test an experiment. But in the integrated circuits industry, processes last only one or two minutes, so you quickly get a lot of information about your basic ideas."

While it is rewarding to help advance integrated circuit technology in the United States, Carol says her chief goal is to help individual companies boost their profits. "I love nothing more than to go into a company and show them how my knowledge can help them. As long as I think that my contributions are going to help their bottom line, I feel victorious."

About a year and a half ago, she developed a theory that explained why companies couldn't get material into the holes of the chips the way they desired. "I developed a rough-cut model that utilizes basic chemical engineering principles. It showed the right trends, so the industry could get in the right mode of operation. It also allowed them to take a major leap forward in yield."

After demonstrating McConica's ideas, several companies incorporated them into chip production. "I captured the essence of the problem, and today it's helping someone's bottom line. To me, that is satisfying."

McConica's findings on integrated circuit processing are sought by large manufacturers like AT&T, small equipment suppliers, and now by a new industry/government consortium (known as Sematech)

. . . Carol is fulfilling a dream she had when she left HP for Colorado State in 1982. "I had hoped that I would be able to have an influence on industry even after I left. I absolutely and totally love industry . . ."

which is trying to counter the foreign semiconductor competition. Sandia National Laboratories, which has funded McConica's research for seven years, asked Carol to support the Sematech effort.

Although it's still premature to gauge Sematech's impact, one of its best achievements so far has been to boost the recognition of equipment suppliers' importance to the integrated circuits industry, McConica points out. Many of those suppliers now ask Carol to help them become more successful as they improve their processes (often for the first time) with in-house scientists. At times, the advice she offers the suppliers about their equipment or facilities is met with disdain.

Becoming a successful company can be painful. "I reveal information about their equipment which they would rather not know. They really don't want to know that their reactor has many nonidealities. It's like raising children. They don't enjoy discipline, but you have to do it for their own good."

Whether promoting the integrated circuits industry through companies like IBM, AT&T, or through small start-up companies, Carol is fulfilling a dream she had when she left HP for Colorado State in 1982. "I had hoped that I would be able to have an influence on industry even after I left. I absolutely and totally love industry. . . . I love the pace of industry, I love the accomplishment of objectives. I thrive on the competition."

And, much like her early enjoyment of the geological adventures with her family, Carol thrives on being free to explore new terrain on her own. Fortunately, her life as a researcher and a teacher allows her to try out new research ideas away from the commercial constraints of manufacturing.

She explains that in academia she can push the boundaries of current integrated circuits technology because she isn't limited to research on equipment and processes that lead only to production. "I am allowed to build my own equipment, which is totally unrelated to someone else's goals. I can try out new ideas and make contributions that people in industry cannot make because they are tied to production."

McConica has long known the thrill of testing new ideas and limits. Her early interest in biology and math was fueled by the fact that nearly every math

and science teacher she had in the ninth through twelfth grades was a woman. The idea that a woman could be a scientist was both acceptable and conventional.

She first discovered the irresistible lure of a research lab while growing up in Boulder—home of the University of Colorado—in the unconventional 60s. At the time, Boulder was a counterculture cocoon that sheltered free thinkers and innovators. Wrapped in a culture that encouraged individual self-realization, Carol found it natural to spend much of her time in CU labs, helping neighbors and family friends with



Carol feels that hands-on experience is invaluable, and many of her classes focus on experiments.

their research. While in high school, she was chosen to conduct research with CU researchers under a National Science Foundation program. "I was able at 17 to do the kind of work that PhD students get to do. If I hadn't had that hands-on research experience, I never would have known how much fun it can be."

Later, as an undergraduate at the University of Denver, Carol's love of learning was further channeled by professors whose primary goal was teaching. She now feels a strong kinship with her own students, remembering the guidance offered by her DU professors, and says, "I felt cared for, I felt nurtured, I felt mentored, I felt accepted, I felt challenged—everything an undergraduate should feel."

Now, as a Colorado State faculty member, McConica is determined to provide the same quality of instruction and commitment to her students. She feels that excellence in engineering instruction comes from hands-on knowledge; therefore, many of her classes focus on experiments.

For instance, if her graduate students are studying reactor design, she will instruct them to build a

simplified version of a reactor and then study flow and diffusion theories. Her students have built plexiglass reactors filled with beads and water in order to study the flow rates of dye and other substances. She believes that a hands-on, senses-oriented approach to teaching is the only way students can really experience the joy of science—and understand its fundamentals.

"I have seen many students who are capable of deriving differential equations in the dark without a pencil. They are brilliant. But they have no concept of engineering. You ask them how they would design some very simple experiments, and they have no idea. I think we are bringing up and importing a whole generation of students who have never been in a hardware store. As educators, we need to remember that profits come from products, not theories."

To counter this lack of practical experience, McConica challenges her students to do things such as disassembling a bicycle down to its last nut and bolt and then putting it back together again. And she is adamant that they also learn how to ask for help if they need it. "By the time I am through with my graduate students, they should have good hands-on ability and interpersonal skills. They should be able to say, 'I don't know,' and to admit their mistakes. Otherwise, they will be impossible to work with in industry."

To better position her students for career success, Carol teaches seminars on issues encountered in the workplace. She addresses, for instance, corporate politics and risk-taking, time management, personality styles, negotiation and listening skills, and quality control. Most of all, she views herself as a conduit through which well-educated and mature students can enter the corporate world. "I see myself as trying to train the best people for industry."

But Carol's loyalty to the corporate arena doesn't blind her to its faults. She is a staunch critic of the corporate world that encourages and rewards achievements at the expense of family stability. She feels that in the drive for success and materialistic glory, some workers and employers have forgotten that families are the ultimate foundation upon which society (and corporations and universities) rests.

She argues that men and women in their 20s to 40s, for instance, should focus on raising and instilling values in their children, but they are instead pressured to become corporate superstars or research wizards. Carol points out that a solution to these skewed values may lie in the philosophy of Confucius, who taught that no community could respect a man who could not lead his own family.

"It would be good for us to study the teachings of Confucius. Somehow our society has forgotten that a prestigious career and a weak family are as useful to society as a house with no foundation. In Indian philosophy, life stages (known as ashrama) are acknowledged. A man is responsible first for learning, and then, in his later years, he must lead his family as a "householder." As he grows older, he leads his community and ultimately prepares for death. It is much more sensible to make our older and wiser workers the vital essence of our institutions while letting the younger members build solid homes in their early years."

The workplace needs to accommodate the multiple roles of men and women and not to penalize those workers who choose to have children and continue their careers," says McConica, the mother of 11-year-old Anna and 14-year-old Ian, who were born while she worked on her degrees. "The national labs, the top five companies, and the top education institutions fail to recognize any existence other than one which is experienced by a single male with no obligations beyond the classroom. They hire based upon graduate GPAs and years elapsed between degrees."

Because of these inequities, McConica sees many young women choosing not to have children, fearing that the workplace will not allow them to have both

children and a career. "In the corporate board rooms of America, there are three taboo subjects: childbearing, childrearing, and death—events certain to happen to most of us. It is comical to me that the very engineers who pretend to understand boundary conditions and initial conditions so well seem to be completely ignorant of the fact that tomorrow's students and employees come from women who have agreed to supply their wombs for the creation of those lives. In today's society, with dual careers, there is little incentive for a woman to make this sacrifice."

Corporations and society must support women and men who choose to balance children and careers, McConica says. She adds that practical solutions could be found in government-mandated parental leaves (including job security), the encouragement of part-time employment and flexible hours, and significant tax credits for the work accomplished by homemakers.

As exciting as corporate achievements, travel, and consulting can be, society must judge itself through its elderly and its children, she says. "I will consider myself a success if my children freely understand that they have choices in their lives and if my students understand that the human side of engineering is just as important as the technical side. It is the balanced, whole person who ultimately builds a strong society." □

ChE letters

HEALTH AND SAFETY TEACHING AIDS

To the Editor:

Mr. J.P. Gupta's article in the summer 1989 issue of *Chemical Engineering Education* outlines one way to teach chemical process safety and health for those undergraduate engineering students who elect this course. The Center for Chemical Process Safety of the American Institute of Chemical Engineers has chosen a different means — teaching health and safety to virtually all students within the framework of required, traditional engineering courses. Teaching health and safety concepts in several courses is an important step toward satisfying "minimum" ABET *Criteria*.

The teaching material, available for the 1990-91 academic year, consists of 90 problems which illustrate safety, health, and loss prevention concepts, such as vapor releases, explosions, and toxic exposure, and which supplement the teaching of traditional engineering courses, including thermodynamics, heat transfer, kinetics, process design. They require mathematical solutions using engineering principles as well as consideration of safety, health, and loss prevention safety issues.

The problems were conceived and developed by chemical engineering faculty of several universities,

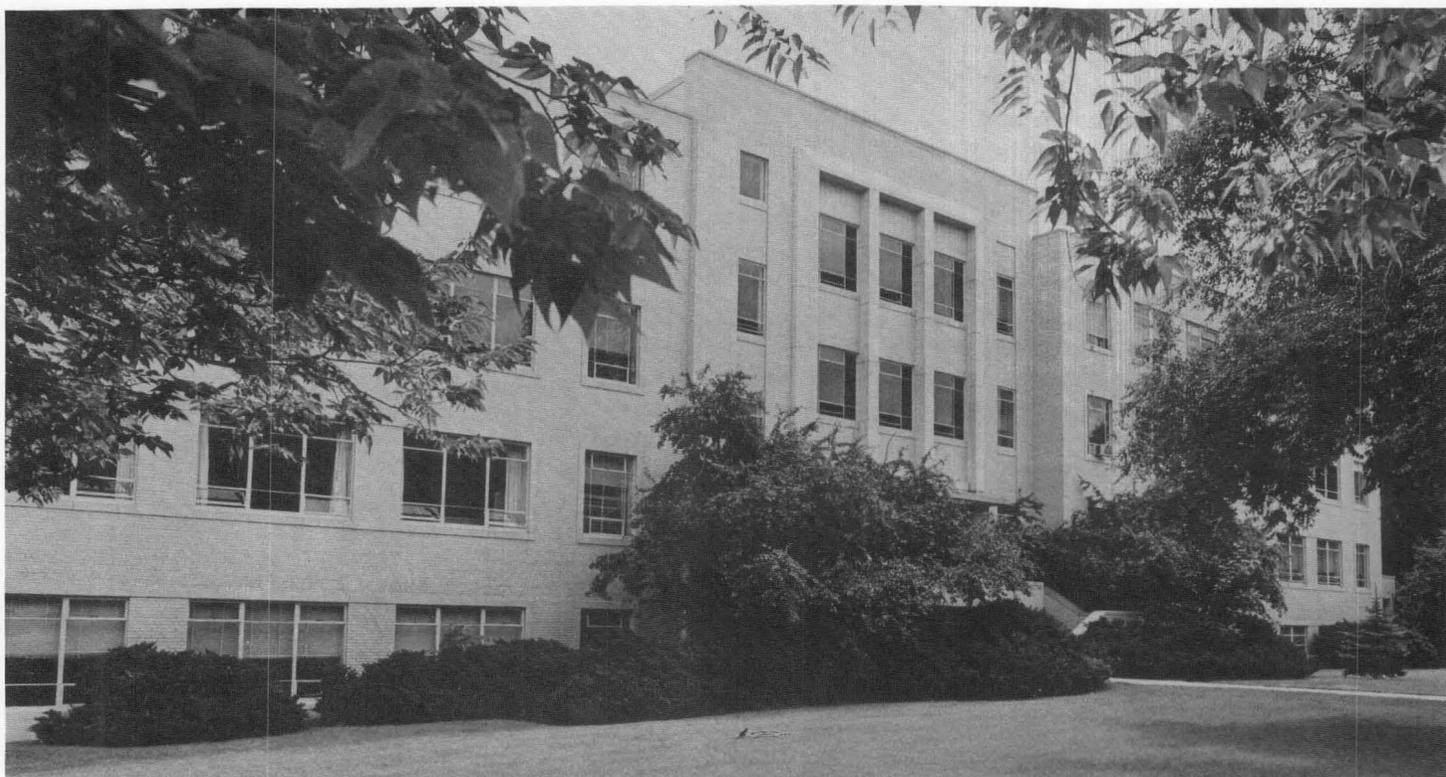
government officials, and industry professionals working under the auspices of the Undergraduate Education Committee of CCPS. To assure realism and ease of use, the material has been reviewed by engineers in industry for accuracy and applicability and has been tested and critiqued by chemical engineering faculty of 40 colleges and universities.

To encourage widespread use of these problems, the Instructor's Guide, with problems, student and instructor notes, and solutions, is available free of charge to faculty who wish to use the problems with the student's book. The Student Problem book, good for all years of study and later reference, will be sold through bookstores at \$18. The U.S. Environmental Protection Agency and National Institute for Occupational Safety and Health which consider this a high priority program are, along with CCPS sponsors, subsidizing project costs.

Information about the Instructor's Guide and Student Problems book is being mailed in February to all chemical engineering faculty in the U.S. and Canada. Faculty members who do not receive this information are urged to contact the Center for Chemical Process Safety at AIChE's offices, 345 East 47th Street, New York, NY 10017, or by calling (212) 705-7319.

F. Owen Kubias

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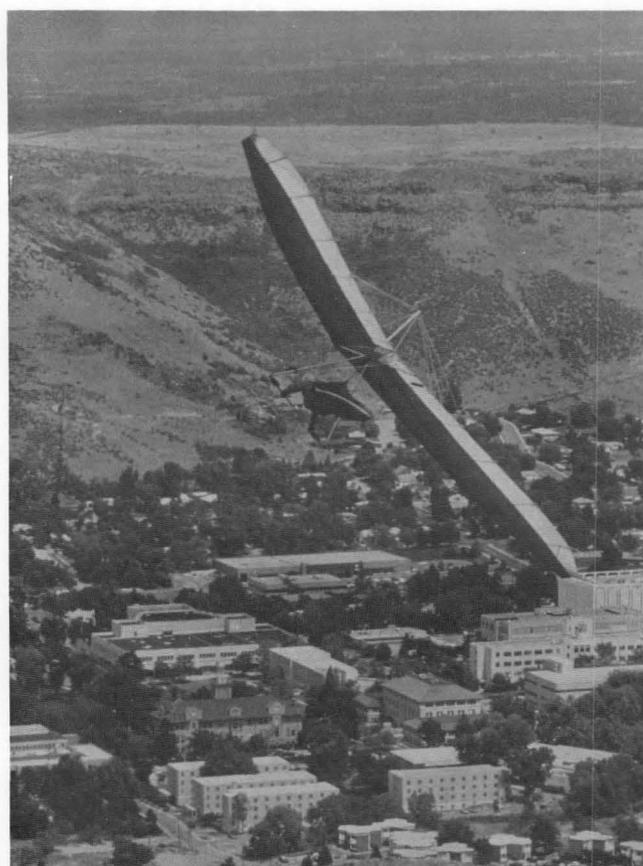
COLORADO SCHOOL OF MINES

E. DENDY SLOAN, JR.
Colorado School of Mines
Golden, CO 80401

THE CHEMICAL ENGINEERING and Petroleum Refining Department at the Colorado School of Mines reflects the physical and intellectual community in which it is situated. Our campus is located in Golden, a suburb of Denver, in the eastern foothills of the Rocky Mountains. The town of Golden contains two main institutions: the Colorado School of Mines and the Coors Brewery. A few years ago a pipeline was installed linking the two facilities, but the administration (overriding student protests) insisted that the pipeline contain only steam, to be used for heating purposes.

The prevailing westerly wind over the Rockies undergoes adiabatic cooling as it rises on the western slope, supplying ski areas such as Aspen and Vail with

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A hanglider's perspective of the campus, taken from a mountain just outside Golden.

the powder for which our state is famous. When the wind descends on Golden it is both warm and dry, providing a climate with more than 300 sunny days per year. The Rocky Mountains offer a great variety of year-round outdoor activities such as skiing, mountain climbing, hiking, mountain-biking, river-rafting, etc. all in spectacular scenery within easy reach of the campus. Perhaps less well-known are the cultural activities in the mountains, such as the Aspen Institute for Humanistic Studies or the various classical and popular music festivals held in the summer. The city of Denver serves as a western cultural center for the nation, offering a diversity of opportunities in the arts, in sports, and in business.

With a population of 14,000, the town of Golden has a relatively small, college-town atmosphere. However, Golden's proximity to several other universities (Denver, Colorado, Metro State, and Colorado State) and facilities such as the Solar Energy Research Institute (SERI) and the National Institute for Standards and Technology (formerly the National Bureau of Standards) creates an intellectual environment normally found only in a much larger metropolitan area.

AN UNUSUAL HISTORY

In 1870, after extensive debate on the relative merits of a school of engineering versus a wagon road for miners, the Colorado legislature decided in favor

In 1870, after extensive debate on the relative merits of a school of engineering versus a wagon road for miners, the Colorado legislature decided in favor of the former.

of the former. The state built the School of Mines to co-exist with a divinity school, called the "University Schools at Golden." The official starting date was listed as 1874, with the initiation of the annual state appropriation. In 1878 the divinity school was destroyed by fire, leaving only the School of Mines planted in the small town twelve miles from the center of Denver.

The school has a long history of concern for the quality of student-faculty interactions, beginning with the first meeting between the student body and the Board of Trustees in 1883. Nontraditional students have always been commonplace in the school; the 1880 president's report to the Board of Trustees lists the average age of the students as thirty-one, with many of them coming from the "rough-and-ready" silver mining communities in Colorado. Before the turn of the century, one of the first (1890) football teams of these miners/students (see photograph) humiliated the fuzzy-cheeked fellows from the University of Colorado by a score of 103 to 0!

As the school grew, emphasis shifted from strictly mining. Currently the Colorado School of Mines (like



Binary Choice

This photo is:

a) The CSM state champion football team, circa 1890

- or -

b) the CSM chemical engineering faculty, circa 1990

the schools of mines in London or Paris) graduates only a few mining engineers, yet many of its traditions (*e.g.*, the silver diploma for graduate degrees) are still associated with the mining industry. The school currently has a student body of about 2500 (one-third of which is composed of graduate students) with about 20% women. Entering freshmen are highly qualified, with an average SAT combined score of 1200. An education at CSM is highly prized, as indicated by the fact that both the entering students' SAT score and the undergraduate tuition are among the highest for any state-assisted school in the nation.

The Colorado School of Mines has developed a unique reputation as a world-class institution for education and research in the mineral, energy, and material fields. As a special-purpose university for science and engineering, today's school offers degree programs in twelve technical disciplines which are related to its mission. For one hundred and fifteen years the school has been committed to providing the education needed by future business and research leaders in the industrial areas it serves.

THE DEPARTMENT

The 1912 catalog lists a degree in chemical engineering which grew out of the applied chemistry department, but the degree was abandoned in 1926 because of financial considerations. Then, in 1946 a petroleum refining degree was offered as an option stemming from the petroleum department. It came to be called the Chemical Engineering and Petroleum Refining degree, in direct contrast to most other chemical engineering departments which originated in chemistry departments. James O. Ball was the first department head—a post which he held for fourteen years until James O. Gary joined the school as head of the department in 1960. With Dr. Gary's promotion to Dean of Faculty in 1972, Phillip F. Dickson became head and remained until an untimely illness forced him to step down. Since 1984, Arthur J. Kidnay has ably led the department.

The department is large enough to provide the diversity in research and teaching which is necessary for a sound educational experience, but it is not so large that personal contact between students and faculty is lost. We have consciously determined to keep the ratio of graduate students-to-faculty at about five to one, with about one-fourth of those enrolled studying for their PhD degree. Our undergraduate program is one of the largest in the country and ranks about twelfth in the number of bachelor degrees granted.

The large size of our department makes it possible for students to construct a program best suited to

TABLE 1
Faculty Research Interests

R.M. Baldwin	• DSc, Colorado School of Mines Fuel Science • Coal Liquefaction
A.L. Bunge	• PhD, University of California, Berkeley Membrane Transport and Separations • Mass Transfer in Porous Media • Ion Exchange and Adsorption Chromatography
J.H. Gary	• PhD, University of Florida Petroleum Refinery Processing • Heavy Oil Processing • Thermal Cracking • Visbreaking • Solvent Extraction
J.O. Golden	• PhD, Iowa State University Phase Change Phenomena • Solvent Extraction • Processing of Polymers • Fluid Mechanics
M.S. Graboski	• PhD, Pennsylvania State (Research Faculty) Fuels Development • Emissions • Alternate Fuels (Coal, Biomass, Heavy Crude)
A.J. Kidnay	• DSc, Colorado School of Mines Thermodynamic Properties of Gases and Liquids • Vapor-Liquid Equilibria • Cryogenic Engineering
R.L. Miller	• PhD, Colorado School of Mines Liquefaction Coprocessing of Coal and Heavy Oil • Particulate Removal • Multiphase Fluid Mechanics • Educational Methods
T.B. Reed	• PhD, University of Minnesota (Research Faculty) Biomass Conversion by Combustion and Gasification • Methanol Production from Wood and Municipal Waste • Diesel Fuels from Cooking Oils • Alternative Fuels
M.S. Selim	• PhD, Iowa State University Heat and Mass Transfer at Moving Boundaries • Sedimentation and Diffusion of Colloidal Suspensions • Heat Effects in Gas Absorption with Chemical Reaction • Entrance Region Flow and Heat Transfer • Surface Phenomena
E.D. Sloan	• PhD, Clemson University Natural Gas Hydrates • Thermodynamic and Transport Properties of Fluids • Adsorption • Educational Methods
V.F. Yesavage	• PhD, University of Michigan Thermodynamics of Polar-Associating Fluids • Properties of Coal Derived Liquids • Equations-of-State for Highly Nonideal Systems • Flow Calorimetry • Surface Phenomena • Treatment of Mixed Wastes • Photochemical Wastewater Treatment

their individual needs. Conversely, the small size of our campus enables a new student to quickly become familiar with the campus and the valuable offerings in other departments. Our department has eight full-time faculty members, all actively engaged in teaching and research, and two research faculty. The research interests of the faculty are listed in Table 1.

The challenges facing the chemical engineering community have changed considerably. Easily exploited resources and reserves of the past are now largely gone, and technologies appropriate thirty years ago are no longer economically feasible or environmentally acceptable. A committee report, "Frontiers in Chemical Engineering: Research Needs and Opportunities," sponsored by the National Research Council, identified eight high-priority areas of national need in chemical engineering. At CSM we have active research in five of those eight areas: (1) liquid fuels (shale, coal, biomass) for the future; (2) responsible management of hazardous substances; (3) surface and interfacial engineering; (4) advanced computational methods and process control; (5) *in-situ* processing of resources.

In addition, we continue to maintain active programs in all the traditional areas of chemical engineering, such as applied thermodynamics, kinetics, catalysis, and heat and mass transfer. Interdisciplinary research is taking place in fields as diverse as materials science, hazardous waste treatment, and transport across human skin. Table 2 lists some of the research projects in our department.

Most graduate research is carried out in the department's modern and well-equipped laboratories which occupy one-half of the third and fourth floors of

Alderson Hall. In 1991 a new wing of Alderson Hall will be constructed which will effectively double the available research space. Graduate students are normally assigned office space separate from research laboratories. Some graduate research is done in conjunction with local industrial and government research laboratories, such as the National Institute for Standards and Technology, the Solar Energy Research Institute, Coors, and IBM. Our goal is to maintain strength in areas critical to existing industries while creating research programs in areas vital to new and emerging technologies.

TABLE 2
Typical Major Research Areas

Center for High Altitude Fuels and Engine Research • *The department is establishing a new research laboratory, dedicated to research on fuels and emissions from internal combustion engines. This lab will contain both stationary gasoline and diesel research engines with sophisticated real-time analytical monitoring capabilities for both engine performance and emissions data. The primary focus of the laboratory will be research on the effect of fuels on emissions for conventional and novel fuels. The laboratory is scheduled for dedication during the spring of 1990 and will be the only facility of its type in the US that is capable of measuring and correlating fuels properties with engine performance and emissions at high altitude.*

Applied Thermodynamics • *CSM is known internationally for research in this area. Thermophysical properties research is included along with phase equilibria of nonideal systems, heat of mixing, and flow calorimetry. Recent work has incorporated supercritical fluid technology, equation-of-state development, advanced computational thermodynamics, and a program to evaluate the impact of thermodynamic property research on the natural gas industry.*

Natural Gas Hydrates • *Very large deposits of low-molecular weight hydrocarbons are present around the world in solid hydrated form. Our studies in hydrate thermodynamics, physical properties, and processing are aimed at both recovery and prevention in various portions of the gas production and processing industry. Our laboratory is the largest in the nation in this area and includes an interdisciplinary effort with several other departments, namely chemistry and geochemistry, geology, physics, and petroleum engineering.*

In-Place Remediation of Contaminated Soils • *Of the options for cleaning contaminated soils, methods which do not require soil excavation prior to treatment offer obvious advantages. The objective of this program is to develop a comprehensive research effort studying in-place methods for remediation in zones above the water table. Present projects include soil flushing with chemically enhanced aqueous solutions, enhanced evaporation by forced aeration, and bioremediation. Centered in chemical engineering, this multidisciplinary program involves faculty from chemistry and geochemistry, geological engineering, civil engineering, environmental science, and petroleum engineering.*

Coal Liquefaction • *A number of fundamental and applied studies in coal liquefaction science and engineering are in progress, aimed at coal reactivity correlation and low-severity liquefaction processes. The reactivity research investigates the relationship between coal chemical structure and the rate and extent of conversion to liquids by direct hydroliquefaction. The low-severity program incorporates reactivity enhancement by mild chemical pretreatment, catalysis by basic nitrogen compounds, and low severity coprocessing studies.*

Further Research Areas • *Other innovative research is being carried out in such areas as:*

Biomass Conversion • Catalytic Hydroprocessing of Lignin • Deactivation of Zeolite-Based Isomerization Catalysis • Development of Novel HDO and Naphtha Isomerization Catalysts • Emulsion Liquid Membrane Studies • Extraction of Brewery Products with Supercritical Fluids • Fuels Testing Center for Pollution Control • Mineral Extraction with Supercritical Water • Moving Boundary Problems • Pedagogical Methods of Integration of Humanities in Engineering • Sedimentation Theory • Suspension Rheology • Solute Transport Across Human Skin • Surface and Interfacial Flows • Photochemical Wastewater Treatment

FACULTY AS PEOPLE

The research interests listed in Table 2 invigorate our faculty's activities. However, members of the faculty are vital people in other ways as well. They are professors in the fullest meaning of the word—their intellectual activity and availability extends beyond the time and space boundaries of the classroom/laboratory.

On the wall of **Bob Baldwin's** office there is a certificate of musical accomplishment from Iowa State—implying that there was a difficult career choice during his student days. Bob teaches in the school's Honors Humanities program and has won several teaching excellence awards. Last year he served as Associate Dean for Undergraduate Studies. When he can manage time away from the Mines campus and the Golden area, Bob is an inveterate globetrotter.

The fact that **Annette Bunge** is the best athlete in the department does damage to our "Rambo" image. Annette coaches the school's mens/women Alpine and Nordic ski teams and participates in all training events with the team. Last year when the team ran a two-mile training run, she had to wait over 1.5 minutes for the second-place finisher. She is an avid outdoorswoman and participates in rock climbing, river-rafting, hiking, crosscountry racing, and diving. She is the recipient of the Dow Outstanding Young Faculty Award from the American Society for Engineering Education (ASEE).

Jim Gary is perhaps our best known faculty member because of his long academic tenure and his classic book in the field of petroleum refining. He came to the school in 1960 and served as Department Head and as Vice President for Academic Affairs and Dean of Faculty (each for about a decade) before resuming an active career in teaching classes and industrial short courses in petroleum processing throughout the world. As the department's only septuagenarian ($\pm 2.9\%$) and one of its most active computer users, he frequently teaches his junior colleagues the newest

in computer hard/software. Jim has received the George R. Brown Medal of Achievement from the school and is a Fellow of both AIChE and AAAS.

John Golden returns to the department after having been led astray into academic administration for the past fifteen years. He has served the School of Mines as Director of Research Development, Dean of Graduate Studies and Research, and Vice President for Academic Affairs and Dean of Faculty. For the 1990-91 academic year he will take a well-deserved administrative leave to relearn some chemical engineering that he forgot during his years of academic administrative combat service.

Mike Graboski returns to the school as research professor after managing his own business in biomass gasification for three years. Mike continues those personal interests he began as a graduate student at Penn



An Ore Cart race on Engineer's Day (the traditional "Spring craziness day" on campus).

State, where he was president of Trout Unlimited. His current hobbies include cross-country skiing, hiking, hunting, and fishing.

Art Kidnay is the department's fearless leader, ranking weightlifter, and intrepid long-distance runner. His colleagues appreciate his magnanimous attitude as well as his limitless capacity for new interests—such as biofeedback tapes to improve running. Art is a Fellow of the AIChE and has won the school's outstanding teaching award.

Ron Miller is the youngest, and by far the most irreverent, faculty member. Students closely identify with Ron—some claiming him as a good friend even after he has taught them! Along with Ron's technical research, he has recently begun pedagogical research to integrate humanities into the initial chemical engineering course. Ron has won school-wide awards for teaching excellence at the University of Wyoming and at the School of Mines.

Tom Reed is a research professor who came to us in 1986 after fifteen years at MIT and nine years at the Solar Energy Research Institute. His initial technical interests were in crystallography and material/energy science, but for the last seventeen years his interests have been in alternative fuels such as methanol and biomass. He has recently started a private company to convert waste cooking oils to diesel fuels.

Sami Selim, the department's mathematical wizard, has a graduate degree in mathematics as well as three degrees in chemical engineering. He specializes in making difficult analytical problems dissolve into thin air, while exhibiting an international flavor of kindness. Sami serves as both the department's opera aficionado and its culinary Epicurean. He has been presented with school-wide teaching excellence awards at three universities, including CSM.

Recently, the only trace of **Dendy Sloan** has been his voice on an answering machine in his office. He was sequestered in the school library until he emerged with the manuscript for *Clathrate Hydrates of Natural Gases*, published in the winter of 1990. His hobbies include attempts at music on the banjo and guitar. Dendy balances a two-career family with his wife, who is an attorney. He is the fifth departmental faculty to be the recipient of a school-wide teaching award.

Vic Yesavage is a displaced New Yorker who rapidly took to the great outdoors. He enjoys family-oriented activities such as camping trips to national parks in the west. Within the department he enjoys the role of graduate advisor to students. In recent years he has become a student of Eastern European history, and he follows the recent developments in that part of the world with great interest.

The faculty feel a collegiality for each other and join in parties, cross-country ski trips, and campouts. These events are filled with appropriate amounts of good cheer, exercise, and comradery to subsequently remind us of our mortality. While we each maintain independence of thought, our faculty is small enough (and friendly enough) to arrive at a consensus on most issues of departmental concern.

Another outgrowth of this collegiality is a cooperative spirit in which most faculty members have engaged in joint research projects. Cooperation between faculty members is but one indication that our department research activities are continuing to evolve. The intellectual abilities of the faculty, along with fresh input from graduate students, are recognized as the best resources of the department. These resources will carry us into new adventures and new ideas in the coming years. □

NO RESPECT!

RICHARD M. FELDER
*North Carolina State University
Raleigh, NC 27695*

The problem is, there's no glamour in being a professor. People don't think of us as powerful and important, like politicians and corporate executives; or as practicing a noble and beneficial profession, like doctors; or as pulling down a bundle for a few minutes work, like doctors, lawyers, and corporate executives; or as romantically unprincipled and somewhat sinister, like politicians, lawyers, and televangelists. In fact, people don't think of us at all. We get no crowds pointing us out and whispering to one another as we walk by; no fathers telling their children that some day they may grow up to be like us; no groupies.

Trying to figure out the reason for this sad state of affairs, I've concluded that we just don't know how to handle ourselves on the job and those other folks do. The solution is clearly for us to copy them. "But how?" I hear you cry. "I am a scholar, at home and happy in the realm of virial gases, canonical ensembles, and stress tensors. What do I know of these worldly things?"

Well, you're in luck—as usual, I have the answers. Here, then, is *Professor Power: Becoming Rich and Famous in a One-Hour Work Week*.



M.D. MODEL—GENERAL PRACTITIONER

Teach five classes each semester. Schedule them all at 9:00 on Tuesday in separate classrooms. To keep the students from getting restless while they're waiting for you, leave some stimulating reading lying around, like a few three-year-old issues of *Centrifugal Pump Digest*. At 10:00 make an appearance in the first classroom, spend about ten minutes teaching something, give an assignment, and dismiss the class, telling them to pay their hourly tuition in the department office before they leave. Do the same thing in your other classes. After the last one, take the rest of the week off to avoid burnout.

DENTIST VARIANT

Same as the G.P., except instead of making the students wait for over an hour before the class starts, make them wait only 45 minutes and then have a teaching assistant give them some drill before you show up for your ten minutes.

MEDICAL SCHOOL FACULTY VARIANT

Put your graduate student advisees on an 80-hour work week. Two weeks before a proposal or paper deadline comes up, make them work 20-hour days, providing them with a cot in the laboratory to get some sleep during the remaining four hours. If anyone in the administration complains, remind them that you could be earning a great deal more in private industry. They won't give you any more trouble.

LAWYER MODEL

Invite the students to call on you any time they have difficulty with the course material. When they come to your office or phone you, keep track of the time you spend and charge \$2.50 a minute for it. If any of them are ever caught cheating, go before the judicial review panel and make tearful references to their previously unblemished record, the hardships they endured as children, and their devotion to their aged parents and half-blind dog. Then make disparaging and unprovable suggestions about the integrity, ulterior motives, and ancestry of the professor who caught them. Apply the usual charges.

POLITICIAN MODEL

On Day 1 of your course, promise that you will 1) teach the students everything they will ever need to know, 2) give all A's, and 3) provide free beer in class. Spend the semester telling them how valuable the course is and how hard you're working to meet their needs, but never actually teach them anything. Cancel about a third of the classes to attend conferences in places like Hawaii and the south of France, calling the trips "fact-finding missions." The day before the students fill out course evaluations, pass out the beer. Then give a comprehensive final, fail most of the class for not learning the material, and explain that it was all the administration's fault. Assure them that next semester things will be different—they'll get A's, free beer, and pizza. Most of them will believe you.

TELEVANGELIST VARIANT

Same as the politician, only 1) promise the students

Continued on page 92.

PROCESS CONTROL EDUCATION IN THE YEAR 2000

A Round Table Discussion

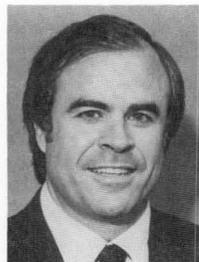
T. F. EDGAR

*The University of Texas at Austin
Austin, TX 78712*

THIS AUTHOR RECENTLY presented a paper on process control education at a joint India-U.S. symposium in Bangalore, India [1]. The paper [2] reviewed the current practices and philosophy of teaching undergraduate process control in a typical chemical engineering department and presented an outline for a course to be taught in the year 2000. This future course would cover the forecasted advances in hardware and software which should take place in the next ten to fifteen years.

A main difficulty with the one-semester process control course at most schools is that its starting point is still the same as it was when the landmark textbook by Coughanowr and Koppel [3] was first published in 1965. In order to incorporate all the advances in control engineering that have taken place in the past twenty-five years (as well as the projected developments) considerable streamlining of the curriculum material must be carried out. The problem faced by most educators is that we tend to adjust courses in a slow feedback mode. We do not adapt a course in a feedforward fashion so that it will match the technology encountered by BS graduates in a modern chemical plant.

In an effort to promote some thought and discussion within the process control community and to begin making curriculum changes now, an outline of a



Thomas F. Edgar is professor and chairman of the Department of Chemical Engineering at The University of Texas, Austin. He earned his BS in chemical engineering from the University of Kansas and his PhD from Princeton University. He has published over 100 papers in the fields of process control, optimization, and mathematical modeling of processes such as separations and combustion. He is coauthor of *Optimization of Chemical Processes* and *Process Dynamics and Control*, and author of *Coal Processing and Pollution Control Technology*.

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TABLE 1
Course Outline for Process Control (ca. 1988)

1. **Introduct. concepts: feedback vs. feedforward control** (1 week)
2. **Mathematical modeling of physical systems** (1 week)
3. **Linear system analysis: Laplace transforms** (2 weeks)
4. **Response characteristics of typical process systems** (1 week)
5. **Controller hardware, instrumentation** (1 week)
6. **Closed-loop analysis, stability calculations** (1 week)
7. **Tuning of PID controllers** (2 weeks)
8. **Frequency response analysis** (1-2 weeks)
9. **Advanced control methods: feedforward, cascade, multivariable, adaptive, supervisory, etc** (3-4 weeks)
10. **Plant control strategies, case studies** (1 week)
11. **Miscellaneous topics**

The above outline excludes time spent in an associated process control laboratory.

future course (discussed later in this paper) was circulated to a cross-section of educators and industrial practitioners for their comments, criticisms, and suggestions. Many of the responses were quite detailed and most interesting, and edited comments are presented in the Appendix to this paper. There is a surprising amount of agreement on the directions in which the field is moving, although there is no clear consensus on how a one-semester course can accomplish the stated objectives. Perhaps a two-semester sequence (such as is practiced in many schools abroad) is the only answer.

GOALS OF AN UNDERGRADUATE PROCESS CONTROL COURSE (1988)

A one-semester or one-quarter undergraduate process control course is required in virtually all US departments of chemical engineering. In some cases a two-quarter or, more rarely, a two-semester course is taught. The content of a typical undergraduate process control course is not intended to train process control specialists. Rather it presents the key concepts in dynamics and control and attempts to inculcate in BS engineers an understanding of transient operations and the influence of feedback control on responses.

A typical course has the following learning objectives:

- *Understanding the difference between dynamic and steady state behavior – courses in chemical engineering generally deal with steady state analysis only. This fact sets apart the subject matter in process control from other courses in the curriculum. Mathematical modeling is a key ingredient.*
- *Becoming proficient in analysis of dynamic systems – the principal tool employed in Laplace transforms. As long as the course focus is on linear continuous systems, Laplace transforms will always be the starting point, unless this is covered in a prior course in mathematics. The amount of emphasis on Laplace transform operations is an important issue, as discussed below.*
- *Learning the effect of feedback control and several industrially-accepted methods of tuning PID controllers – this leads to the issues of stability and performance in designing feedback controllers. Computer simulation with interactive graphics is a key pedagogical tool.*
- *Appreciating the benefits of advanced methods such as feedforward and cascade control – students should know under what conditions various methods should be implemented.*
- *Exposure to modern instrumentation and controller hardware as practiced in industry – in particular, a digital control system interfaced to an actual process. A laboratory experience should be included in the control course or as part of a unit operations laboratory.*

Table 1 shows the typical course content for a 15-week process control course based on 1980s textbooks such as Stephanopoulos [4], Smith and Corripio [5], or the new book by Seborg, Edgar, and Mellichamp [6].

There is wide disagreement on the amount of time that should be dedicated to mathematical modeling, since every additional hour spent there must be taken away from other material. Exemplary systems can be studied, such as the stirred tank heater which is described by a first-order linear differential equation. However, systems of industrial relevance are quite complex, and developing models for these systems in a few weeks of a process control course is clearly beyond the capabilities (from a fundamental point of view) of a typical undergraduate student. Nevertheless, such models can be presented to the student by employing simulators with rich graphics capabilities. The objective of such a simulator is to give the student a "feel" for dynamic behavior. However, it is unrealistic to expect the student to become even marginally competent in simulation or associated numerical analysis issues in this course.

Laplace transforms are the basic mathematical tool in process control, and the teaching of this subject (along with frequency response) has historically been viewed as a major part of a process control course.

The basic ideas in stability and PID controller tuning are important, but interactive software can be employed to solve realistic problems after a few tutorial examples. Root locus should only be briefly mentioned.

However, given the emergence of mainframe and personal computer software for linear systems analysis and simulation, does the current heavy emphasis on Laplace transform manipulations need to be re-evaluated? The early dependence on Laplace transforms arose out of necessity because computational and graphical tools were not available. Rigorous analysis was necessary to obtain transient responses. As a tool for complex systems, Laplace transform analysis to obtain time-domain responses is of marginal utility, especially when time delays exist in the process. The key to reducing the current course effort on linear systems analysis is the good interactive software which is available today [1]. It also would be helpful to modernize and focus the differential equation course which is taught by our colleagues in the mathematics department.

Controller hardware and instrumentation is a subject which requires continual updating as new products are introduced. While there is a lot of material here, most of it is descriptive in nature and tends to be vendor-specific. It should be mandatory that some background on the digital version of the PID controller be provided here since all controllers sold today are digital units (that appear to be analog). Programmed logic controllers (PLC) should also be covered.

The basic ideas in stability and PID controller tuning are important, but interactive software can be employed to solve realistic problems after a few tutorial examples. Root locus should only be briefly mentioned.

There are many ways to tune a PID controller [6]. Methods based on stability considerations alone are generally not satisfactory; performance-based methods are both stable and predictable with respect to the design criteria. For simple systems, most tuning methods give approximately the same results. The effect on model errors should also be addressed, leading to a robust PID controller. In controller design the quality of the results depends directly on the level of computational effort. The Ziegler-Nichols algebraic correlations based on the process reaction curve and the quarter-decay ratio give inconsistent performance. Improved performance can be achieved by frequency response. While application of this technique can be tedious, especially when undertaken manually,

interactive computer graphics permits the design of a PID controller to be completed very quickly. Unfortunately, many engineers who are responsible for controller tuning were subjected to the manual trial and error approach while they were students and have never since looked at this option. The fact that frequency response is rarely used in industry needs to be addressed (and corrected) by the educational sector.

The understanding of modern control systems provided by vendors or design firms requires consideration of a number of advanced control strategies. In the early 1970s, there were only a handful of plants using feedforward control. This algorithm is now considered to be the standard approach when combined with feedback control. Just as significant, cascade control is routinely used in computer control systems. Multivariable and adaptive control are of lesser importance, although industrial activity in these areas is growing rapidly. Industry is especially interested in self-tuning (adaptive) controllers because of reduced manpower requirements and improved performance with a negligible cost difference.

Plant control strategy is a topic properly emphasized throughout the text by Stephanopoulos [4]. While it may be arguable that the average undergraduate student is not intellectually mature enough to absorb this type of material on top of everything else, case studies which analyze a group of interconnected unit operations rather than a single process unit have merit as the "capstone" component of a course in process control. Safety issues also should be covered here.

Table 1 has omitted many specific topics that could be covered in an up-to-date control course; see Table 2. Many of these topics will increase in importance in the future.

PROCESS CONTROL IN THE YEAR 2000

What will the state of affairs be in the year 2000? While most educators believe the undergraduate students of that era will be more facile with the use of computers, it is unlikely that there will be a quantum jump in the mathematical preparation of those students. So the starting point of a typical course will be about the same. However, the industrial environment where process control is carried out will probably be quite different than it is today. Because of greater integration of the plant equipment, tighter quality specification, and more emphasis on maximum profitability while maintaining safe operating conditions, the importance of process control will be increased. Very sophisticated computer-based tools will be at the

disposal of plant personnel, who will at least need to understand the functional logic of such devices. Controllers will be self-tuning, operating conditions will be optimized frequently, total plant control will be implemented using a hierarchical (distributed) multivariable strategy, and expert systems will help the plant engineer make intelligent decisions (those he or she can be trusted to make). Plant data will be analyzed continuously, reconciled using material and energy balances with optimization, and unmeasured variables will be reconstructed using parameter estimation techniques.

How much emphasis needs to be placed on advanced techniques in the year 2000 course? Should we abandon analog (continuous) analysis methods in favor of digital ones such as z-transforms? What about the PID controller? Will it be replaced by a more general approach based on nonlinear programming? The answers to these questions are complicated by the fact that advancements in undergraduate education do not really cause a new industrial environment. There is probably much more influence at the graduate level. The second problem is that there is a great lack of uniformity in the modernization of chemical plants with respect to process control.

By the year 2000, the analog systems currently in use will have been replaced by digital systems. There will probably be sufficient computing capability available in each process plant (via distributed control) to implement any or all advanced techniques. There will still be single-loop panel-based controllers and control systems utilizing personal computers; while these can communicate with higher level computers, they will employ many different algorithms and functions than those offered in the standard PID controller today. So this may be the time when the standard undergraduate control course can be largely converted to digital control. Laplace transforms could be eschewed in favor of discrete time analysis (difference equations) and z-transforms.

Table 3 shows a 15-week lecture course for the

TABLE 2
Additional Topics for Undergraduate Process Control

- | | |
|--|---|
| <ul style="list-style-type: none"> • Alarms • Computer control systems, data acquisition • Predictive control • Simulation • Distributed control • Unit operations control applications • Batch sequence control • Process control languages | <ul style="list-style-type: none"> • Statistical process control • Process control data base management • Real-time computing, architecture • Expert systems, AI • Digital control algorithms • State space analysis • Supervisory control • Model identification |
|--|---|
-

year 2000 and indicates the emphasis of various topics. The selection of topics can be justifiably criticized because it presupposes a reasonable level of training in fields such as optimization. It also demands that Laplace transforms and linear dynamic systems be (appropriately) taught in the mathematics department. However, fifteen years from now we could use nonlinear programming tools in the same way as we employ numerical analysis for simulation today. The student does not need a deep understanding of the numerical details involved in order to have confidence in the answers. Even today linear and nonlinear programming tools have matured to the point that they are used routinely in commercial operations and serve as the basis for management and operating decisions [7]. Optimization can also provide a unified approach for model identification and parameter estimation.

The course in Table 3 would emphasize developing familiarity with the techniques of process control, with a distinct unit operations flavor. A one-semester

course would be insufficient to train specialists in process control, more so than it is in 1988. However, the ability of an engineer to creatively solve process control problems can be enhanced by continuing education and experience.

Obviously the content of the undergraduate process control will not exhibit a step change near the year 2000 but will evolve more or less continuously. This will require the interim development of educational materials to supplement existing courses. Probably the biggest discontinuity will arise in the conversion from continuous-time analysis (*e.g.*, Laplace transforms) to discrete-time, but this transition may never occur completely.

SUMMARY

Process control is a rapidly changing field, and its high technology nature demands continual updating of process control courses and laboratories. Perhaps the major issue to be addressed for the future is the role of continuous time analysis (*vs.* discrete-time) and increased use of simulation. A larger role for optimization in process modeling and controller design is envisioned.

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APPENDIX

Manfred Morari: Caltech

If you consider Laplace transforms simply as a tool for solving differential equations, then this aspect of Laplace transforms is obviously obsolete, and the use of Laplace transforms for obtaining system responses should be totally de-emphasized in the future curriculum. I, however, look at Laplace transforms and frequency response analysis more as a means of understanding the issues of stability, performance and robustness. There is simply no replacement in sight which conveys these issues with the same clarity.

a. The effect of a time delay variation, for example, on the stability and performance of a control system can be easily explained and nicely understood from a Nyquist curve analysis. Any other method would involve only trial and error via simulation and would not transmit the same degree of insight.

b. With the proper training, an undergraduate can learn to look at a Bode plot (obviously generated by CAD software) and determine from one curve the speed of response, the likelihood of overshoot,

TABLE 3

Course Outline for Process Control (ca. 2000)

Topics	Comments
Dynamic Simulation (2 weeks)	Concept of time constants for various physical systems, nonlinear behavior, commercial simulation packages
Response characteristics (1 week)	First, second, and higher order; unusual response characteristics (with examples)
Development of discrete-time models (1 week)	Fitting of discrete-time equations to data, use of convolution models
Analysis of discrete-time systems (2 weeks)	z-transforms, transfer functions, stability analysis
Conventional and predictive controller structures (2 weeks)	Conventional digital feedback vs. predictive control, supervisory control, cascade implementation of control trajectories
Optimization methods for controller design (2 weeks)	Optimal tuning of PID controllers, nonlinear programming formulation of design problem (<i>e.g.</i> , dynamic matrix control or DMC), constraint handling
Tuning of controllers/robustness (1 week)	Effect of tuning parameters for PID/predictive controllers, treatment of model errors
Feedforward, adaptive, and multivariable control (2 weeks)	Extension of optimization methods to cover disturbance rejection, model parameter changes, and multivariable interactions
Digital hardware/implementation (1 week)	Equipment features and configurations, sampling, filtering
Expert systems (1 week)	Structure and purpose of expert systems, alarm analysis, selectors

NOTE: Laboratory experiments employing a modern digital control system are recommended to supplement the lectures described above.

steady state offset, the behavior of the system for a range of different disturbances, the possible sensitivity of the closed loop system to modeling errors, if non-minimum phase characteristics are present, etc. To obtain the same information and insight from either an analysis of difference equations or extensive simulations would be essentially impossible, or, to say the least, rather involved.

"Will the PID controller be replaced by a more general approach based on nonlinear programming?" Largely not. The one important issue absent from your paper is modeling. The PID controller provides reasonably good control with a minimum of modeling effort. The information required to set up a nonlinear program for online control is much larger and in most cases the effort is not justifiable. This is also the reason why fewer model predictive control schemes have been implemented than the public has been led to believe.

Irv Rinard: CUNY

One concern is that process control has traditionally been taught from the bottom up. Now that is okay if we are training our students to be process control engineers. But if the plant control engineers are going to be chemical engineers who occasionally have to worry about process control along with a lot of other things, bottom up is probably not appropriate. They spend a semester getting to the point where they can analyze and design a SISO feedback controller, then they go out into a chemical plant only to find out that PID controller tuning is not the plant's critical control problem.

Along the lines of what you have suggested, perhaps there should be two undergraduate control courses: one an overview course which everyone would take, and a second course for those who intend to go into the systems engineering side of the business.

Another concern is that the focus of process control has been too narrow. Algorithms and their implementation have received most of the attention. Students go forth only to learn that measurements can be biased, or noisy, or fail altogether; that control valves stick; and that other critical items are either messed up or maxed out. Tuning a loop is more than just determining P, I, & D: it is also zeroing and spanning, fixing and adjusting, and sometimes even rewiring. Ninety percent of a proper computer control algorithm is data checking. While the topics of data reconciliation and fault diagnosis are on your agenda for the year 2000, they belong properly and prominently in the very first undergraduate course.

Along the same lines, students go forth thinking that the regulatory control system is it. They are almost totally unaware that the most important control system in the plant is not the regulatory control system, but the safety system. The former affects the size of your paycheck: the latter, whether or not you'll be around to collect it. Only Rijnsdorp has given this subject any coverage in a control textbook, at least as far as I can recall offhand.

What I would like to see is a revision of the entire curriculum to make it more model-based. Students should connect the basic idea of dynamic simulation to the solution of differential equations early on. Then, in the various courses, the appropriate models would be developed as a pedagogical tool. For instance, in thermodynamics, instead of learning about flash calculations in the abstract, the students could develop a dynamic model of a flash drum: in unit operations, dynamic models of heat exchangers and distillation columns. Then, when they get to the process control course, they already have the basic background in process modeling. I have found in teaching process control that modeling is what the students are weakest in. Emphasizing it throughout the curriculum might help. Perhaps this is an issue that CACHE should take up.

Jim Doss: Tennessee Eastman

In order to streamline the curriculum, a first step would be to put Laplace transforms into the mathematics courses. However, students tend not to retain the mathematical theory but to remember the experiences from control laboratory experiments and simulations. It is also important to emphasize the use of computation, especially with computer graphics. Students need to learn more about modeling and identification of process models. More digital control needs to be presented, and a parallel presentation of s and z transforms (such as in Saucedo and Schiring's textbook) might be necessary in the future. However, other digital devices such as

PLCs and their use in interlocks are important, combined with discussion on alarms and process safety. Finally, students need to understand the concept of total plant control.

Wayne Bequette: Rensselaer Polytechnic Inst.

It is interesting that ChEs handle process control so well, despite the fact that we are trained (at the BS level, where 90% of the control engineers come from) on black box or linear system models. Our knowledge of "real" processes comes from our background in steady state modeling and design. Rarely in a typical BS curriculum are we teaching students using complex, nonlinear dynamic models. Our ideas, when we get into industry, about what effect certain manipulated variables have on certain output variables are based solely on our steady state background. I guess that one of the most important experience that an undergraduate control student can have is controlling laboratory equipment. A good dynamic process simulator can provide almost as good of an educational experience.

Sometimes it is amazing how well ChEs control processes in the real world, with such a poor theoretical background. It is well known, of course, that it takes a year or two of experience before a BS candidate can make a real contribution—but this is true of most industrial positions, not just process control engineering. In addition, most problems will be solved by the simplest method available, so the lack of theory is not a major hindrance.

I believe that for the vast majority of control loops, there will be no issue of digital vs. analog control. The lowest level of control (constituting > 80% of the loops) will continue to be a simple PI flow controller. The sampling rate is high at this level, so there is not a vast difference between digital and analog control. The main advantage of digital at this level is the ease of maintenance issue. That will be the main advantage of most loops for a period of time, because, if a particular control strategy is ineffective, digital technology allows a quick retrofit.

Brad Holt: University of Washington

Some of the key questions really must be dealt with. Should we be teaching continuous or discrete control theory? Can we teach the course using discrete theory completely and yet convey to the students the feel for dynamics and modeling that we do with continuous theory? How does modeling fit into such a course? Do we teach them difference equations or discrete approximations to ordinary differential equations? There simply is not time in such a course to teach both continuous and discrete theory, but almost all of the discrete texts that I have seen really assume a continuous background. Although I feel that teaching the course from the discrete standpoint would be very valuable, I haven't figured out how to do it and convey all of the ideas and information that we do now.

One important area which I feel that you could have said more is in how to actually design controllers. Most of the control books present P, PI, and PID as "the" controllers. You select one of these and then follow some rules to tune it. The books do not do a good job of suggesting when they will work well, when they don't and why there are problems. This year I taught the seniors an IMC based control philosophy as the first step. We started with feedforward controllers and how to design them, progressed to IMC as a technique to handle disturbances and uncertainty, and finally introduced the standard control configuration as the normal implementation method. This led to PI and PID controllers, how to tune them, and when they are likely to work. The students really feel that they know how to "design" controllers. They understand the role of uncertainty, the importance of models, and why systems with non-minimum phase elements are difficult to control. Although I will do some things differently next year, the experiment worked well.

Daniel Rivera: Shell Development

The course should begin by reflecting on fundamental system properties that establish chemical process control as a field in its own right. The effect of deadtime, inverse response, constraints, uncertainty, and operating requirements on achievable closed-loop performance should be emphasized. Discussing these issues can be done at the beginning of the course because these represent inherent limitations independent of control design. All of the course material should revolve upon technologies to meet these requirements.

The benefits of Laplace and frequency-domain methods should not be rejected because of implementation considerations. Frequency-domain analysis is useful even when controller design is performed in the time domain. The recent theory on robustness of control systems is one such example. What is probably more reasonable is to replace such exercises as inverting Laplace transforms and the like with instruction on the use of frequency-domain techniques for performance and robustness analysis.

Why should the undergraduate curriculum have to wait until the year 2000 to include a treatment of model uncertainty and constrained control? While a thorough treatment of these topics is probably most suited for graduate level courses, there is enough existing theory to justify, at the very least, a conceptual introduction to these subjects.

Lin Tung: Fisher Controls

ChE's should understand the process as well as control and should have some background in control strategies for various unit operations. Increased use of the concepts should not be at the expense of process understanding. PID control will still be a key control concept in 2000 (and probably not be replaced by nonlinear programming), although as part of distributed control systems (DCS). DCS system concepts should be presented and students should be exposed to such equipment (most vendor systems employ the same basic ideas although the equipment may differ). We need to upgrade the operator's educational level; in Europe BS engineers are used (why use a high school graduate to control a multi-million dollar process?).

Ed Bristol: Foxboro

Teaching of PID tuning should have a strong root locus component (the closed-loop response is shaped by the dominant three poles). We need to get students to think more in the frequency domain and to develop a practical feel for dynamics and control. An experienced tuner is like an experienced car driver. Theory should be used to gain insight, not just to implement a tool. Control engineers should not restrict themselves to facts that can be proven mathematically. We want methods that work even when the theory does not. Model uncertainty (such as nonlinearity, model order, or noise) should in practice lead one to use a simpler approach, while many theories tend to give more complex answers.

Christos Georgakis: Lehigh University

Regarding the observation that we might abandon the continuous time domain for the discrete time one, you are right that the widespread use of digital control computers is pushing us in this direction. However, many chemical processes are slow, and if slow composition measurements are not used, then the sampled character of the digital control computer has no effect on the performance of the controller. In this case, continuous time might be sufficient. I, however, agree with you that the sampled data concerns should start being incorporated in the first process control course. The extent will depend on what is the philosophy of the most popular texts between now and the year 2000.

I expect that "expert systems" will have an impact on process control education much earlier than the year 2000 and to a larger extent than you estimate in your paper. In my definition of "expert systems" I include systems that are not necessarily "expert" but complement the numerical calculations, of, say, a PID algorithm with symbolic calculations (or logic, if you wish) to design the overall control system. A selector is the simplest example. While in practice we use override controls and PLCs, we do not teach our students about them in a systematic way.

Joel Hougen: Consultant (U. of Texas, retired)

We need to strongly emphasize accurate instrumentation and the importance of obtaining good data. Many existing plants are instrumented without much thought about needed performance characteristics. Students need to appreciate the importance (and lack) of field instrument calibration and the difficulty of obtaining fundamental plant models (hard to predict steady state or dynamic characteristics in advance). Undergraduates should have the experience of successfully verifying simple dynamic models in the laboratory. A reasonable goal is $\pm 2\%$ accuracy in material balances. For most processes, simple dynamic models are adequate and PID controllers are satisfactory. However, Ziegler-Nichols tuning is not

appropriate for today's controllers to achieve high performance. A great amount of process understanding is necessary to develop process control strategies; algorithms are secondary. In the course, theory should connect to reality (and not just be a mathematical exposition).

George Stephanopoulos: M.I.T.

Prerequisites for the design of good controllers are: the in-depth understanding of open-loop process dynamics and closed-loop behavior under various control modes (proportional/integral/derivative). A good coverage of these two subjects gives a strong imprint of analytical attitude, which completely characterizes the educational experience in the course.

But within such an environment the following issues are hardly ever raised: What are the operational objectives in the plant? How does one convert informal operating requirements (e.g., minimize operational cost) to formal and explicit control objectives?

Even for the design of single loops, some important considerations are only lightly touched upon. For example: How does one systematically develop the process model needed for a particular control task? What is the effect of model inaccuracies on the stability and performance robustness of a control loop? How does one design a control loop in the presence of input and output constraints?

While the above questions are asked by practicing engineers on a daily basis, it is not true that they are difficult to answer or require an extensive expansion of lecture hours.

The continuing preoccupation with the analytical leg of process control is partly due to our inability to deal with non-analytic, factual, poorly articulated, often contradictory and qualitative knowledge. We do not know how to handle conflicting facts, or we downplay the importance of qualitative knowledge. Our ability to harvest the added opportunities offered by knowledge-based systems depends on our awareness of the new computing technology. Object-oriented programming is indispensable in capturing structured knowledge around processing units, controllers, control design tasks, order-of-magnitude reasoning, etc.

Yaman Arkun: Georgia Tech

Dynamic modeling should be covered throughout the ChE curriculum. The control course should focus on the utilization of dynamic models for control purposes rather than setting them up from first principles which can be best accomplished in other core ChE courses. It is better to spend the time on relevant control issues like the extent of required modeling sophistication, e.g., nonlinear vs. linear approximations, effects of parameter uncertainties, neglecting secondary physical phenomena, etc.

I personally do not devote more than two lectures to Laplace transforms. I believe the home for detailed treatment of Laplace transforms is in a math course. However, the topic is important as it naturally bridges linear dynamic models with continuous transfer functions and frequency response analysis. The emphasis on frequency response should remain since practical and fundamental problems such as stability, performance, and robustness with uncertainty can be nicely interpreted using Bode, Nyquist plots, and M -circles without resorting to trial and error dynamic simulations.

In the very near future, I believe we will see more coverage of discrete-time systems and model predictive control in the undergraduate control courses. The reason for this is the industrial success of MPC and the fact that it does provide a framework within which a wider scope of realistic control problems can be conveniently couched and conveyed to the students. The issues of process economics, operational constraints, changing objectives with time, and the utilization of process models online are difficult if not impossible to illustrate using PID or other more classical controllers. Any undergraduate textbook in this area will have to be supplemented with simulation software which implements MPC. Development of case studies mimicking the exercise a control engineer goes through in practice will be invaluable. Such projects would be assigned at the beginning of the course very much like a senior design project and solved in parallel with the lectures covering areas such as problem formulation, model development and discrimination, control structure selection, and finally, tuning and performance assessment. We have done this using PID, feedforward, and cascade controllers, and I can envision doing it in the near future using MPC and more challenging industrial problems. □

THE UNSTRUCTURED STUDENT-DESIGNED RESEARCH TYPE OF LABORATORY EXPERIMENT

A. MACIAS-MACHIN,¹ GUOTAI ZHANG,²
and OCTAVE LEVENSPIEL

Oregon State University
Corvallis, OR 97331-2702

THE STANDARD LABORATORY experiment in chemical engineering centers around a fixed piece of equipment, so the whole exercise is pretty much unchanged from year to year. But in these times when use of the personal computer is widespread, student reports of these experiments can easily be saved, merged, and passed on year after year, in ever-improved form—sometimes with little thought on the part of the preparer.

We would like to encourage the increased use of a different kind of exercise: the research type of laboratory experiment. Here, instead of showing the students the equipment to be used, and telling them what to do and how to write it up (eight sections in the report, starting with introduction, theory, *etc.*), tell them what you want to discover and let them choose their own way of doing it.

In this paper, this type of experiment is discussed and illustrated with one example. The main idea is as follows:

1. Tell the team of students the question you want answered. Choose a question which can be answered in more than one way—something which is not in their textbooks and which will require that they develop their own analysis;



Agustin Macias-Machin, assistant professor at the Polytechnic University of Canary Islands (Spain) is presently at Oregon State University on a two-year visiting faculty appointment. He is doing research on various projects, all focusing on solar energy storage in phase change materials, which is a critical problem for the Canary Islands.

¹On leave from Polytechnic University of Canary Islands, Spain
²On leave from East China University of Chemical Technology, Shanghai

something which was not asked last year or the year before.

2. The students should consider the alternatives and decide among themselves, after discussion, how to go about answering the question.
3. Once a decision is made, the students should present their plan to the instructor in order to see if equipment is available. At this point, they might be asked (gently, of course) if they would like to reconsider part of their plan.
4. The students are then to proceed with the experiment, to compare their results with the literature, and to write up their findings—not a big report, but one which is to the point.

EXAMPLE OF THE MINI-RESEARCH EXPERIMENT

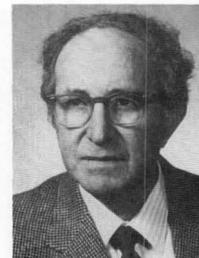
The Question

Tell the student team that you want them to find *h* for melting ice, maybe because you have been asked to look into the feasibility of capturing antarctic icebergs for towing to parched lands for fresh water (make up a good story). More precisely, tell them to

Guotai Zhang is an associate professor at the East China University of Chemical Technology (Shanghai) and is director of the hydrocarbon processing laboratory there. He is presently a visiting researcher at Oregon State University studying ways of fluidizing extremely fine particles which do not want to fluidize.



Octave Levenspiel is professor of chemical engineering at Oregon State University and is particularly interested in chemical reactors. He has written a number of books and was one of the earliest recipients of ASEE's Lectureship Award. He recently received an honorary doctorate from France for his "internationally outstanding scientific reputation."



We would like to encourage the increased use of a different kind of exercise: the research type of laboratory experiment. Here, instead of showing the students the equipment to be used and telling them what to do . . . tell them what you want to discover and let them choose their own way of doing it.

develop an expression for h for downfacing ice surfaces in quiescent water at different temperatures, to compare this with what's available in literature, and to recommend an expression for use.

Tell them that there is no experimental set-up for this purpose. However, say that the laboratory has vats, thermometers, scales, and calipers available, and that Professor X has a refrigerator with a freezer section in his office which he may allow them to use if asked nicely.

Tell the team to report back to you when they are ready and to tell you what they plan to do, what equipment they've assembled, and what they found in the literature. We suggest reserving about one-third of the marks for this presentation, to see if they really have thought the problem through. The whole experiment should take two laboratory periods.

One Way to Answer the Question

1. Take half of a fast-food hamburger styrofoam container, fill it with water, and freeze it.
2. Place it face down in a vat of water, remove any air bubbles that are present, and then measure the thickness of the slab of ice with calipers at various times. That is all there is to the experiment itself.
3. The analysis needed to find h should not be difficult, but since it will not be found in any book they will have to develop it themselves. They should be able to do it. Don't help them. They should find that the slope of the thickness-time curve is all they need. Figure 1

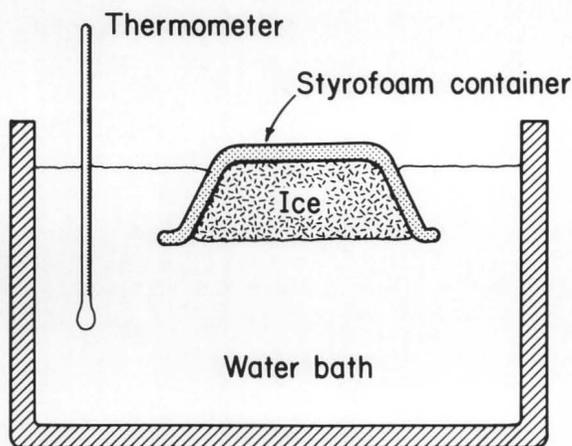


FIGURE 1. Experimental set-up.

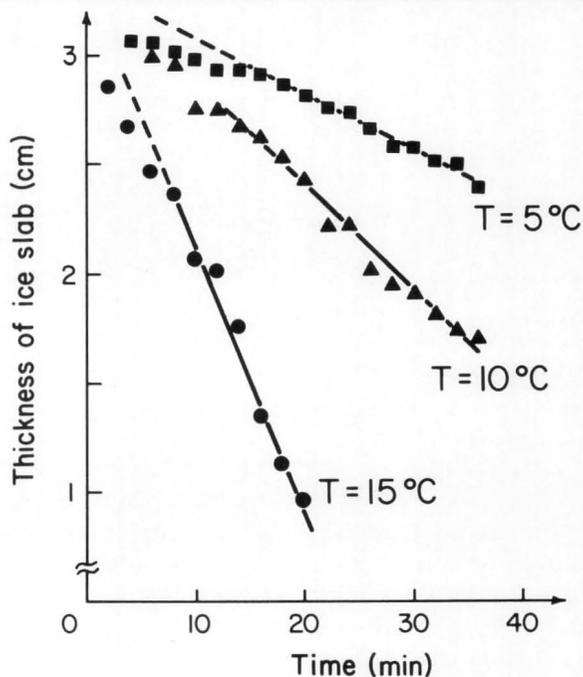


FIGURE 2. Typical findings for the thickness of ice layer vs. time for horizontal downfacing slabs of ice in water at various temperatures.

shows the procedure, and Figure 2 shows what we found when we did this experiment.

4. In the analysis and discussion of their results, you may want to look for the following points:
 - Were the students able to find a literature correlation for h for cold downfacing plates in water? Did they check Penny?
 - Did it occur to them that h for melting ice may differ from h for ordinary flat surfaces, and did they search for this h value in the literature? Did they even consider this whole matter? (Extra points!)
 - Did they compare their values with the literature values and discuss the differences?
 - If they found a lower initial slope in Figure 2, as we did, did they try to explain why this was so? Or did they just least-square the whole set of data? (Poor.)
 - Did they at least plot the data and look at it? Or did they just generate a computer program which calculated h without human intervention or judgement? (Terrible!)
5. As for the experimental procedure:
 - Did they try to insulate the top and sides of their block of ice, somewhat as we did, or did they plunge the whole

Continued on page 116.

FROM MOLECULAR THEORY TO THERMODYNAMIC MODELS

Part 2: Mixtures

STANLEY I. SANDLER

University of Delaware
Newark, DE 19716

IN THE PREVIOUS paper we showed how one could establish a theoretical basis for both understanding and testing the molecular level assumptions contained in common pure fluid equations of state and for developing new ones. We now extend this analysis to mixtures and will consider activity coefficient models and equation of state mixing rules.

THE GENERALIZED VAN DER WAALS PARTITION FUNCTION FOR MIXTURES

The starting point is again the canonical partition function, here for N_1 molecules of species 1, N_2 molecules of species 2, etc., contained in a volume V at temperature T

$$Q(N_1, N_2, \dots, V, T) = \sum_{\text{states}} e^{-E_i(N_1, N_2, \dots, V, T)/kT} \quad (1)$$

where E_i is the energy of the i^{th} quantum state. From this partition function all other thermodynamic properties can be computed (Eqs. (1-2 to 4) of [1]). (We will refer to equations from [1] using the designation l.)

Following the same analysis as in [1] of separating the translational, rotational, vibrational, electronic, and interaction energy states, we obtain the following expression for the generalized van der Waals partition

Using the terminology of (1), this term is referred to as the configurational contribution to the free energy. The second term is the residual term; it arises from the soft repulsive and attractive forces among the molecules—that is, from the molecular interactions.

function for a mixture of simple molecules

$$Q = \left(\prod_i \frac{1}{N_i!} (q_t q_r q_v q_e) N_i \right) V_f^N(T, V, N_1, N_2, \dots) \exp\left(\frac{-N\Phi(T, V, N_1, N_2, \dots)}{2kT}\right) \quad (2)$$

where

$$\Phi(N_1, N_2, \dots, V, T) = \frac{-2kT}{N} \int_{T=\infty}^T \frac{E^{\text{CONF}}(N_1, N_2, \dots, V, T)}{kT^2} dT \quad (3)$$

$$= \frac{2T}{N} \int_{1/T=0}^{1/T} E^{\text{CONF}}(N_1, N_2, \dots, V, T) d\left(\frac{1}{T}\right)$$

with

$$E^{\text{CONF}}(N_1, N_2, \dots, V, T) = \sum \sum E_{ij}^{\text{CONF}}(N_1, N_2, \dots, V, T) \quad (4)$$

and $N = \sum N_i$. Once the mixture free volume V_f and the average configurational energy for each species i interacting with species j molecules, E_{ij}^{CONF} , is known, Eq. (2) can be used to obtain the equation of state and other thermodynamic properties of a mixture.

Alternatively, instead of using the mixture partition function directly, we can consider the difference between the partition function of the mixture and those of the pure components to obtain the change in properties on forming a mixture from the pure fluids. In particular, to obtain an excess Helmholtz free energy change on mixing that is equal to the excess Gibbs free energy at constant temperature and pressure from which we can obtain activity coefficients, the mixing process must be one in which we start with the pure components at temperature T and pressure P , where their molar volumes are \underline{V}_i , and then adjust the pressure of the mixture so that there is no volume change on mixing; that is, that [2]

$$\underline{V}_{\text{mix}} = \sum x_i \underline{V}_i$$

In this case we have

$$\begin{aligned}
A_{T,V}^{EX} &= G_{T,P}^{EX} \\
&= A_{\text{mix}}(T, V, N_1, N_2, \dots) - \sum A(T, V_i, N_i) - kT \sum N_i \ln x_i \\
&= -kT \ln \left(\frac{V_f(N_1, N_2, \dots, V_{\text{mix}})^N}{\prod_i \left[V_{f,i}(N_i, V_i) \left(\frac{N}{N_i} \right)^{N_i} \right]} \right) \\
&\quad + \frac{1}{2} [N\phi(T, V_{\text{mix}}, N_1, N_2, \dots) - \sum N_i \phi_i(T, V_i, N_i)] \\
&= -kT \ln \left(\frac{V_f(N_1, N_2, \dots, V_{\text{mix}})^N}{\prod_i \left[V_{f,i}(N_i, V_i) \left(\frac{1}{x_i} \right)^{N_i} \right]} \right) \\
&\quad - kT \int_{T=\infty}^T \frac{[\sum \sum E_{ij}^{\text{CONF}}(T, V, N_1, \dots) - \sum E_i^{\text{CONF}}(T, V_i, N_i)] dT}{kT^2} \\
&= A_{\text{CONF}}^{EX} + A_{\text{RES}}^{EX} \quad (5)
\end{aligned}$$

The first term on the right-hand side of the equation, which arises from the difference in free volume terms, is the excess Helmholtz free energy of mixing that persists at very high temperatures; it depends upon the hard-core size and shape differences between the molecules. Using the terminology of [1], this term is referred to as the configurational contribution to the free energy. The second term is the residual term; it arises from the soft repulsive and attractive forces among the molecules—that is, from the molecular interactions.

There are two different ways to proceed in thermodynamic modeling. One, for high pressure mixtures (especially of hydrocarbons and inorganic gases), is to use an equation of state to describe both the vapor and liquid phases. The other, for mixtures at low pressure and with more complicated molecules, is to use an equation of state only for the vapor phase and an excess Gibbs free energy (activity coefficient) model to describe the liquid phase. While it is common to think of these two methods of thermodynamic modeling as being completely distinct, we see from Eq. (2) (the derivative of which leads to the equation of state) and from Eq. (5) (the composition derivative of which leads to activity coefficients) that both have the same origin: the statistical mechanical partition function. Consequently, any assumptions made about the mixture free volume and configurational energy will lead to an equation of state and its mixing rule as well as to an activity coefficient model. As we will soon see,

the assumptions which lead to the usual equations of state produce only the simplest excess Gibbs free energy models, while the assumptions which lead to the most commonly used free energy models result in equation of state mixing rules which do not satisfy an important theoretical boundary condition.

LOCAL COMPOSITIONS AND THERMODYNAMIC MODELS

For demonstration purposes we will consider a mixture of square-well molecules (see [1] for a definition of this potential). Following the analysis in [1] we obtain

$$E_{ij}^{\text{CONF}} = -\frac{N_j}{2} N_{ij} \epsilon_{ij} \quad (6)$$

where N_{ij} is the average number of i molecules interacting with a central j molecule at the temperature and density of interest. Thus, N_{ij} may be thought of as a species-species coordination number. In order to proceed further we need to have information about the free volume in the mixture and the species coordination numbers N_{ij} as a function of temperature, composition, and density. We will now consider each of these terms separately.

For mixtures of hard spheres (or the hard-core part of square-well fluids) the free volume can be approximately estimated using the van der Waals expression

$$V_f = V - (\sum N_i) b \quad \text{with} \quad b = \sum \sum x_i x_j b_{ij}$$

[Further using $b_{ij} = (b_{ii} + b_{jj})/2$, which is correct for hard spheres, we have $b = \sum x_i b_i$.] Using this result in Eqs. (1 and 1-3) gives the usual van der Waals configurational or free volume part of the equation of state

$$P^{\text{CONF}} = kT \left(\frac{\partial \ln V_f^N}{\partial V} \right)_{N,T} = NkT \left(\frac{\partial \ln V_f}{\partial V} \right)_{N,T} = \frac{NkT}{V - Nb} \quad (7)$$

Similarly using this expression for the free volume in the configurational contribution to excess Helmholtz free energy, Eq. (5), gives

$$\begin{aligned}
A_{\text{CONF}}^{EX} &= -kT (N \ln V_{f,\text{mix}} - \sum N_i \ln V_{f,i} + \sum N_i \ln x_i) \\
&= -kT \ln \left(\frac{(V - \sum N_i b_i)^N x_i^{N_i}}{\prod (V_i - N_i b_i)^{N_i}} \right) = kT \sum N_i \ln \frac{\Phi_{f,i}}{x_i} \quad (8)
\end{aligned}$$

where

$$\Phi_{f,i} = (V_i - N_i b_i) / (V - N_i b_i)$$

is the free volume of pure species i divided by the total free volume in the mixture.

If we assume that the free volume fraction of species i is equal to its volume fraction, Eq. (8) becomes the well-known Flory expression for the configurational free energy term [3]. Clearly other assump-

tions can be made; for example, we can also use the Carnahan-Starling free volume expression (Eq. (1-15)) and its analogue for mixtures, though at the cost of greater mathematical complexity.

The simplest species-species coordination number model is that the mixture is random, that is

$$N_{ij} = \frac{N_i}{V} C$$

where C is the same constant for all species-species interactions. This is the generalization of the van der Waals assumption that the coordination number is a linear function of density that we used in [1]. Using this in Eq. (2 to 4, and 1-3) we obtain

$$P^{res} = \frac{N^2}{V^2} \frac{C}{2} \sum \sum x_i x_j \epsilon_{ij} = -\frac{1}{V^2} \sum \sum x_i x_j a_{ij} \quad (9)$$

where

$$a_{ij} = -CN_a^2 \epsilon_{ij} / 2$$

in analogy with [1].

Combining the configurational (Eq. 7) and residual (Eq. 9) contributions gives the van der Waals equation of state (Eq. 1-14b) with the following mixing rules

$$a = \sum \sum x_i x_j a_{ij} \quad (10a)$$

and

$$b = \sum \sum x_i x_j b_{ij} \quad (10b)$$

Eqs. (10 a,b) are known as the van der Waals one-fluid mixing rules. The first part of the name refers to its originator, and the second to the fact that they lead to mixture being described by the same equation of state as the pure fluid, but with composition-averaged parameters.

It is known from statistical mechanics [4] that the mixture second virial coefficient, that is, the coefficient B_{mix} in the expansion for a mixture

$$\frac{PV}{RT} = 1 + \frac{B_{mix}(T)}{V} + \dots \quad (11)$$

has a quadratic composition dependence. Since the low density expansion of any cubic equation of state results in the second virial being a linear function of the equation of state parameters a and b (for example, $B_{mix}(T) = b - (a/RT)$ for the van der Waals equation), the known quadratic composition dependence of $B(T)$ requires that Eqs. (10 a,b) be satisfied at low density. This is an important theoretical low-density boundary condition. In fact, in chemical engineering the mixing rules of Eqs. (10 a,b) are generally used at all densities. One present area of equation of state research is density-dependent mixing rules which have a more complicated composition dependence at high density but reduce to Eqs (10 a,b) at low density.

Using the random mixing assumption in Eq. (5) with the further approximation that the molar volume

of each species is approximately the same leads, for a binary mixture, to

$$A_{RES}^{EX} = G_{RES}^{EX} = \frac{1}{2} \left[N\phi_{mix} - \sum_{i=1}^2 N_i \phi_i \right] = -C \frac{N^2}{V} x_1 x_2 (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) \quad (12)$$

which is the one-constant Margules expression [5], or the two-constant Margules expression if we do not assume that the molar volumes are equal. Thus, from the analysis so far we see that the Margules equation with a Flory-Huggins correction (or without it if we neglect the contribution of Eq. 8) for the excess free energy and activity coefficients, and the van der Waals one-fluid mixing rules have the same origin in molecular theory, the random mixture.

From statistical mechanics we can easily show that the exact low density result for the species-species

TABLE 1
Local Coordination Number Models
and Equations Which Result

Local Coordination Number Model	Equation of State Mixing Rule	Free Energy (Activity Coefficient) Model
$N_{ij} = \frac{N_i}{V} C$	vdW 1-fluid	Margules
$N_{ij} = \frac{N_i}{V} C_{ij}$	vdW 1-fluid	Margules
$N_{ij} = \frac{N_i}{V} C_{ij} e^{\epsilon_{ij}/kT}$	vdW 1-fluid	Margules
$\frac{N_{ij}}{N_j} = \frac{N_i}{N_j} \frac{v_i}{v_j}$ with $N_{ij} + N_{ji} = N_{cj}$ and θ_{ij} independent of T and V	nonquadratic, density independent $a = \frac{\sum \sum x_i x_j v_i a_{ij}}{\sum x_i v_i}$ if $N_{cj} = \frac{N}{V} C_j$	Van Laar and regular solution [6] if $A_{CONF}^{EX} = 0$ or Flory-Huggins if Flory term used for A_{CONF}^{EX}
$\frac{N_{ij}}{N_j} = \frac{N_i}{N_j} \frac{v_i}{v_j} e^{(\epsilon_{ij} - \epsilon_{jj})/kT}$ with $N_{ij} + N_{ji} = N_{cj}$	as above	Wilson [7] equation
Surface area fractions	nonquadratic, density independent	UNIQUAC [8] equation when Guggenheim-Staverman expression used for A_{CONF}^{EX}

coordination number in a mixture of square-well molecules is

$$\lim_{\rho \rightarrow 0} N_{ij}(N_1, N_2, \dots, V, T) = \frac{N_i}{V} \frac{4\pi}{3} \sigma_{ij}^3 (R_{ij}^3 - 1) e^{\epsilon_{ij}/kT} \quad (13)$$

This is an interesting result since it requires that the local composition of i molecules around a j molecule is proportional not only to the mole fraction of species i , but also terms that depend on the sizes and energies of interaction of the i and j molecules. Thus, in general, the mole fraction of i and j molecules around a central molecule will be different than their bulk mole fractions. That is, the random mixing model is incorrect, unless all species have the same size ($\sigma_{ii} = \sigma_{jj} = \sigma_{ij}$), well width ($R_{ii} = R_{jj} = R_{ij}$), and energy of interaction ($\epsilon_{ii} = \epsilon_{jj} = \epsilon_{ij}$). We refer to departures from random mixing as a local composition effect.

Assuming that Eq. (13) is valid at all densities, we obtain for the residual part of the equation of state

$$\begin{aligned} P^{\text{RES}} &= -\frac{N^2}{V^2} \frac{2\pi}{3} kT \sum \sum x_i x_j \sigma_{ij}^3 (R_{ij}^3 - 1) (e^{\epsilon_{ij}/kT} - 1) \\ &= -\frac{N^2}{V^2} \sum \sum x_i x_j a_{ij} \end{aligned} \quad (14)$$

where

$$a_{ij} = \frac{2\pi}{3} kT \sigma_{ij}^3 (R_{ij}^3 - 1) (e^{\epsilon_{ij}/kT} - 1)$$

Thus, again the van der Waals one-fluid mixing rules and the Margules expansion for the activity coefficient (which we leave as a proof for the reader) are obtained, though this time from a non-random, local composition model. In fact we can generalize the analysis to show that any assumption in which the local composition N_{ij} is a linear function of the density of species i (regardless of its temperature dependence) results in the van der Waals one-fluid mixing rules and the Margules Gibbs free energy or activity coefficient model. Table 1 contains a number of local composition models and the equation of state mixing rules and activity coefficient models which result.

A different class of thermodynamic models results from starting instead from assumptions about the ratio of local compositions, which we will write as

$$\frac{N_{ij}}{N_{jj}} = \frac{N_i}{N_j} \theta_{ij}$$

For example, from Eq. (13), we have

$$\lim_{\rho \rightarrow 0} \frac{N_{ij}}{N_{jj}} = \frac{N_i}{N_j} \frac{\sigma_{ij}^3}{\sigma_{jj}^3} \frac{(R_{ij}^3 - 1)}{(R_{jj}^3 - 1)} e^{(\epsilon_{ij} - \epsilon_{jj})/kT}$$

so that

$$\lim_{\rho \rightarrow 0} \theta_{ij} = \frac{\sigma_{ij}^3}{\sigma_{jj}^3} \frac{(R_{ij}^3 - 1)}{(R_{jj}^3 - 1)} e^{(\epsilon_{ij} - \epsilon_{jj})/kT} \quad (15)$$

However, to proceed with generalized van der Waals theory, each of the N_{ij} are needed, not merely their ratio. A common (implicit or explicit) additional assumption contained in many activity coefficient models is that the total coordination number for each species

$$N_{cj} = \sum_i N_{ij}$$

while it may be a function of temperature and density, is independent of composition. That is,

$$N_{cj} \neq N_{cj}(x_1, x_2, \dots, x_N) \quad (16)$$

This assumption has its origin in lattice-based models of liquids which generally require that the lattice on which molecules are placed is fixed, so that the coordination number of each lattice site is unchanged with composition. This assumption is correct if the random mixing assumption, $N_{ij} = CN_i/V$, is valid, but is incorrect otherwise.

For a binary mixture using Eq. (16) to solve for N_{ij} in terms of θ_{ij} leads to

$$N_{jj} = \frac{x_j}{x_i \theta_{ij} + x_j} N_{cj} \quad \text{and} \quad N_{ij} = \frac{x_i \theta_{ij}}{x_i \theta_{ij} + x_j} N_{cj} \quad (17)$$

Table 1 also contains the activity coefficient models which result from the combination of Eqs. (5 and 17) with various choices for θ_{ij} . Note that we have not shown the corresponding equation of state mixing rules in this table. This is because the mixing rules which result from using Eq. (17) do not satisfy the low density boundary conditions of Eqs. (10 a,b). For example, the combination of Eqs. (2, 17, 1-13) with the assumption that the total coordination number is a linear function of density yields the van der Waals equation of state residual term (Eq. 9) with

$$a = \sum \sum \frac{x_i x_j \theta_{ij}}{x_i \theta_{ij} + x_j} a_{ij} \quad (18)$$

if θ_{ij} is independent of temperature and a somewhat more complicated expression if it is not. The important observation is that this mixing rule is not quadratic in composition because of the denominator (unless $\theta_{ij} = 1$). However, using this local composition model also leads to a residual contribution for the free energy (or activity coefficient) of the widely used regular solution or van Laar form if θ_{ij} is taken to be the ratio of some measure of the molecular sizes. Further, combining this residual term with the Flory expression for the configurational term, Eq. (8), gives the Flory-Huggins model [9].

In Table 2 we display a collection of recently proposed density dependent local composition models which lead to density dependent equation of state mixing rules that are quadratic only at low density, and to one new activity model to be discussed shortly.

COMPARISON WITH COMPUTER SIMULATION

Given the collection of local composition models in Tables 1 and 2, we can now ask two questions. First, is the local composition effect real? That is, do local compositions exist in the vicinity of a molecule that are different from the bulk compositions? Second, if the answer to the first question is yes, which of the local composition models in these tables is correct, if any? To answer these questions we again turn to the Monte Carlo computer simulation method used in [1], but now for binary mixtures of square-well molecules. For each species we use the potential of Eq. (1-8) with the following combining rules to obtain the parameters for the interactions between the unlike molecules

$$\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}} \quad \text{and} \quad \sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$$

(In our simulations we also chose $R_{11} = R_{22} = R_{12} =$

TABLE 2
Local Coordination Number Models Which Result in Density-Dependent Equation of State Mixing Rules

Local Coordination Number Model	Equation of State Mixing Rule	Free Energy (Activity Coeff.) Model
Whiting & Prausnitz [12]	complicated, see ref. 12	None given
$\frac{N_{ij}}{N_j} = \frac{N_i}{N_j} e^{(\epsilon_{ij} - \epsilon_{jj})N_{ij}/kT}$ $N_{ij} + N_{jj} = N_{cj} = C_j \rho$	quadratic only at low density	
Hu, <i>et al.</i> [13]	complicated, see ref. 13	None given
$N_{ij} = \frac{4\pi}{3}(R_{ij}^3 - 1)\sigma_{ij}^3 \frac{N_i}{V} \exp\left(\frac{\alpha\epsilon_{ij}}{kT}\right)$ $\alpha = 0.60 - 0.58(\rho \sum x_i \sigma_{ij}^3)^{0.1865}$	quadratic at low density	
$N_{ij} = \frac{x_i N_m V_{a,ij} e^{\epsilon_{ij}/2kT}}{V + V_{a,ij}(e^{\epsilon_{ij}/2kT})}$	Eq (22) quadratic at low density	Eq (23)

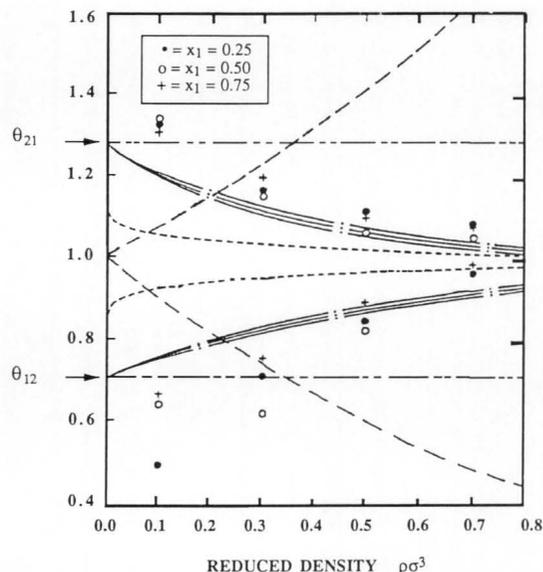


FIGURE 1. The local composition ratios θ_{21} and θ_{12} as a function of reduced density $\rho\sigma^3$ for the square-well fluid with $2\epsilon_{11}/kT = \epsilon_{22}/kT = 1.2$ and $\sigma_{11} = \sigma_{22}$. The points were obtained using Monte Carlo simulation [10]. The arrows (-) are the theoretical low density limits, --- is the Whiting-Prausnitz model [12], - - - is the Wilson model, - · - · is the model of Hu *et al.* [13], and - - - - results from the model of Eqn. (20) for different mole fractions.

1.5.) The results obtained in [10] for the species-species combination numbers N_{ij} for mixtures of square-well molecules of equal size, but different well-depths, are shown in Figure 1, and in [11] for mixtures of molecules of equal well-depths, but unequal size, in Figure 2. In the first of these figures we have plotted the ratio

$$\theta_{ij} = \frac{N_{ij}}{N_j} \frac{N_j}{N_i}$$

which would be unity if there were no local composition effects (that is, if $N_{ij}/N_{jj} = N_i/N_j$), while in Figure 2, based on Eq. (13), we have plotted the ratios

$$\theta_{ij} \frac{\sigma_{ij}^3}{\sigma_{jj}^3} = \frac{N_{ij}}{N_j} \frac{N_j}{N_i} \frac{\sigma_{ij}^3}{\sigma_{jj}^3}$$

In this case if the local compositions were proportional to the covolume fractions, the ratios would be unity, while if the mixtures were random the ratios would be equal to the constant $\sigma_{ij}^3/\sigma_{jj}^3$ independent of temperature, density, and composition.

The first important observation from Figures 1 and 2 is that the local composition or nonrandom mixing effect is real; the local composition ratio is not

equal to the bulk composition ratio (*i.e.*, θ_{ij} is not equal to unity in Figure 1, or $\sigma_{ij}^3/\sigma_{jj}^3$ in Figure 2). Further, the local composition ratios are a strong function of density, but only a weak function of mole fraction. Also, for mixtures of equal size molecules (Figure 1), where local compositions result only from attractive forces, the local composition or nonrandomness effect is strongest at low densities and weakens as the density increases. There is a simple physical explanation for this. At low densities the molecules are, on the average, widely separated, and while few molecules approach each other, when they do the effect of the attractive potential well is strong. On the other hand, at high density the spacing between molecules is small so that each molecule is constantly in the attractive well of several of its neighbors. In this case the attractive potential provides an almost uniform background in which the molecules move, and the hard cores, which exclude a molecule from certain regions, play a dominant role. It is for this reason that for the case of equal size, unequal attractive energy mixtures the local composition effect is large at low density (where the difference in the attractive wells is important) and small at high density (where the effect of the equal-size hard cores predominates).

For the case of unequal size molecules, the size difference plays an important role at all densities, as may be surmised from Eq. (15). Consequently, by using covolume fraction ratios, the remaining local composition effects are small in magnitude and relatively simply dependent on both density and composition. Figure 1 also contains the predictions of various thermodynamic models when their parameters are identified with those in the intermolecular potential. In Figure 2 we show only the predictions of our local

composition model since those of most other models are so seriously in error as to be off the scale of the figure! The second observation, then, is that only our recently proposed local composition model (to be discussed in the next section) is in even approximate agreement with simulation results.

Another observation is that the local composition ratios obtained from simulation are only very slightly dependent on composition; indeed, to the accuracy of the simulations they may be independent of composition. Thus, in agreement with the assumptions in a number of thermodynamic models, θ_{ij} may not be a function of mole fraction. This implies that the simple quadratic equation of state mixing rules of Eq. (11) may be adequate at all densities—at least for molecules that can be modeled by the square-well potential.

In fact, in our studies of the high pressure phase behavior of light hydrocarbons and inorganic gases [14], we found that the simplest and most accurate cubic equation of state correlation was obtained using Eqs. (10 a,b) with the combining rules

$$a_{ij} = \sqrt{a_{ii}a_{jj}} (1 - k_{ij}) \quad (19a)$$

and

$$b_{ij} = \frac{1}{2} (b_{ii} + b_{jj}) (1 - d_{ij}) \quad (19b)$$

where k_{ij} and d_{ij} are fitted to experimental data. We can understand the success of this simple procedure from the fact that the simulation results establish that the composition dependence which underlies the van der Waals one-fluid mixture rules is approximately correct, so that the adjustable parameters in the combining rules (Eqs. 19 a,b) can be made to compensate for any remaining small errors.

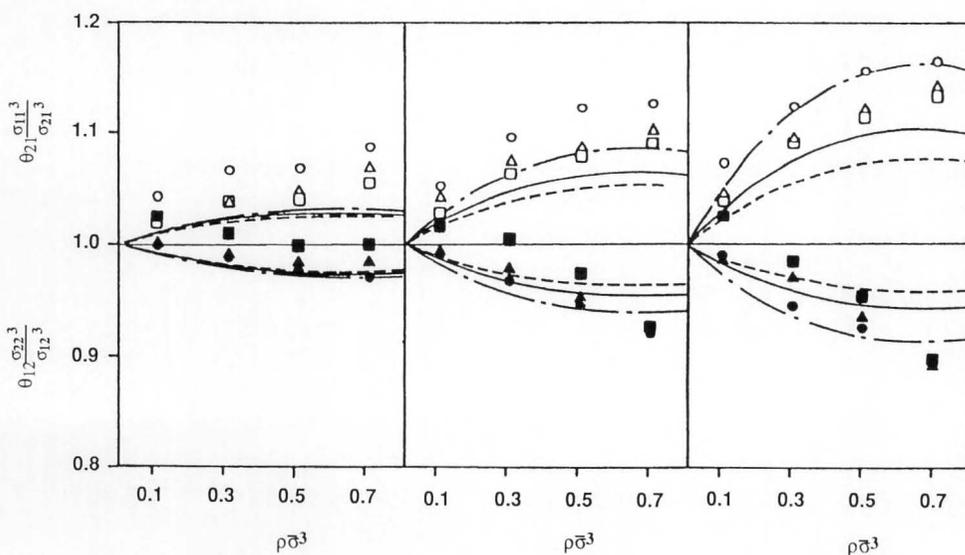


FIGURE 2. The local composition ratios $\theta_{21}\sigma_{11}^3/\sigma_{21}^3$ and $\theta_{12}\sigma_{22}^3/\sigma_{12}^3$ obtained from Monte Carlo simulation [11] as a function of reduced density $\rho\bar{\sigma}^3 = \rho\sum x_i\sigma_{ii}^3$ for the square-well fluid with $\epsilon_{22}/kT = 0.4$ for various values of the diameter ratio σ_{22}/σ_{11} . The points \square , Δ , and \circ are for the mole fractions $x_1 = 0.25$, 0.50 , and 0.75 , respectively, and the lines — — —, —, and - - - are the predictions of Eqn. (20) at the same compositions. Other local composition models would not appear on the scale of this figure. The exact low density result for both these local composition ratios is unity.

To test the assumption of the independence of the total coordination number on composition, N_{ci} obtained from simulation is plotted as a function of composition for various different densities, temperatures, and molecular size ratios in Figure 3. There we see that it is only in the case of molecules of nearly equal diameters that the total coordination number is approximately independent of composition, as assumed in Eq. (16). In general, this lattice-based assumption is incorrect; a more nearly correct assumption is that the total coordination number is a linear function of composition. This observation calls into question one of the assumptions underlying the van Laar, Wilson, UNIQUAC, and some other activity coefficient models.

Consequently, the effectiveness of these models may be more a result of the limited density range in which they are used, their flexible mathematical form, and the adjustable parameters they contain, than their theoretical correctness. Indeed, we find that we can choose a set of parameters in any local composition model which leads to reasonable agreement with our simulation data over a limited range of density, though these parameters are not related to the parameters in the interaction potential model.

A NEW LOCAL COMPOSITION MODEL

One local composition model that we have found [15] to be in approximate agreement with simulation data over a large range of density, temperature, and molecular size and energy differences, is

$$N_{ij} = \frac{x_i N_m V_{o,ij} e^{\epsilon_{ij}/2kT}}{V + V_{o,ij} (e^{\epsilon_{ij}/2kT} - 1)} \quad (20)$$

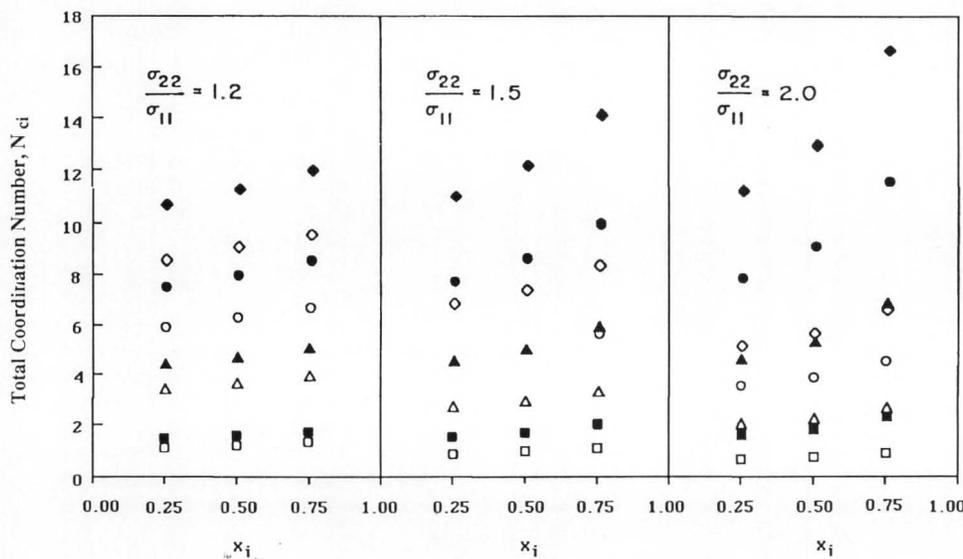


FIGURE 3. The total coordination numbers N_{c1} and N_{c2} for the same square-well mixture considered in Fig. 2 obtained from Monte Carlo simulation [11]. The unfilled and filled points are N_{c1} and N_{c2} , respectively, corresponding to following densities: (\square, \blacksquare) $\rho\bar{\sigma}^3 = 0.1$, (Δ, \blacktriangle) $\rho\bar{\sigma}^3 = 0.3$; (\circ, \bullet) $\rho\bar{\sigma}^3 = 0.5$; and (\diamond, \blacklozenge) $\rho\bar{\sigma}^3 = 0.7$. The important observation is that the total coordination number for each species is a function of mole fraction.

where

$V_{o,ij} = N\sigma_{ij}^3/\sqrt{2}$ and N_m is the coordination number at close-packing (18 if $R_{ij} = 1.5$).

This model is an empirical extension of Eq. (1-18) for a pure fluid. Example results from Eq. (20) are given in Figures 1 and 2; though not perfect, it is clearly more accurate than other local composition models.

Using Eq. (20) in Eqs. (2 to 4 and 1-3) results in the mixture form of Eq. (1-19) which we write as

$$\frac{PV}{RT} = \left(\frac{PV}{RT}\right)^{HS} - \frac{N_m a}{V + a} \quad (21)$$

with the following density-dependent mixing rule

$$a = \frac{\sum \sum \frac{x_i x_j a_{ij}}{V + a_{ij}}}{\sum \sum \frac{x_i x_j}{V + a_{ij}}} \quad (22)$$

where

$$a_{ij} = V_{o,ij} (e^{\epsilon_{ij}/kT} - 1) \quad \text{and} \quad \left(\frac{PV}{RT}\right)^{HS}$$

is the mixture hard-sphere compressibility factor from the van der Waals or other free volume models.

There are two features of Eq. (22) to be noted. First, that at low density ($V \rightarrow \infty$), Eq. (22) reduces to Eq. (10a), as it should. Second, that the number of terms in the summations, and therefore the order of Eq. (21) with respect to volume, increases with increasing number of components; thus, Eq. (22) is not a one-fluid mixing rule. From our comparisons with experimental data [14], we find that if one does not use correlative binary parameters (*i.e.*, $k_{ij} = d_{ij} = 0$ in Eqs. 19 a,b) the mixing rule of Eq. (22) leads to a slightly better prediction of high pressure phase be-

TABLE 3
Correlation of Low Pressure Binary
Aqueous-Organic Mixtures
Using Two-Parameter Activity Coefficient Models

	Average error In pressure mm Hg	Average error In vapor mole fraction	Variation of parameters over temperature range (%)
Two-Constant Margules	13.56	0.0162	± 11.4
van Laar	8.52	0.0107	± 9.4
Wilson	8.95	0.0088	± 40.3
UNIQUAC	9.20	0.0101	± 206.7
Equation 23	6.73	0.0060	± 9.0

second components were acetaldehyde, acetone, 1-butanol, 2-butanone, butyl acetate, cyclohexanone, diethylamine, diethyl ether, 1,4-dioxane, ethanol, methanol, methyl acetate, methyl diethylamine, 3-methyl pyridine, 1-propanol, 2-propanol, pyridine, tetrahydrofuran, and thiazole

havior (especially in the critical region) than do the van der Waals one-fluid mixing rules. However, when binary parameters are used ($k_{ij} \neq 0$), Eq. (22) and its analog for other equations of state is not significantly better than the simpler Eq. (10).

The excess free energy or activity coefficient model that results from the combination of Eqs. (5) and (20) is

$$G_{T,P}^{EX} = G_{T,P}^{EX} \Big|^{CONF} - N_m RT \sum \sum x_i x_j \ln \frac{b_{ij}}{b_{ii}} \quad (23)$$

where

$$b_{ij} = 1 + \frac{V_{o,ij}}{2 \sum_i x_i V_{o,ii}} \left(e^{\epsilon_{ij}/2kT} - 1 \right) \quad \text{and} \quad b_{ii} = \frac{1}{2} \left(e^{\epsilon_{ij}/2kT} - 1 \right)$$

As shown in Table 3, this new activity coefficient model correlates data for aqueous-organic mixtures better than other two-parameter activity coefficient models [16]. However, we have found that for other mixtures the ability of this new equation to correlate experimental data is approximately equal to that of other activity coefficients now in use.

CONCLUSIONS

In this paper we have presented the generalized van der Waals partition function for mixtures and have shown both how it can be used to understand the models we use in thermodynamics in terms of species-species and total coordination numbers, and how to develop new models. Using computer simulation, we have shown that the local composition effect is real.

That is, that the local mole fractions in the vicinity of a molecule in a fluid mixture are different than the bulk mole fractions. Based on these simulations, we conclude that some of the thermodynamic models we commonly use contain assumptions which are not supported by the results of computer simulations for mixtures of square-well (and other) molecules. Thus, the success of current mixture equations of state and activity coefficient models may be more a result of the limited ranges to which they are applied and the adjustable parameters used than their underlying theoretical basis.

The overall conclusion of this (and the previous) paper that I would like the reader to come away with is, that while thermodynamic modeling is a mature subject, there is still a need for much additional, theoretically based research. Unlike the past, when models were developed by insight, intuition, and/or empiricism, we now have tools such as statistical mechanical theory, computer simulation, and (though not discussed here) a variety of experimental techniques for determining local composition effects and developing models, as well as the generalized van der Waals partition function presented here, to go from such microscopic models to macroscopic equations. Research based on these tools should lead to better models of broader applicability. In particular, since we see from the equations presented here that both activity coefficient models and equations of state have their roots in the partition function, a reasonable goal would be to develop equations of state and mixing rules to describe all mixtures, no matter how complex, and to dispense with activity coefficient models completely.

ACKNOWLEDGEMENTS

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Continued on page 116.

STOCHASTIC MODELING OF CHEMICAL PROCESS SYSTEMS

Part 2: The Master Equation

R. O. FOX and L. T. FAN
Kansas State University
Manhattan, KS 66506

THE GENERAL PHILOSOPHY of stochastic modeling was discussed in the first part of this series on stochastic modeling of chemical process systems. Moreover, a particular class of stochastic models was outlined, based on the master equation. In Part 2, the master equation will be discussed and an approximate solution technique known as the System Size Expansion will be presented. The formal apparatus developed here will be utilized in the third part of the series to model a chemically-reacting system.

In developing stochastic models based on the master equation, it is assumed: (1) that a population of discrete entities exists and evolves through interaction between the entities; (2) that the entities possess certain characteristics such as size, temperature, and chemical makeup, which distinguish groups of entities from other groups; and (3) that the entities exist in Euclidian space of zero or higher order. A stochastic model for this population can be derived based on the concepts of probability theory. The resultant expression for the joint probability of the random variables designating the distinct groups of entities in the population is known as the master equation [1,2]. The master equation arises directly from the assumption that the interactions between entities possess the Markov property; changes in the system depend solely on the present state of the population and not on its past states.

In what follows, the random variable N denotes the number of entities in a specific group in the population. Subscript j signifies the number of entities possessing feature j ; each feature is assigned a positive integer. Similarly, multiple subscripts will designate distinct groups of characteristics, *e.g.*,

$$\{N_{i,j}; j \in \{1,2,3,\dots\}, i \in \{-\infty,\dots,-2,-1,0,1,2,\dots,+\infty\}\}$$

can denote the number of entities with feature j , located at point i on a discretized number line. The joint

probability of the random variables $\{N\}$ will be denoted as $P(\{n\},t)$ or simply P , when $\{n\}: n \in (0,1,2,3,\dots)$, *i.e.*, when the state space of N consists of the positive integers. However, for convenience of mathematical manipulation it will be desirable to approximate n as a positive real number *i.e.*, $\{n\}: n \in (0,+\infty)$, when performing the System Size Expansion introduced in the following section; the joint probability p becomes a joint probability density function denoted as $p(\{n\},t)$, or simply p . In both expressions, t refers to time since the model describes a process evolving in time. $P(\{n\},t)$ is interpreted as

$$P(\{N_1 = n_1, N_2 = n_2, \dots\}, t)$$

which is the joint probability that the random variable N_1 has a value of n_1 , the random variable N_2 a value of n_2 , and so on at time t . It is also necessary to define a conditional probability, $P(\{n\}_1, t_1 | \{n\}_0, t_0)$, which is the probability that the random variable N_1 has a value of n_{11} , the random variable N_2 a value of n_{21} , and so on at time t_1 , given that the random variable N_1 has a value of n_{10} , and so on at time t_0 .

THE MASTER EQUATION

Letting $t_0 = t$ and $t_1 = t + \tau$, where τ is a small time interval tending toward zero, the conditional probability $P(\{n\}_1, t + \tau | \{n\}_0, t)$ can be expanded in a Taylor series

$$P(\{n\}_1, t + \tau | \{n\}_0, t) = \left[1 - \tau \sum_{\{n\}} W_1(\{n\}_0, \{n\}) \right] \delta^k(\{n\}_1 - \{n\}_0) + \tau W_t(\{n\}_0, \{n\}_1) + o(\tau^2) \quad (1)$$

The quantity $W_t(\{n\}_0, \{n\}_1)$ is the transition probability per unit time that the population changes from state $\{n\}_0$ to state $\{n\}_1$ in the time interval between t and $t + \tau$. The quantity

A stochastic model for this population can be derived. . . . The resultant expression for the joint probability of the random variables designating the distinct groups of entities in the population is known as the master equation . . . [which] arises directly from the assumption that the interactions between entities possess the Markov property . . .

$$\tau \sum_{\{n\}} W_t(\{n\}_0, \{n\}) - \tau W_t(\{n\}_0, \{n\}_0)$$

is the total probability of transition from state $\{n\}_0$ to any other state during the time interval between t and $t + \tau$. Thus, $\tau W_t(\{n\}_0, \{n\}_1)$ is the probability of a transition from $\{n\}_0$ to $\{n\}_1$ during the time interval between t and $t + \tau$, and

$$\left[1 - \tau \sum_{\{n\}} W_t(\{n\}_0, \{n\}) \right] \delta^k(\{n\}_1 - \{n\}_0) + \tau W_t(\{n\}_0, \{n\}_0)$$

is the probability that no transitions occur during the time interval between t and $t + \tau$.

Assuming that the states of the population possess the Markov property, $P(\{n\}_1, t + \tau)$ can be expressed as

$$P(\{n\}_1, t + \tau) = \sum_{\{n\}_0} P(\{n\}_1, t + \tau | \{n\}_0, t) P(\{n\}_0, t) \quad (2)$$

Taking the limit of this expression as $\tau \rightarrow 0$ yields the master equation:

$$\frac{dP(\{n\}_1, t)}{dt} = \sum_{\{n\}} W_t(\{n\}, \{n\}_1) P(\{n\}, t) \quad (3)$$

where $W_t(\{n\}_1, \{n\}_1)$ is defined as

$$W_t(\{n\}_1, \{n\}_1) = - \sum_{\substack{\{n\} \\ \{n\} \neq \{n\}_1}} W_t(\{n\}, \{n\}_1) \quad (4)$$

MASTER EQUATION EXPANSION

The master equation, as given in Eq. (3), is in the form of an ordinary differential equation. Since $P(\{n\}, t)$ appears only to the first power, the equation is linear. However, if the state space is large, Eq. (3) is a large system of coupled equations—one for each possible state. For example, for the set of two random variables

$$\{n\}_i = \{n_1, n_2\}_i : n_j \in \{0, 1\}, i \in \{1, 2, 3, 4\}, j \in \{1, 2\}$$

there are four possible events

$$\{n\}_1 = \{0, 0\}, \{n\}_2 = \{1, 0\}, \{n\}_3 = \{0, 1\}, \{n\}_4 = \{1, 1\}$$

Note that the state space of either of the two random variables, N_1 and N_2 , consists of two events, *i.e.*, $\{0, 1\}$. The resultant system of differential equations could comprise four coupled equations. In general, if $k(j)$ is the number of events in the state space of random

variable N , then the number of coupled differential equations could be equal to

$$\prod_j k(j)$$

Even if j is equal to 1, this could still result in a very large system of equations. For example, if the state space of random variable 1 consists of all the integers [$k(1)$ equal to $+\infty$], the number of equations will be infinite. It is necessary, therefore, to develop an approximation procedure for the solution of such equations.

The use of the System Size Expansion is predicated upon the fact that often, for a system involving interactions between entities in the population, the magnitude of the change in the number of entities in the system following a transition is an extensive variable, *e.g.*, the number of molecules, but the dependence of the rate of transition on the number of entities is expressed as an intensive variable, *i.e.*, the concentration of molecules. As an example, consider a system consisting of two populations A and B, undergoing second order interactions between them in a volume Ω . Suppose that q members are in population A and r members are in population B, and that a transition takes place when a member of population A meets a member of population B. In most cases, the rate of such a transition will not only be proportional to q times r , but also inversely proportional to the volume squared. This follows intuitively from the image of the entities moving freely in the volume Ω . Decreasing Ω will increase the number of collisions between members of populations A and B. The rate of transition is thus dependent on the density or concentration of entities in the system.

Under the assumption that the System Size Expansion is valid, the term representing the rate of transition $W_t(\{n\}, \{n\}_1)$ in the master equation, Eq. (3), is first rewritten as $W_t(\{n\}; \{n\}_1 - \{n\})$, where $\{n\}_1 - \{n\}$ is the magnitude of the change in the random variables $\{N\}$ during a transition. Letting $\{\xi\} = \{n\}_1 - \{n\}$, the rate of transition can be expressed as $W_t(\{n\}; \{\xi\})$. It can further be rewritten as

$$W_t(\{n\}; \{\xi\}) = \Omega \Psi_t \left(\left\{ \frac{n}{\Omega} \right\}; \{\xi\} \right) \quad (5)$$

if it is assumed to be a homogeneous function of the random variable. The rate of transition is now a function of the intensive random variables $\{N/\Omega\}$, and the

System Size Expansion can be introduced.

Making a change of variables and introducing the new random variables $\{Z\}$ and the deterministic variables $\{\phi\}$ such that

$$\{N\} = \Omega\{\phi(t)\} + \Omega^{\frac{1}{2}}\{Z\} \quad (6)$$

the rate of transition is rewritten as

$$W_t(\{n\}; \{\xi\}) = \Omega \Psi_t \left(\left\{ \phi(t) + \Omega^{\frac{1}{2}} z \right\}; \{\xi\} \right) \quad (7)$$

It will be seen later that the deterministic variables $\{\phi\}$ correspond to the macroscopic behavior of the system. The master equation, Eq. (3), is then of the form

$$\frac{dP \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\}_1, t \right)}{dt} = \sum_{\{\xi\}} \Omega \Psi_t \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\}; \{\xi\} \right) P \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\}, t \right) \quad (8)$$

To proceed with the expansion, it is useful to define the first and second jump moments, A_i and $B_{i,j}$, respectively, and \tilde{A}_i and $\tilde{B}_{i,j}$ as follows:

$$\begin{aligned} A_i(\{n\}) &= \sum_{n_{ii}} (n_{ii} - n_i) W_t(\{n\}, \{n\}_1) \\ &= \sum_{\xi_i} \xi_i W_t(\{n\}; \xi_i) = \Omega \sum_{\xi_i} \xi_i \Psi_T \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\}; \xi_i \right) \end{aligned} \quad (9)$$

$$\tilde{A}_i \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) = \Omega^{-1} A_i(\{n\}) \quad (10)$$

and

$$\begin{aligned} B_{i,j}(\{n\}) &= \sum_{n_{ii}} \sum_{n_{jj}} (n_{ii} - n_i)(n_{jj} - n_j) W_t(\{n\}, \{n\}_1) \\ &= \sum_{\xi_i} \sum_{\xi_j} \xi_i \xi_j W_t(\{n\}; \xi_i, \xi_j) \\ &= \Omega \sum_{\xi_i} \sum_{\xi_j} \xi_i \xi_j \Psi_T \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\}; \xi_i, \xi_j \right) \end{aligned} \quad (11)$$

$$\tilde{B}_{i,j} \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) = \Omega^{-1} B_{i,j}(\{n\}) \quad (12)$$

The expression $W_t(\{n\}; \xi_i \xi_j)$ denotes the dependence of the rate of transition on both n_i and n_j . If no such dependency exists, either ξ_i or ξ_j is identically zero. The master equation, Eq. (8), can then be expanded in powers of Ω to yield

$$\begin{aligned} \frac{\partial p(\{z\}, t)}{\partial t} - \Omega^{\frac{1}{2}} \sum_i \frac{d\phi_i}{dt} \frac{\partial p(\{z\}, t)}{\partial z_i} \\ = -\Omega^{\frac{1}{2}} \sum_i \frac{\partial}{\partial z_i} \left[\tilde{A}_i \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) p(\{z\}, t) \right] \\ + \frac{1}{2} \sum_i \sum_j \frac{\partial^2}{\partial z_i \partial z_j} \left[\tilde{B}_{i,j} \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) p(\{z\}, t) \right] + O \left(\Omega^{-\frac{1}{2}} \right) \end{aligned} \quad (13)$$

where $p(\{z\}, t)$ is the probability density function of the new random variables $\{Z\}$, and $O(\Omega^{-1/2})$ represents terms of order $\Omega^{-1/2}$ and smaller.

To proceed further, the expansions of \tilde{A}_i and $\tilde{B}_{i,j}$ in powers of Ω must be performed; they yield

$$\tilde{A}_i \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) = \tilde{A}_i(\{\phi(t)\}) + \Omega^{-\frac{1}{2}} \sum_j z_j \tilde{A}_{i,j}(\{\phi(t)\}) + O(\Omega^{-1}) \quad (14)$$

$$\tilde{B}_{i,j} \left(\left\{ \phi(t) + \Omega^{-\frac{1}{2}} z \right\} \right) = \tilde{B}_{i,j}(\{\phi(t)\}) + O \left(\Omega^{-\frac{1}{2}} \right) \quad (15)$$

These expressions define the expansion coefficients \tilde{A}_i , $\tilde{A}_{i,j}$, and $\tilde{B}_{i,j}$. The expanded master equation, Eq. (13), thus becomes

$$\begin{aligned} \frac{\partial p}{\partial t} - \Omega^{\frac{1}{2}} \sum_i \frac{d\phi_i}{dt} \frac{\partial p}{\partial z_i} = -\Omega^{\frac{1}{2}} \sum_i \tilde{A}_i \frac{\partial p}{\partial z_i} - \sum_i \sum_j \tilde{A}_{i,j} \frac{\partial}{\partial z_i} [z_j p] \\ + \frac{1}{2} \sum_i \sum_j \tilde{B}_{i,j} \frac{\partial^2 p}{\partial z_i \partial z_j} + O \left(\Omega^{-\frac{1}{2}} \right) \end{aligned} \quad (16)$$

The terms of order $\Omega^{1/2}$ on both sides of this expression cancel if ϕ_i obeys

$$\frac{d\phi_i}{dt} = \tilde{A}_i(\{\phi(t)\}) \quad (17)$$

Letting Ω approach infinity (thermodynamic limit), the last term on the right-hand side of Eq. (16) vanishes, thereby yielding

$$\frac{\partial p}{\partial t} = - \sum_i \sum_j \tilde{A}_{i,j} \frac{\partial}{\partial z_i} [z_j p] + \frac{1}{2} \sum_i \sum_j \tilde{B}_{i,j} \frac{\partial^2 p}{\partial z_i \partial z_j} \quad (18)$$

where \tilde{A}_i , $\tilde{A}_{i,j}$, and $\tilde{B}_{i,j}$ are given by Eqs. (14) and (15). Equations (17) and (18) are the expressions resulting from the System Size Expansion.

Even in the form given by Eq. (18), the master equation for the system may still involve a large number of variables $\{Z\}$, since the number of random variables is equal to the number of distinct populations in the system, which may be large. Nevertheless, Eq. (18) is a linear Fokker-Planck equation whose solution yields a multivariate, normal distribution; the linear-

ity is in reference to the coefficients $\tilde{A}_{i,j}$ and $\tilde{B}_{i,j}$. In general, a Fokker-Planck equation is said to be linear if it can be written in the form of Eq. (18) and the coefficients do not depend on the random variables $\{Z\}$. Although the coefficients, $\tilde{A}_{i,j}$ and $\tilde{B}_{i,j}$, are linear, they are time-dependent through the dependence on $\{\phi\}$, obeying the system of coupled, possibly non-linear, differential equations given by Eq. (17). To solve the Fokker-Planck equation, Eq. (18), it is necessary to first solve Eq. (17) for $\{\phi\}$.

Solving Eq. (17) for $\{\phi\}$ can itself be a highly arduous task, especially if the equations are non-linear. Methods for solving the Fokker-Planck equations with the constant coefficient matrices, $\tilde{A}_{i,j}$ and $\tilde{B}_{i,j}$, are available, but the addition of a time-dependence quickly increases the complexity of the problem. Such difficulties can be circumvented in cases where a complete expression for $p(\{z\}, t)$ can be substituted by expressions for its moments in general, and for its means, $\langle Z_i \rangle$, and the cross-moments $\langle Z_i Z_j \rangle$ in particular. This is accomplished by multiplying both sides of Eq. (18) by z_i or $z_i z_j$, and integrating over all variables from $-\infty$ to $+\infty$; this yields

$$\frac{d}{dt} \langle Z_i \rangle = \sum_j \tilde{A}_{i,j} \langle Z_j \rangle \quad (19)$$

and

$$\frac{d}{dt} \langle Z_i Z_j \rangle = \sum_k [\tilde{A}_{i,k} \langle Z_k Z_j \rangle + \tilde{A}_{j,k} \langle Z_k Z_i \rangle] + \tilde{B}_{i,j} \quad (20)$$

These expressions give rise to the governing differential equation for the covariances of $\{Z\}$ as

$$\frac{d}{dt} \text{Cov}[Z_i, Z_j] = \sum_k [\tilde{A}_{i,k} \text{Cov}[Z_k, Z_j] + \tilde{A}_{j,k} \text{Cov}[Z_k, Z_i]] + \tilde{B}_{i,j} \quad (21)$$

Returning to the original random variables $\{N\}$ and using their definitions in terms of $\{\phi\}$ and $\{Z\}$, the expressions for their means and covariances can be obtained from Eqs. (19) and (21), respectively, as

$$\frac{d}{dt} \langle N_i \rangle = \Omega \frac{d\phi_i}{dt} + \Omega^2 \frac{d}{dt} \langle Z_i \rangle = \Omega \tilde{A}_i + \Omega^2 \sum_j \tilde{A}_{i,j} \langle Z_j \rangle \quad (22)$$

and

$$\begin{aligned} \frac{d}{dt} \text{Cov}[N_i, N_j] &= \Omega \frac{d}{dt} \text{Cov}[Z_i, Z_j] \\ &= \sum_k [\tilde{A}_{i,k} \text{Cov}[N_k, N_j] + \tilde{A}_{j,k} \text{Cov}[N_k, N_i]] + \Omega \tilde{B}_{i,j} \end{aligned} \quad (23)$$

Note that Eq. (19) is identical to the linear equation resulting from linear stability analysis of Eq. (22). Consequently, the real parts of the eigenvalues of the coefficient matrix, $\tilde{A}_{i,j}$, will be negative if the macroscopic behavior of the system is stable with respect

to fluctuations. Since $\langle Z_i(0) \rangle$ is equal to zero, $\langle Z_i(t) \rangle$ will be zero as long as the system is macroscopically stable. When this is not the case, the System Size Expansion is no longer valid and must be replaced by an alternate technique. Macroscopically, such behavior may correspond to a bifurcation point where two or more solutions branch from the original stable state. Probabilistically, the density function for the system would then no longer be unimodal; it is this property which invalidates the System Size Expansion at such points.

DERIVATION OF CORRELATION FUNCTIONS

The foregoing derivations of the expressions for the means and covariances of the random variables have yielded little information about the dynamic characteristics of the fluctuations. The auto- and cross-correlation functions, however, can provide this information. These functions yield measures of the influence of the value of a random variable at time t on the values of the random variables at time $t + \tau$. Two processes with equal means and variances but different auto-correlation functions can behave differently. For a Markov process, the auto- and cross-correlation functions can be easily derived [1]; the governing equations for them are the same as that for $\langle Z_i \rangle$, Eq. (19). Defining the correlation matrix as

$$K_{i,j}(\tau) = \langle Z_i(0) Z_j(\tau) \rangle \quad (24)$$

the following set of differential equations can be derived by relating $K(t)$ to $\text{Cov}[Z_i, Z_j]$;

$$\frac{d}{dt} K_{i,j}(\tau) = \sum_k \tilde{A}_{j,k}^s K_{i,k}(\tau); \quad K_{i,j}(0) = \text{Cov}[Z_i, Z_j]^s \quad (25)$$

where

$$\begin{aligned} \tilde{A}_{j,k}^s &= \tilde{A}_{j,k}(\{\phi^s\}) \\ \{\phi^s\} &= \text{steady-state values of } \{\phi(t)\} \\ \text{Cov}[Z_i, Z_j]^s &= \text{steady-state covariance of } Z_i \text{ and } Z_j \end{aligned}$$

Equation (25) is a direct result of the linear nature of Eq. (19) and of the fact that the process is Markovian. It also follows from Eqs. (24) and (25) and the relationship between the random variables $\{Z\}$ and the original random variables $\{N\}$ that the correlation functions for the random variables $\{N\}$ can be found by solving Eq. (25) subject to the initial conditions

$$K_{i,j}(0) = \text{Cov}[N_i, N_j]^s$$

where

$$\text{Cov}[N_i, N_j]^s = \text{steady-state covariance of } N_i \text{ and } N_j$$

In Part 3, the final part of this series, the master equation and the System Size Expansion are applied to modeling of a chemically-reacting system.

ACKNOWLEDGEMENTS

This material is mainly based upon work supported under a National Science Foundation Graduate Fellowship awarded to the first author.

NOTATION

A_i	first jump moment
\tilde{A}_i	A_i / Ω
$\tilde{A}_{i,j}$	coefficient in expansion of \tilde{A}_i
$B_{i,j}$	second jump moment
$\tilde{B}_{i,j}$	$B_{i,j} / \Omega$
$\text{Cov}[N_i, N_j]$	$\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle$, covariance of N_i and N_j
$\text{Cov}[Z_i, Z_j]$	$\langle Z_i Z_j \rangle - \langle Z_i \rangle \langle Z_j \rangle$, covariance of Z_i and Z_j
$K_{i,j}(\tau)$	correlation matrix defined as $\langle Z_i(0) Z_j(\tau) \rangle$ for Z_i and Z_j , or as $\langle N_i(0) N_j(\tau) \rangle - \langle N_i(0) \rangle \langle N_j(\tau) \rangle$ for N_i and N_j
N_j	number of entities possessing feature j
$N_{i,j}$	number of entities possessing feature i and feature j
$\langle N_i \rangle$	expected value of random variable N_i
$p(\{n\}, t)$	joint density function of continuous random variables $\{N\}$
$P(\{n\}, t)$	joint probability of random variables $\{N\}$
$P(\{n\}_1, t \{n\}_0, t_0)$	conditional probability of random variables $\{N\}_1$ at time t given the value of random variables $\{N\}_0$ at time t_0
$W_t(\{n\}_0, \{n\}_1)$	rate of transition from state $\{n\}_0$ to state $\{n\}_1$
Z_i	fluctuating component of random variable N_i
$\langle Z_i \rangle$	expected value of random variable Z_i
$\langle Z_i Z_j \rangle$	expected value of product of random variables Z_i and Z_j

Greek Letters

$\delta^k(x)$	Kronecker delta where $\delta^k(0) = 1$ and $\delta^k(x) = 0$ for $x \neq 0$
ξ_i	magnitude of change in random variable N_i
τ	small time interval tending toward zero
ϕ_i	deterministic variable corresponding to macroscopic behavior of N_i
$\Psi_t\left(\left\{\frac{n}{\Omega}\right\}; \{\xi\}\right)$	homogeneous intensity of transition function
Ω	system volume

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1. Gardiner, C.W., *Handbook of Stochastic Methods*, Springer, New York (1983)
2. van Kampen, N.G., *Stochastic Processes in Physics and Chemistry*, North-Holland, New York (1981) □

RANDOM THOUGHTS

Continued from page 71.

straight A's for the rest of eternity; 2) pocket their tuition; and 3) don't give them the beer.

CORPORATE EXECUTIVE MODEL

Demand a high six-figure salary when offered the position of chancellor. When you get it, use the interest on your university's \$200 million endowment to buy your way into financial control of a small but productive college in another state. Fire all their deans and department heads and put your own people in those positions. Move their best professors to your university, fire the others who don't have tenure, take any of their laboratory equipment you can use and sell the rest. Then fold the college and use the losses to offset the profits from the equipment sale, leaving yourself with a net annual corporate tax liability of \$3.27. Keep doing this. When you've ruined enough small productive colleges to get your salary up to seven figures, announce that it is in the university's best interests to teach all classes in Japanese. Sell controlling interest in the university to the Kyoto Institute of Technology, participate in the dedication of the sushi bar where the Burger & Brew used to be, and retire just in time to miss the cafeteria riot and the disgusting things those ungrateful student hooligans do with all that raw fish.

◇ ◇ ◇ ◇ ◇

And that's all there is to it. With these few simple techniques we can easily transform our images and start to enjoy the good life.

On the other hand, there may be something to say for the status quo. As things stand now, most of us do our jobs without exploiting anyone's vulnerability or innocence, enriching ourselves at their expense, or trampling on their dignity. We may have to forego the Swiss bank accounts this way, but it still seems like a good bargain. We just have to be sure that our success is measured by the quality of our teaching and research and by nothing else...but then we're educators and scholars by profession, so there's no problem.

And now if you'll excuse me, I've got to get my notes together for the meeting at 10:00 where we review Greg Furze and Roger Snavelly for promotion and tenure. Furze gets great teaching reviews and he's written a couple of research papers that people think very highly of, but there's not much by way of grants. Snavelly is another story. He brings in a mint in funding, but his teaching evaluations are grim and his graduate students complain that they hardly ever see him, even though he keeps them here for as long as seven years. Should be an interesting meeting. □

• 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 1990 fall issue should write to the editor, indicating the subject of the contribution and the tentative date it will be submitted.
Deadline is June 1st.

ChE book reviews

HEAT TRANSFER EQUIPMENT DESIGN

by R.K. Shah, E.C. Subbarao and R.A. Mashelkar
Hemisphere Publishing Corporation,
79 Madison Avenue, New York 10016-7892,
804 pages, \$159.50 (1989)

Reviewed by

C.M. Hackenberg
Universidade Federal do Rio de Janeiro

This book is a very well-arranged collection of lectures, the majority of which were presented by invited authors at an Advanced Study Institute on Heat Transfer Equipment, held in Poona, India, in June of 1986. The Institute was organized to provide an international forum for the dissemination of information on the thermal hydraulic fundamentals and design of heat transfer equipment. A keynote lecture on energy conservation and waste energy recovery in industry was presented in order to give an estimate of the amount of energy used in industry in the form of heat as well as to allow for a discussion of the most adequate energy efficient technology.

The book contains nine chapters, and all the topics are well-referenced. One will not find a very extended analysis of the heat transfer fundamentals, but the given information is sufficient to refresh the latent knowledge of practicing engineers, and it also encourages the expert to pose new research questions to the applications of more advanced studies.

The opening chapter is a general review of the classification of heat transfer equipment, heat exchanger design methodology, and basic thermal design methods. Uncertainties on the design and operation of systems of heat exchangers and of the problems related to the heat transfer modeling in heat exchange equipment from laboratory work to industrial design are also taken into consideration.

The second chapter briefly treats the codes and standards of the mechanical design of exchangers, including an appraisal of the state-of-the-art for tubular units. The "meat" of the book begins in chapter three, which presents the convection fundamentals and their application to the single phase heat exchangers. The usual correlations utilized for the evaluation of the heat transfer coefficients are briefly discussed. It is nice to find, in this chapter, a concise presentation of computational fluid dynamics applied to the prediction of the heat transfer, mechanical, and thermal-stress behavior. A general notion of the nature and capabilities of the PHOENIX program, which first emerged in 1981, is also presented.

Chapter four concerns the procedures of the thermal design of single-phase exchangers. Here one finds an overall design methodology for shell and tube exchangers which offers an approximate sizing technique for preliminary design. This can be handy for checking the results of computer-based design methods, as we all know.

The brief lectures presented in this chapter include computational applications to several types of heat exchangers going through air-cooled equipment and the syntheses of optimal heat exchanger networks. Going further, one finds a short analysis of the plate heat exchangers and their design theory, followed by the plate-fin and tube-fin design procedures. Furthermore, other lectures discuss the design of electronic equipment based on the thermal analysis, nuclear and fluidized bed heat exchangers, direct fire heaters, and high temperature waste-heat recovery. There is also a nice discussion on mechanically-aided heat exchanger design.

In chapter five there is a brief discussion of the fundamentals of two-phase flow heat transfer for boiling in tubes and tube bundles. Then the Nusselt classical theory for laminar film condensation on a vertical plate, a horizontal tube, and a bank of horizontal tubes is reviewed. The condensation on enhanced surfaces is also

Continued on page 99.

CHEMICAL COMPATIBILITY OF POLYMERIC MATERIALS

Some Simple Guidelines

KENNETH A. SOLEN, MARVIN C. KUCHAR

Brigham Young University

Provo, UT 84602

THE AUTHORS PRESENT here some principles for specifying general classes of polymers to be used in contact with acids, bases, oxidants, certain other common antagonists, and specific solvents. These principles are appropriate for an undergraduate chemical engineering general course in materials, where extensive detail and discussion about a myriad of chemical reactions and polymer variations cannot be treated.

Many chemical engineers face the problem of selecting equipment made from or lined with polymers, and the compatibility of the equipment surface with the chemical to be handled is a significant consideration. It is obviously important to know whether chemical reactions will occur between the chemical and the polymer walls and whether solvent effects will cause polymer swelling, dissolution, or alterations in mechanical properties. Yet, our chemical engineering department, like many others, can afford only one re-

Kenneth A. Solen received his BS from the University of California, Berkeley, in 1968, and his PhD from the University of Wisconsin, Madison, in 1974, both in chemical engineering. He also earned an MS in physiology from the University of Wisconsin, Madison, in 1972. After post-doctoral research fellowships at the University of Iowa Medical School and the University of Oregon Health Sciences Center, he joined the faculty at Brigham Young University in 1976. He is currently a professor of chemical engineering.



Marvin C. Kuchar received his BS and his PhD degrees from Brigham Young University in 1958 and 1963, respectively, in organic chemistry. After working as a Senior Research Chemist for E.I. DuPont de Nemours he joined the faculty at Brigham Young University in 1979. He is currently an associate professor of chemistry and is Chairman of the Department of Textiles.

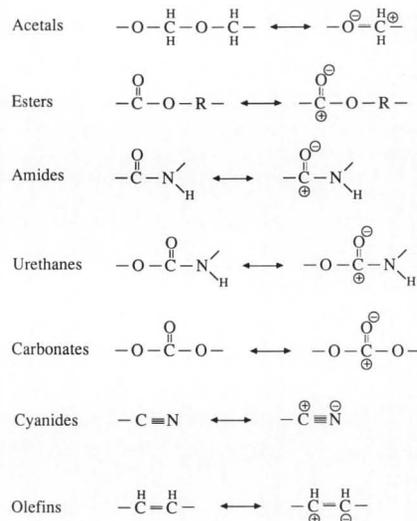


FIGURE 1. Dipole resonant forms in some common classes of polymers.

quired undergraduate course in engineering materials. The course is based on one of the popular general textbooks on engineering materials which covers a wide spectrum of topics including metallurgy, ceramics, semiconductor materials, and polymers. However, the polymer treatment is limited and focuses largely on forming and molding the polymers (*i.e.*, mechanisms and kinetics of polymer formation and rheology of polymer melts) and on physical properties. Thus, we felt that supplementary coverage was necessary.

Our goal is to explain polymer-chemical compatibility, as much as possible, in terms of unifying principles. The alternative would be to memorize extensive information about the very large number of specific reactions encountered between nearly-infinite combinations of polymers and chemicals. Even with the application of some central principles, the number of exceptions and variations would require significant discussion and tabulation. Such a treatment is attempted in a few books dedicated to the description of polymers

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(see references 1-3 for example), but general textbooks about engineering materials can hardly begin such coverage. Further, while the vendors of polymer equipment provide "technical specifications" about chemical compatibility, those specifications are typically tables of chemicals matched against their products with empirical recommendations such as "good," "fair," and "not recommended." Other tables specify the maximum usable temperature recommended for each chemical-polymer pair, but do so also in an empirical fashion. A further complication is that each manufacturer adds specific agents to its polymer formulations to modify the properties of the final product, thereby adding even greater uncertainty to the application of general principles. However, chemical engineers, with their background in organic and physical chemistry, should know some basic rules which will allow at least preliminary selection of polymer types and evaluation of vendor claims for a particular application.

This paper summarizes some basic principles for predicting relative chemical attack from acids, bases, oxidants, and certain other common antagonists and also for predicting relative solvent effects in polymers. This material is presented in two or three lectures in our chemical engineering materials course after reviewing with the students the structures and names of common polymers, discussing structural characteristics (density, crystallinity, *etc.*), and comparing the properties of thermoplastic and thermosetting polymers. The brief treatment described below provides some understanding (as opposed to memorization) which will allow preliminary evaluation of polymer equipment for handling chemicals and which

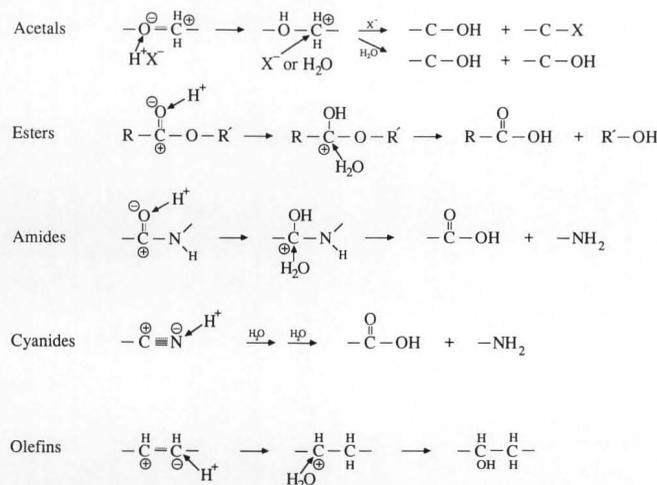


FIGURE 2. Examples of the attack of dipolar resonance forms of polymers by acids.

The paper summarizes some basic principles for predicting relative chemical attack from acids, bases, oxidants, and certain other common antagonists, and also for predicting relative solvent effects in polymers.

will also serve as a framework upon which information about specific reactions and cases can later be added.

UNDESIRABLE CHEMICAL REACTIONS

Acid-Base Attack

The susceptibility of many polymers to attack by surrounding acids and bases is related to the degree of "charged dipole formation within the polymer structure. A review of atomic structure will convince the student that the relative electronegativities of C, N, and O are in the order $O > N > C$. This helps to explain that the combination of these elements in a polymer structure results in the distortion of electron clouds away from carbon atoms, with a resultant dipole as one resonant form (Figure 1). The student should also be aware, however, that even olefinic double bonds have resonant dipole forms. Non-oxidizing acids generally attack by attraction of the H^+ ion to the negative side of the dipole resonant structure and formation of a complex. The unstable complex then further reacts with the negative ion of the acid or with water (in the case of aqueous solutions) to split the polymer chain at that point (Figure 2). The attack of a polymer by a base proceeds in a similar fashion, with the initial attraction of the OH^- and complex formation at the positive site of the resonant dipole and then subsequent resolution of the unstable complex (Figure 3).

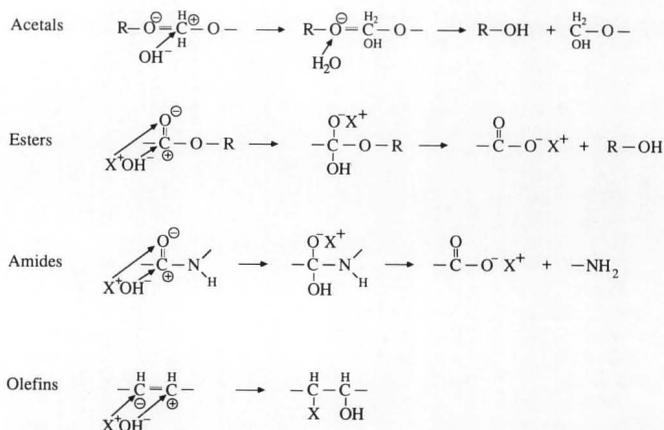


FIGURE 3. Examples of the attack of dipolar resonance forms of polymers by bases.

In our materials course, the emphasis is not so much on the reaction mechanisms as on the principle that more polar resonant forms will cause greater attack in general. Hence, polyamides (*e.g.*, nylon), olefins (*e.g.*, natural rubber and styrene butadiene), and polyesters (*e.g.*, polymethylmethacrylate, PMMA) will be relatively susceptible to acid-base attack. Examples include the partial hydrolysis of poly(methylacrylamide) in base to the free acid form, the conversion of acetals by alkali and acid to produce alcohols, the cleavage of polyester chains by hot alkali treatment, *etc.* Polyurethanes are not quite as susceptible, because the urethane nitrogen atom stabilizes the resonant form and reduces the polarity. At the other extreme, polyethylene (PE), with no polar resonance, will generally not be attacked by acids and bases (which explains why acids and bases can be stored in polyethylene containers).

Of course, very strong acids and bases (especially oxidizing acids) can attack even polyethylene or polypropylene (PP) by directly attacking the C-H bonds, especially the weaker bonds on the methyl side groups of the PP. Where these very strong reagents are to

TABLE 1
Relative Rates of Oxidation Versus Structure [4]

<u>Structure</u>	<u>Relative Rate of Oxidation</u>
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-) \\ \uparrow \qquad \qquad \qquad \uparrow \end{array}$	10
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{CH}-\text{O}-) \\ \uparrow \end{array}$	9
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{CH}-) \\ \uparrow \end{array}$	6.5
$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ (-\text{CH}_2-\text{CH}-) \\ \uparrow \end{array}$	2.8
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{O} \\ \\ \text{C}=\text{O} \\ \\ -\text{CH}_2-\text{CH}- \\ \uparrow \end{array}$	1.4

be encountered, the PE chain is used with fluorine substituted for both of the hydrogens on every other carbon atom (polyvinylidene fluoride, PVDF) or on every carbon atom (polytetrafluoroethylene, PTFE) to reduce such attack. The electron-rich fluorine acts by stabilizing the polar resonant forms.

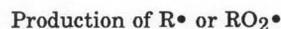
Chlorine is also used for a replacement for hydrogen on every other carbon, either substituted for one of the hydrogen atoms on that carbon (polyvinylchloride, PVC) or for both hydrogen atoms of that carbon (polyvinylidene chloride, PVDC). However, the larger chlorine atom creates some steric stress because of its size and has a greater tendency to be removed. Hence, its resistance to acid-base attack is limited.

Oxidation

Synthetic polymers are oxidized by oxygen in the atmosphere, particularly in the presence of light (in the absence of light the reaction is relatively slow) and by liquid oxidants, such as permanganate, peroxides, epoxides, oxidizing acids (*e.g.*, nitric, sulfuric, and chromic), and even water. The resulting changes in polymer chemistry yield a more brittle polymer with corresponding loss of strength.

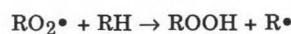
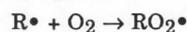
Oxidation of polymers can be generalized into the following reactions (4):

Initiation:

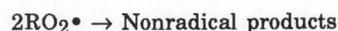


(where R is some portion of the hydrocarbon chain)

Propagation:



Termination:



Particularly susceptible locations include carbon atoms which are 1) adjacent to double-bond carbon atoms (polymers such as polyisoprene or polybutadiene that contain unsaturated linkage are susceptible to attack by ozone as well as oxygen), 2) connected to ether oxygen atoms, and 3) tertiary carbons (Table 1, poly(vinylchloride) is very susceptible to oxidation, and, of the major polymer systems, polypropylene is more susceptible than polyethylene).

Oxidation can be reduced by adding inhibitors or by altering polymer structure. UV screeners are

added to all polymer formulations for equipment use. The substitution of fluorine in place of hydrogen (PVDF, PTFE, etc.) significantly reduces susceptibility to oxidation, because the electronegative fluorine causes charge repulsion of the oxidant. Also, polystyrene, with its electron-rich aromatic ring to protect potential oxidation sites, is less susceptible to oxidation than is polyethylene.

Special Addition/Substitution Reactions

Several chemical agents add to the double bonds of unsaturated polymers, and some may even attack saturated compounds. The most common of these are:

CHLORINATION: Chlorine gas, hydrochloric acid, chlorosulfonic acid, and phosphorus-containing chlorides are among the agents which will cause chlorine attack of polymers. Not only will chlorine be added to unsaturated bonds (e.g., conversion of PVC to a dichloride), but polyethylene can also be chlorinated. Chlorination of natural rubber involves a complex series of addition, substitution, crosslinking, and cyclization reactions.

HYDROGENATION: Polymers with unsaturated bonds may be subject to hydrogenation, particularly at high temperatures in the presence of high-pressure hydrogen gas. For example, polyisoprene can be hydrogenated to yield poly-isopentane, and polystyrene can be converted to poly-vinylcyclohexane.

NITRATION: Nitric acid is the most common source of this attack. Polymers with aromatic groups are susceptible to nitration reactions on the aromatic ring. For example, polystyrene in the presence of both nitric and sulfuric acids yields the corresponding poly(nitrostyrene). With aliphatic polymers, the nitro group attaches to the chain or to a suitable substituent on the chain.

Many additional specific reactions could be included, but only a few of the more common ones are described, and the students are warned that they must do their own homework on the job for each application which presents itself.

High-Temperature Effects

In addition to the fact that high temperatures cause softening (loss of strength) of polymers, organic polymers are unstable at temperatures above 150-200 degrees centigrade and undergo some chemical reactions. The kinds of reactions include:

ISOMERIZATION: Polymers containing certain side chains such as cyano(nitrile), chloro, carboxylic acid, or ester groups, when subjected to high temperatures, undergo isomerization to yield new products. A classic example is the cyclization of natural rubber to produce cyclohexane rings in the polymer chain. (This reaction is exploited by the Goodyear Tire and Rubber Com-

pany to produce Pliolite rubber using chlorostannic acid as a reagent.)

DEPOLYMERIZATION: High temperatures can cause depolymerization to yield the monomer or chain cleavage to yield low molecular weight products or degradation of side chains. The result is a general breakdown of the polymer. For example, poly(tetrafluoroethylene), poly(methyl methacrylate) and poly(alpha-methyl styrene) undergo complete conversion to the monomer when heated to high temperatures.

The students should be alerted to the possibility of polymer degradation from factors other than contact with reactive chemicals. Such factors include X-ray irradiation, electric discharge, ultra-violet radiation, etc., which may result in cleavage and reformation of the polymer chains. However, no simple theories are available to predict the effects of such phenomena.

With this background, the students are prepared to understand some of the general trends seen in the empirical tables provided by the polymer vendors. For example, the extracted information in Table 2 shows that polyamides, polyesters, and rubber are not good candidates for use in the presence of acids and bases, while PE and PVDF are much better candidates.

TABLE 2
Selected Data on Chemical Resistance at 70°F
from Gates Rubber Co.
Chemical Resistance for Industrial Hose Stocks

	Nat. Rubber & Styrene But.	Cross-linked PE (Gatran)	PVDF + HFPP (Viton)	Polyester Elastomer (Hytrel)	Polyamide (Nylon)
Acetic Acid (25%-50%)	N	G	N	G	N
Agua Regia	N	G	G	N	N
Chromic Acid (10%)	N	E	E	N	N
Chromic Acid (25%)	N	G	E	N	N
Chromic Acid (50%)	N	N	E	N	N
HCl(15-37%)	G	G	E	N	N
Nitric Acid (10-60%)	N	G	E	N	N
Sulfuric Acid (10%)	E	E	E	N	N
Sulfuric Acid (30%)	G	E	E	N	N
Sulfuric Acid (50%)	N	E	E	N	N
Sulfuric Acid (93%)	N	E	E	N	N
Sodium Hydroxide (40%)	E	E	G	G	N
" (50,115°F)	E	G	N	-	N
" (50,180°F)	N	N	N	-	N
" (60%)	G	-	N	-	N
Potass. Hydroxide (30%)	G	G	G	N	N
Potass. Permanganate	N	E	G	-	N

E = Excellent: G = Good: N = Not Recommended: - = Insufficient Data

SOLVENT EFFECTS

Solvents interrupt the weak, secondary bonds between polymer chains. With thermosetting polymers, this can result in swelling of the polymer. In thermoplastic polymers, where chains are not necessarily covalently attached to each other, solvent effects can include the "dissolving" of some polymer material (*i.e.*, liquifying and removing it from the original bulk of polymer). Obviously, the extent of the solvent effects is influenced by the access of the solvent to the polymer chains, so amorphous, low-density (loosely-packed) polymers with minimal cross-linking or with long cross-links will be more susceptible.

To actually dissolve a polymer, the solvent must completely surround the chains, so short-chain polymers are more susceptible. For example, foams typically have very low molecular weights, are very amorphous, and dissolve relatively easily (a good demonstration here is to compare the effects of a mild acid on a styrofoam cup versus a polystyrene beaker). This principle is used to good advantage by manufacturers who solvent-treat polymer formulations to carry away low-molecular weight chains to produce high-molecular weight products.

The prediction of which solvents will be more effective with a given polymer begins with the hypothesis that solvents must compete with the cohesive forces between polymer chains. Such forces can be characterized by the "cohesive energy density" which, for liquids, can be defined as the energy needed to vaporize a certain volume of the liquid. Thus

$$\text{Cohesive Energy Density} = \delta^2 = E_0/V_0$$

where

$$E_0 = \text{latent energy of vaporization of volume } V_0$$

$$\delta = \text{"solubility parameter"}$$

The hypothesis is that a solvent with an energy density similar to that of the polymer will be able to exchange weak bonds with the polymer molecules (chains) and to disrupt the polymer. This is presumably the reason for observation of the "like-attracts-like" relationship (polar solvents attack polar polymers, aromatic solvents attack aromatic polymers, alkane solvents attack alkane polymers, *etc.*). If the hypothesis is correct, a value of δ exists for the polymer (determined from exposure to solvents, since polymers are not volatile) at which a maximum solvent effect will be achieved (*i.e.*, when $\delta_{\text{solvent}} \approx \delta_{\text{polymer}}$). In fact, swelling and/or dissolution in most polymers is observed when δ_{solvent} is within $\pm \approx 2\text{-}3$ (cal/cm³)^{1/2} of a central value, which is then reported as δ_{polymer} (examples of this effect are given in references 4 and

5). Values of δ for polymers and solvents are tabulated in several references (4, 6), and it is instructive to have the students plot a vendor's recommendations of solvents for a polymer against the values of δ_{solvent} , such as illustrated in Figure 4 for a PVDC formulation from Dow Chemical Company.

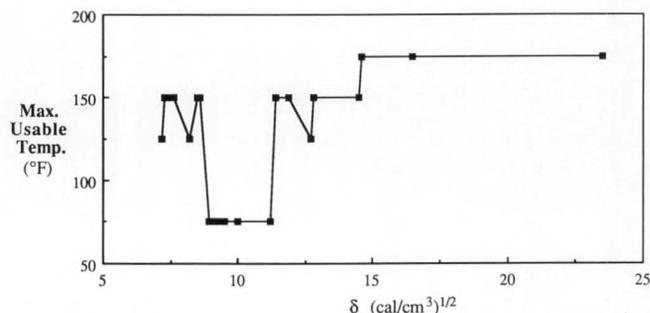


FIGURE 4. Recommended maximum usable temperatures of solvents with PVDC (Saran®) extracted from Dow Chemical Company "Chemical Resistance Guide for Systems Using Plastic Lined Piping Products" (values of δ were compiled from reference 4).

The value here is that for a particular polymer, given the value of δ for that polymer or given a table with recommendations for a few solvents, the student will be able to quickly guess if a particular solvent is safe or questionable by referring to the value of δ for that solvent. For example, suppose that an engineer wishes to know if dimethyl sulfoxide will cause serious swelling and/or dissolution with the PVDC from Dow Chemical Company. First of all, a dilemma arises, because the value of δ for PBDC is reported by Hall (6) as 9.8 (cal/cm³)^{1/2} and by Rodriguez (4) as 12.2 (cal/cm³)^{1/2}. From Figure 4, it is obvious that the formulation from Dow Chemical Company is closer to the material reported by Hall, and that dimethyl sulfoxide ($\delta = 13.0$ (cal/cm³)^{1/2}) will probably not induce significant solvent effects with this polymer.

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REVIEW: Equipment Design

Continued from page 93.

presented and recalls Gregorig wavy surfaces. This chapter concludes with a nice review of the in-tube condensation which describes recent improvements in the methods for predicting flow patterns, pressure drop, and heat transfer during condensation in horizontal and vertical tubes.

The thermal design of two-phase exchangers is treated in chapter six, with a well-posed set of condenser design approaches for pure vapor, mixture of vapors, and multicomponent mixtures with the presence of non-condensables. Special care is devoted to the design methods for the cross-flow and reflux condensers. A critical evaluation of cooling tower design methodology is presented which outlines exact design procedures and assesses the errors associated with the approximate method. Next there is a brief discussion of the basic heat pipe theory, followed by the preliminary design considerations. Thus, an overall design methodology is presented for heat pipe exchangers. Detailed solution procedures are outlined for rating and sizing problems with an example. The chapter concludes with a review of the types of heat pumps, their economics, and the state-of-the-art of chemical absorption heat pumps for industrial applications.

Chapter seven on heat transfer augmentation is primarily directed to enhanced forced convective vaporization and condensation inside tubes. A nice review is presented, and the two-phase different approach is compared to the heat transfer evaluation of single phase behavior. This is followed by a discussion of the performance evaluation criteria for enhanced tube geometries used in two-phase heat exchangers, which is resolved in terms of the heat transfer area ratio.

Chapter eight includes a brief introduction to the fundamentals of rheology and the thermal design of heat exchangers for non-Newtonian fluids. Specific information on the role of rheological behavior and geometry on heat transfer is presented. One should notice that special emphasis has been given to the adoption of Newtonian fluid correlations in dealing with non-Newtonian materials.

To complete the design analysis, chapter nine goes through a treatment of flow-induced vibration mechanisms, and some correlations for their prediction in heat exchangers are discussed. A single-component, two-phase (boiling or condensation) flow instability analysis is also presented which concentrates on the practical aspects of two-phase flow instability in large steam or vapor generators.

While reviewing the book, I got the impression that the authors accomplished the main objective of the Institute. The material presented may be utilized in modern engineering education. The book is not a teaching text in the usual sense—there are too many gaps for a new learner to bridge. But it may be utilized, with a

reasonable amount of success, in an advanced design course of heat transfer equipment. □

ChE book reviews

GRANULAR FILTRATION OF AEROSOLS AND HYDROSOLS

Chi Tien

Butterworths, 80 Montvale Ave., Stoneham, MA 02180; 1989 pages, \$69.95 (1989)

**Reviewed by
Richard H. Heist
University of Rochester**

This book deals with granular filtration of liquid and gaseous suspensions and is directed specifically at this one type of separation process. It fills a gap in the separations literature since most of what has been published is spread throughout the journal literature. This book will be particularly useful to anyone new to the field of granular filtration who wants to get started as quickly as possible. Although the author asserts that the level of the text is consistent with material in accredited chemical and mechanical engineering degree programs, I am not so sure this is true. However, the text could certainly be used as a text or a supplemental text in graduate level, research-oriented courses dealing with separations.

Although both the filtration of liquid suspensions in granular media and aerosol filtration in granular beds are usually treated as two distinct subjects, the author departs from this traditional practice and takes a unifying approach with the result that a majority of the chapters in the book apply equally well to both processes. The principles presented and discussed in the text provide the framework for obtaining information that will aid in the design, operation, and control of granular filtration systems.

In Chapter One the author provides a brief overview of granular filtration, a bit of historical perspective, and a comparison with other, related separation technologies. Several examples of commercial scale granular filtration applications for both liquid and gaseous suspensions are discussed.

In Chapter Two, the governing equations that describe the macroscopic behavior of granular filtration are derived. The formulation, solution, and application of these equations to provide information describing the time dependence of effluent concentration and pressure drop are the primary focuses of this chapter. The author also provides an interesting description of filtration as a stochastic process.

Continued on page 105.

THE USE OF LOTUS 1-2-3 MACROS IN ENGINEERING CALCULATIONS

EDWARD M. ROSEN

*Monsanto Company
St. Louis, MO 63167*

THERE IS A GROWING recognition of the potential usefulness of spreadsheet programs throughout the chemical engineering curriculum. This has been confirmed by the Education and Accreditation Committee of AIChE in its listing of the CACHE Corporation's recommendation of "Desired Computer Skills for Chemical Engineering Graduates" [1]. One of the desired skills is the use of the spreadsheet.

For educational use, the spreadsheet provides some appealing features:

- *The student must have a complete understanding of the problem. He does not use a "canned" program which may hide the solution method.*
- *The spreadsheet allows the student to view the problem's solution directly without the need to print out iterations or look at an output file.*
- *The spreadsheet facility is generally available when other computational facilities may not be.*

For industrial users, the spreadsheet is also of considerable interest:

- *The user can use one system for a variety of problems. He need not learn multiple systems to carry out his job.*
- *There is a certain level of integration the user of the spreadsheet program can achieve by reading files from and sending files to other programs.*

Edward M. Rosen is a senior fellow in the Monsanto Chemical Company. He received his BS and MS degrees in chemical engineering from Illinois Institute of Technology and his PhD from the University of Illinois. He is coauthor (with E. J. Henley) of the book *Material and Energy Balance Computations* (John Wiley, 1969). A past chairman of the CAST Division of AIChE, he is currently chairman of the Process Engineering Task Force of the CACHE Corporation.



The use of the spreadsheet in chemical engineering calculations has been recently reviewed [2]. However, the use of macros was not indicated. Such macros extend the usefulness of the spreadsheet into a variety of applications which would be quite improbable without them. In this discussion, the macros of the popular spreadsheet program LOTUS 1-2-3 [3] will be used (Version 2.01).

MACROS

Macros were originally intended to simply allow the user to store a series of keystrokes so that they wouldn't have to be reentered in routine applications. Macros, however, allow programming in a broader sense. The early version of LOTUS 1-2-3 macros (/X commands) were difficult to use and to follow. However, with Release 2 the Advanced Macro Commands have become available. These are named in such a way as to be much more understandable, and one can follow a listing with comparative ease.

One of the limitations of the standard worksheet is that it doesn't allow for the use of "loop within loop" calculations which arise so often in chemical engineering. However, with macros, this limitation is removed and the capability to use subroutines, much as in FORTRAN, is possible.

A related limitation of the standard spreadsheet is the inability to jump to an arbitrary location as a result of a conditional evaluation. With macros, this is not only possible but also invaluable.

Since learning the macro language takes time and effort, it is fair to ask whether it is worthwhile to learn macros—especially if a calculation can be carried out in another way, say by using FORTRAN or BASIC. The answer certainly depends on system availability, accessibility, familiarity, and the time available for solution. However, it is worthwhile to note that the advanced macro capability of LOTUS 1-2-3 can be made useful with about one day's effort.

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SUBROUTINES

There are differences in using subroutines in LOTUS 1-2-3 as compared to FORTRAN. The first is the ability in LOTUS 1-2-3 to address and manipulate any cell in the spreadsheet whether or not it is passed as an argument to the subroutine. Results from the subroutine cannot be placed in a relative location (*i.e.*, the address cannot be passed on output). Instead the output must be picked up from locations designated by the subroutine.

These comments are illustrated in Figure 1 which shows the coding for a general purpose subroutine, ROOTX, based on Wegstein's method [4] for solving a one dimensional equation in the form

$$f(x) = x \quad (1)$$

The subroutine operates in two modes. If 'code'

(cell P6) is set to 0, then the working cells (P7 to P16) are cleared, and control is returned to the calling routine. If 'code' is set to 1, then ROOTX will return a new x for each pair of values x and f(x) supplied as arguments which are passed to cells P4 and P5 using the DEFINE keyword. Note that the upper and lower bounds on the slope in Wegstein's method are set in cells P1 and P2.

The calling program is given in the macro \q. It is set up to solve either of two problems determined by cell H1 (Problem Selection). The arguments passed to the subroutine, H3, x, and H4, f(x), are specified in the call to the subroutine, *i.e.*, {ROOTX H3,H4}. The new value of x generated by ROOTX is picked up from location P4 and passed to location H3 with the macro command {LET H3,P4}. The convergence criterion is given in the calling program and can be problem dependent.

To Run:	H1:	Prob No.	2	P1:	upper	0.8
Set H1				P2:	lower	-9
& H3	H3:	x	409.9927	P3:		
Then alt q	H4:	f(x)	409.9927	P4:	x	409.9927
				P5:	f(x)	409.9927
Problem 1		van der Waals Constants		P6:	code	1
from Myers				P7:	counter	4
& Seider	H8:	a=	1351000	P8:	x1	409.3106
Page 455	H9:	b=	38.64	P9:	f1	410.0009
	H10:	R=	82.06	P10:	x2	409.9942
van der	H11:	T=(deg K)	173.15	P11:	f2	409.9927
Waals Eqn	H12:	P=(atm)	50	P12:	slope	-0.01200
				P13:	t	0.988133
Initial v	H14:	RT	14208.68	P14:	t*delta	-0.00151
in H3: 600	H15:	a/v^2+p	77.30286	P15:	term1	0.683556
				P16:	denom	0.683556
Soln: 222.4454	EVAL	(LET H14,H10*H11)				
		(LET H15,H8/(H3*H3)+H12)				
		(LET H4,H14/H15+H9)				
Problem 2	H25:	3339.3		P21:	ROOTX	(DEFINE P4=VALUE,P5=VALUE)
from Reklaitis	H26:	451.1603		P22:		(CALC)
Page 445	H27:	613.8811		P23:		(IF P6=0)(BRANCH P25)
	H28:	188.4174		P24:		(BRANCH P27)
	H29:	18.65373		P25:		/CP6-P7..P16-
Initial T				P26:		(RETURN)
in H3: 700				P27:		(LET P7,P7+1)
				P27:		(LET P8,P10)
				P29:		(LET P9,P11)
				P30:		(LET P10,P4)
				P31:		(LET P11,P5)
Soln: 409.9927	EVAL1	(LET H25,3339.3)		P32:		(LET P15,ABS(P10-P8))
		(LET H26,1.138E-2*(H3^2-298^2)/2.)		P33:		(IF P15>0)(BRANCH P36)
		(LET H27,0.4338E-4*(H3^3-298^3)/3.)		P34:		(LET P16,1)
		(LET H28,0.37E-7*(H3^4-298^4)/4.)		P35:		(BRANCH P37)
		(LET H29,1.01E-11*(H3^5-298^5)/5.)		P36:		(LET P16,P10-P8)
		(LET H4,298+(H25+H26-H27+H28-H29)/29.88)		P37:		(LET P12,MIN(P1,MAX(P2,(P11-P9)/P16)))
				P38:		(LET P13,1/(1-P12))
				P39:		(LET P14,P13*(P11-P10))
				P40:		(LET P4,P4+P14)
				P41:		(IF P7=1)(LET P4,P5)
				P42:		(RETURN)
\q	(LET P6,0)	Clear				
	(ROOTX H3,H4)					
	(LET P6,1)	Set ROOTX				
G47:	(IF H1=1)(BRANCH G50)	Select Prob 1 or 2				
	(EVAL1)					
	(BRANCH G51)					
G50:	(EVAL)					
G51:	(IF ABS(H3-H4)<1.E-6)(BRANCH G55)	Test Convergence				
	(ROOTX H3,H4)	Get new x				
	(LET H3,P4)	Set x to f(x)				
	(BRANCH G47)	Evaluate function				
G55:	(CALC)	Complete				

FIGURE 1. Use of subroutine ROOTX in Macro \q.

Depending on the problem specification given by H1(1 or 2) the macros EVAL or EVAL1 are used to evaluate $f(x)$. Problem 1 (EVAL) is taken from Myers and Seider [5] in which the value of v is sought in the van der Waals equation in the form $v = f(v)$. Problem 2 is taken from Reklaitis [6] in which a temperature is sought in an equation in the form $T = f(T)$. The solutions found in each case agree with those given by the authors. Note that in each case (EVAL and EVAL1) the value of H4, $f(x)$, is calculated from the value of H3, x .

PARTIAL DIFFERENTIAL EQUATIONS

The use of the spreadsheet to solve the steady state Laplace equation in two dimensions and the simple parabolic equation in one dimension and time was discussed in [2]. In each of these cases the problem could be set up in a single two dimensional table and solved by an appropriate finite difference formulation using the standard spreadsheet. However, this is not possible in the following case.

Consider heat transfer in a cylinder of radius a and height L :

$$\rho c \frac{\partial T}{\partial \theta} = k \left(\frac{1}{R} \frac{\partial T}{\partial R} + \frac{\partial^2 T}{\partial R^2} + \frac{\partial^2 T}{\partial Z^2} \right) \quad (2)$$

where

- ρ = density
- c = heat capacity
- k = thermal conductivity
- T = temperature
- R = radial coordinate
- Z = height coordinate
- θ = time

with boundary conditions

$$\begin{aligned} \text{at } \theta = 0 & \quad T = T_i \quad \text{at } 0 < R < a \quad \text{and } 0 < Z < L \\ \text{at } \theta \geq 0 & \quad T = T_w \quad \text{at } R = a \quad \text{and } Z = 0 \quad \text{and } Z = L \end{aligned}$$

In order to put Eq. (2) into dimensionless form, let

$$r = \frac{R}{a}, \quad z = \frac{Z}{a}, \quad u = \frac{(T - T_i)}{(T_w - T_i)}, \quad t = \frac{\omega \theta}{a^2} \quad \text{where } \omega = \frac{k}{\rho c} \quad (3)$$

Then

$$\frac{\partial u}{\partial t} = \left(\frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2} + \frac{\partial^2 u}{\partial z^2} \right) \quad (4)$$

with boundary conditions

$$\begin{aligned} \text{at } t = 0 & \quad u = 0 \quad \text{at } 0 < r < 1 \quad \text{and } 0 < z < 1 \\ \text{at } t \geq 0 & \quad u = 1 \quad \text{at } r = 1 \quad \text{and } z = 0 \quad \text{and } z = 1 \end{aligned}$$

Eq. (4) may be solved by finite differences using the

stable Crank-Nicolson method [7,8]. Let

- i = index in the r direction
- j = index in the z direction
- n = index in time t

Then using finite difference approximations

$$\frac{\partial u}{\partial t} \cong \frac{u_{i,j,n+1} - u_{i,j,n}}{\Delta t}$$

$$\frac{\partial^2 u}{\partial r^2} \cong 0.5 \left(\frac{u_{i+1,j,n} - 2u_{i,j,n} + u_{i-1,j,n}}{(\Delta r)^2} + \frac{u_{i+1,j,n+1} - 2u_{i,j,n+1} + u_{i-1,j,n+1}}{(\Delta r)^2} \right)$$

$$\frac{1}{r} \frac{\partial u}{\partial r} \cong \frac{1}{2i\Delta r} \left(\frac{u_{i,j,n} - u_{i-1,j,n}}{\Delta r} + \frac{u_{i,j,n+1} - u_{i-1,j,n+1}}{\Delta r} \right)$$

$$\frac{\partial^2 u}{\partial z^2} \cong 0.5 \left(\frac{u_{i,j+1,n} - 2u_{i,j,n} + u_{i,j-1,n}}{(\Delta z)^2} + \frac{u_{i,j+1,n+1} - 2u_{i,j,n+1} + u_{i,j-1,n+1}}{(\Delta z)^2} \right)$$

Substituting these approximations into Eq. (4) and solving for $u_{i,j,n+1}$ there results

$$u_{i,j,n+1} = \frac{1}{A - \frac{B}{i}} \left(\begin{aligned} & (D + B/i)u_{i,j,n} + (B - B/i)(u_{i-1,j,n} + u_{i-1,j,n+1}) \\ & + B(u_{i+1,j,n+1} + u_{i+1,j,n}) \\ & + C(u_{i,j-1,n+1} + u_{i,j-1,n} + u_{i,j+1,n+1} + u_{i,j+1,n}) \end{aligned} \right) \quad (5)$$

where

$$\begin{aligned} A &= \frac{1}{\Delta t} + \frac{1}{(\Delta r)^2} + \frac{1}{(\Delta z)^2} \\ B &= \frac{1}{2(\Delta r)^2} \\ C &= \frac{1}{2(\Delta z)^2} \\ D &= \frac{1}{\Delta t} - \frac{1}{(\Delta r)^2} - \frac{1}{(\Delta z)^2} \end{aligned}$$

Eq. (5) allows the computation of u at time $n+1$ from the values at time n . This permits the following scheme:

1. Set up a table to store the values of u at time n . Initially this will be all zeros, except at the boundaries. Call this table the Storage Table (C100..AC125). It is shown in Figure 2 with the cells labeled.

FIGURE 2. Spreadsheet solution to Eq. (4) using Macro \a.

Solution to Parabolic Equation				\a (BREAKON)			
Two Dimensional Unsteady State in Cylindrical Coordinates				(IF E4<2)(BRANCH G2B)			
To Run set E4 to 1 (& alt a) and then 2				(LET B4,0)			
Counter: B4:	50	Set 1-Initialize E4:	2	G5:	/CEB4-B7..B10-	Time in hrs	3.47222222 0.00000716
		Set 2-Run			/CEB4-A11..A1100-	(AT) and	4.629629629 0.000003741
Completed					/CEB4-A21..A2100-	Scaled	5.787037037 0.000014418
Iter B7:	50				/DFC99.AC99--	Temperature	6.964444444 0.00004122
Time Hrs B8:	57.87037037			G10:	-1-1--	at	8.101851851 0.000112568
Temp B9:	0.162792552				/DFB100.B125-	a/2 and L/2	9.259259259 0.000248133
Target B10:	0.785714285				0-1--	(A2)	10.416666666 0.000485837
Times B11:	50				/CEB6-C100..AC100-		11.57407407 0.000863705
Physical Properties:					/CEB6-AC101..AC125-		12.73148148 0.001410828
Radius	Meters	E62:	0.5	G15:	/CEB6-C125..AC125-		13.80080808 0.002184161
Height	Meters	E63:	1		/DFC199.AC199--		15.04629629 0.003186492
Init Temp	Cent	E65:	75		-1-1--		16.20370370 0.004445556
Wall Temp	Cent	E66:	5	G20:	/DFB200.B225-		17.36111111 0.005974040
Target Temp	Cent	E67:	20		0-1--		18.51851851 0.007778144
Density	KG/M ³	E69:	1000	G25:	/CEB6-C200..AC200-		19.67592592 0.009858463
Thermal Cond	W/(M°C)	E70:	0.15		/CEB6-AC201..AC225-		20.83333333 0.012210978
Heat Cap	J/(KG°C)	E71:	2500		/CEB6-C225..AC225-		21.99074074 0.014828040
Thermal Diff	M ² /J	E74:	6.0000E-08	G30:	/CEB4-C101..AB124-		23.14814814 0.017699274
Omega					(LET APP, TIME HRS)		24.30555555 0.020812363
Table Increments:					(LET A199, TIME HRS)		25.44296296 0.024153711
Delta r (R/a)		E77:	0.04	G35:	(LET E93,0)		26.62037037 0.027708980
Delta z (Z/a)		E78:	0.08		(LET A100,0)		27.77777777 0.031463521
Delta Dimensionless Time		E79:	1.0000E-03		(LET A200,0)		28.93518518 0.035402703
a*a/Omega		E80:	4.1667E+06	G40:	(CALC)		30.09259259 0.039512162
Table Values:					(IF E4=1)(QUIT)		31.25 0.043777984
Initial Temperature (scaled)		E84:	0	G45:	(LET E93,1)		32.40740740 0.048186832
Final Scaled Temperature		E85:	0.7857142857		(LET B4,B4+1)		33.56481481 0.052726031
Wall Temperature (Scaled)		E86:	1		(LET A200, (E79*B4+E80)/3600.)		34.72222222 0.057383614
A		E88:	1781.25		(LET A100,A200)		35.87962963 0.062148349
B		E89:	312.5	G50:	(LET B7,B4)		37.03703703 0.067009744
C		E90:	78.125		(LET B8,A200)		38.19444444 0.071958031
D		E91:	218.75		(LET B10,E85)		39.35185185 0.076984146
Initiator		E93:	1		(CALC)		40.50925925 0.082079706
					(RECALC C201..AB224,(B4<0),12)		41.66666666 0.087234963
					/RVC201..AB224-		42.82407407 0.092448781
					C101..AB124-		43.98148148 0.097708587
					(LET B9,0.25*(O112+O113+P112+P113))		45.13888888 0.103010338
					(CALC)		46.29629629 0.108348481
					(IF B4=1)(GOTO A11-		47.45370370 0.113717919
					(IF B4=1)(DOWN 1)(LEFT 1)		48.61111111 0.119113971
					/RVBB--		49.76851851 0.124532344
					(RIGHT 1)		50.92592592 0.129969097
					/RVB9--		52.08333333 0.135420614
					(IF B9=B10)(QUIT)		53.24074074 0.140883577
					(IF B7=B11)(QUIT)		54.39814814 0.146354939
					(BRANCH G2B)		55.55555555 0.151831904
							56.71296296 0.157311892
							57.87037037 0.162792552

Storage table after 50 iterations.

TIME HRS	Center Line				P97/P197		Q97/Q197		Z97/Z197		AA97/AA197		AB97/AB197		AC97/AC197	
	C97/C197	D97/D197	E97/E197		P98/P198	Q98/Q198			Z98/Z198	AA98/AA198	AB98/AB198	AC98/AC198				
57.87037037	0	1	0	1	12	13			22	23	24	25				
101/201:	1	0.8019503696	0.801785688	0.8019503696	0.8282357983	0.8351236273			0.9502170828	0.9669669609	0.9836623894	1				
102/202:	2	0.616361832	0.616042838	0.616361832	0.6672779054	0.6806200387			0.9035656241	0.9360117568	0.9683524371	1				
103/203:	3	0.4533459104	0.452891384	0.4533459104	0.5258953404	0.5449065092			0.8625868594	0.908820593	0.9549041101	1				
104/204:	4	0.3190524537	0.318486287	0.3190524537	0.4094218807	0.4331029499			0.8288267437	0.8864192765	0.9438247564	1				
105/205:	5	0.2152089802	0.214556496	0.2152089802	0.3193564049	0.3466482528			0.8027200517	0.8690963093	0.9352570679	1				
106/206:	6	0.1397606841	0.139045490	0.1397606841	0.2539176133	0.2838327042			0.7837509686	0.8565094415	0.9290317776	1				
107/207:	7	0.0881935758	0.087435520	0.0881935758	0.2091912275	0.2408991162			0.7707853961	0.8479061644	0.9247767107	1				
108/208:	8	0.0550020135	0.054216366	0.0550020135	0.1804025826	0.2132643534			0.7624396849	0.842368376	0.9220377909	1				
109/209:	9	0.03487747	0.034075089	0.03487747	0.1629476435	0.1965090051			0.7573794531	0.8390106594	0.9203771053	1				
110/210:	10	0.0234283931	0.022616488	0.0234283931	0.1530174582	0.1869768206			0.754500637	0.8371004192	0.9194323234	1				
111/211:	11	0.017458014	0.016641140	0.017458014	0.1478392427	0.1820061544			0.7529994459	0.8361043026	0.9189396559	1				
112/212:	12	0.0149517193	0.014132758	0.0149517193	0.1456655323	0.1799195729			0.7523692811	0.8356861562	0.9187328457	1				
113/213:	13	0.0149517192	0.014132758	0.0149517192	0.1456655323	0.1799195729			0.7523692811	0.8356861562	0.9187328457	1				
114/214:	14	0.0174580139	0.016641140	0.0174580139	0.1478392426	0.1820061544			0.7529994459	0.8361043026	0.9189396559	1				
115/215:	15	0.023428393	0.022616488	0.023428393	0.1530174581	0.1869768205			0.754500637	0.8371004192	0.9194323234	1				
116/216:	16	0.0348774697	0.034075088	0.0348774697	0.1629476434	0.1965090049			0.7573794531	0.8390106593	0.9203771053	1				
117/217:	17	0.0550020132	0.054216365	0.0550020132	0.1804025825	0.2132643533			0.7624396849	0.842368376	0.9220377909	1				
118/218:	18	0.0881935755	0.087435519	0.0881935755	0.2091912273	0.2408991161			0.770785396	0.8479061644	0.9247767107	1				
119/219:	19	0.1397606837	0.139045489	0.1397606837	0.2539176131	0.2838327041			0.7837509686	0.8565094415	0.9290317776	1				
120/220:	20	0.2152089798	0.214556496	0.2152089798	0.3193564047	0.3466482527			0.8027200517	0.8690963093	0.9352570679	1				
121/221:	21	0.3190524533	0.318486287	0.3190524533	0.4094218805	0.4331029497			0.8288267437	0.8864192765	0.9438247564	1				
122/222:	22	0.45334591	0.452891384	0.45334591	0.5258953403	0.5449065091			0.8625868594	0.908820593	0.9549041101	1				
123/223:	23	0.6163618318	0.616042837	0.6163618318	0.6672779053	0.6806200386			0.9035656241	0.9360117568	0.9683524371	1				
124/224:	24	0.8019503694	0.801785687	0.8019503694	0.8282357983	0.8351236273			0.9502170828	0.9669669609	0.9836623894	1				
125/225:	25	1	1	1	1	1			1	1	1	1				

D201: [W12] @IF(\$E93=0,0,(D101*(E891)+E89*(E201+E101)+E89*(C201+C101)+E89*(D102+D100+D200+D202))/(E88))
 E201: [W14] @IF(\$E93=0,0,(E101*(E891)+E89/E89)+E89*(F201+F101)+E89*(1-1/E89)*(D201+D101)+E89*(E102+E100+E202+E200))/(E88-E89/E89))

2. Set up a second table (the Calculate Table, C200..AC225) which will calculate the values of u at time $n+1$ from the formula of Eq. (5). Since the value of $u_{i,j,n+1}$ depends on the values at $n+1$ as well as at n , iterate until convergence (say at least twelve iterations). The cells are labeled together with the cells for the Storage Table.

Figure 2 illustrates the spreadsheet setup for a cylinder of radius 0.5 meters and a height of 1 meter with the following physical properties:

$\rho = 1000 \text{ kg/m}^3$	density
$k = 0.15 \text{ watts/(m deg C)}$	thermal conductivity
$c = 2500 \text{ J/(kg deg C)}$	heat capacity

The increments chosen (based on a table of 25 cells by 25 cells) were

$$\begin{aligned}\Delta r &= 0.04 \\ \Delta z &= 0.04 * \text{Height/Radius} = 0.08 \\ \Delta t &= 0.001\end{aligned}$$

The macro \a is set to run in two modes. If E4 is set to 1, then the tables are both set to zero (the Calculate Table is set to zero by having E93 set to zero as shown in the commands for cells D201 and E201) and the boundary values are set to 1. If E4 is set to 2, then the macro allows the Calculate Table to be generated from the Storage Table. The values are copied from the Calculate Table to the Storage Table after the temperatures at time $n+1$ are determined and the process is repeated until a fixed number of

TABLE 1
Spreadsheet Value
of u versus the Analytical Solution at $L/2$

R	r	Spreadsheet			Analytical
		$\Delta r = 0.025$	$\Delta r = 0.04$	$\Delta r = 0.04$	Solution
		$\Delta z = 0.050$	$\Delta z = 0.08$	$\Delta z = 0.08$	
		$\Delta t = 0.001$	$\Delta t = 0.001$	$\Delta t = 0.0005$	
0.	0.	0.01421	0.01413	0.01413	0.01599
0.1	0.2	0.02897	0.02891	0.02892	0.03064
0.2	0.4	0.09399	0.09312	0.09313	0.09694
0.3	0.6	0.2684	0.2666	0.2666	0.2723
0.4	0.8	0.5922	0.5907	0.5907	0.5950
0.5	1.0	1.0	1.0	1.0	1.0

steps (*i.e.*, time) is taken or a particular temperature is exceeded. The macro uses columns AY and AZ to record time and temperature at the location $a/2$ and $L/2$. The results are shown in Figure 2. The computation stopped after 50 time steps (57.87 hrs) which was reached before the specified target temperature. Each of the time steps takes about 45 seconds on a Vectra ES/12 (80286) with a math coprocessor (80287).

The Calculate Table was constructed by copying the contents of cell D201 to cells D202..D224 and the contents of cell E201 to E202..AB224. By symmetry the values of column C were set to those of column E.

Carslaw and Jaeger [8] give an analytical solution for this case:

$$u = 1 - \frac{8}{\pi a} \sum_{k=0}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^k J_0(R\alpha_m)}{(2k+1)\alpha_m J_1(a\alpha_m)} \cos\left(\frac{(2k+1)\pi x}{2h}\right) \exp\left(-\omega h(\alpha_m^2 + (2k+1)^2\pi/4h^2)\right) \quad (6)$$

where

$$\begin{aligned}h &= L/2 \\ -h &< x < h\end{aligned}$$

and α_m is calculated from the roots of the zeroth order Bessel function J_0 : *i.e.*,

$$\begin{aligned}\alpha_1 &= (\text{1st root})/a \\ \alpha_2 &= (\text{2nd root})/a \\ &\dots \\ \alpha_m &= (\text{mth root})/a\end{aligned}$$

The upper limit on m was taken as 40 and the upper limit on k was 50. The first forty roots of the zeroth order Bessel function were taken from Jahnke and Emde [10].

Table 1 compares Eq. (6) to the spreadsheet solution at $L/2$ ($x=0$) at a number of values of R . Since the spreadsheet solution is not given exactly at $L/2$, the average value of the surrounding cells at a given r was used. The table also gives values found when the time increment was reduced to 0.0005 and the values of the coordinate increments were $\Delta r = 0.025$ and $\Delta z = 0.050$.

Reducing the values of Δr and Δz (a 40 x 40 table) improved the accuracy somewhat, but cutting the value of Δt did not. Eq. (3) may be used to convert the dimensionless solution to the scaled solution sought. An error of 0.005 in u corresponds to an error in T of 0.5 deg C if $(T_w - T_i) = 100$.

CONCLUSIONS

Macros allow the use of the spreadsheet for a greater variety of problems than can be done without

them. The LOTUS 1-2-3 advanced macro commands are relatively easy to learn and apply. Their use should be considered.

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REVIEW: Aerosols and Hydrosols

Continued from page 99.

In the third chapter, the author focuses on procedures for modeling granular media in filters. Rather than utilizing a "black box" approach to describe the filter (inherent in the methods described in Chapter Two) in order to determine concentration histories and pressure drops, the specifications of the collector's structure, geometry, size, size distribution, and the fluid flow fields around the particles are considered.

In Chapter Four, a variety of mechanisms for the deposition of particles on collectors from flowing suspensions are discussed. Expressions for collection efficiencies for these various deposition mechanisms are derived, utilizing the media modeling methods described in Chapter Three.

In the fifth chapter, the author illustrates that trajectory analysis, along with the media models described in the third chapter, can be used to estimate filtration rates. Because of complexities associated with representing fluid drag forces acting upon suspended particles and also representing particle surface geometry as deposition proceeds, the method of trajectory analysis is limited mainly to clean filters.

In Chapter Six we find that because of distinct differences in the particle deposition mechanisms, it

becomes necessary for the author to depart from the integrated approach he has followed up to this point and to treat aerosols and hydrosols separately. In this chapter he focuses on prediction and measurement of initial collection efficiencies for the granular filtration of aerosols. Collection efficiencies are predicted using the trajectory analysis methods discussed in the fifth chapter. A variety of experimental methods for determining initial collection efficiencies are briefly discussed, and appropriate experimental results are provided. Empirical correlations and their relative merits are also discussed.

In the seventh chapter, the author describes the prediction of initial collection efficiencies for hydrosols using trajectory analysis. Results of these calculations are compared with experimental data. Limitations of the trajectory analysis approach and possibilities for improving it are discussed.

In Chapter Eight the author begins to look at the entire process of particle deposition, not just the initial stages which have been addressed up to this point. Dendrite growth of deposited particles and stochastic simulations of particle deposition are the focus of much of this chapter. The author points out that much of what is covered in this chapter is still in the developmental stage and, as such, is included to demonstrate general principles and the potential of the methods.

Finally, in Chapter Nine, the author focuses on a number of actual investigations (case studies) dealing with the granular filtration of aerosols and hydrosols. Topics discussed include filter ripening, effects of deposit morphology on filter performance, effects of deposition on aerosol filtration, aerosol deposition in fluidized filters, and the increase in hydrosol filter coefficient.

In summary, the author has done a nice job of writing about a sharply focused area of separations which, up to now, has been largely dealt with in scientific journals. A great deal of information has been brought together in a coherent, logical format. It is particularly useful because it tells you how to do things. The book is fairly easy to read, and the figures, graphs, and tables are clear and easy to understand. The author does not get bogged down in tedious mathematical derivation. That which is not shown directly is usually referenced adequately. The text is designed to bring someone who is interested in further work in the area "up to speed" in a reasonable period of time. The references are extensive and will be particularly helpful to anyone interested in the field. Since the subject matter of the book is admittedly narrow, it would only be useful as a course text or supplemental text for advanced, research oriented graduate courses. □

INCORPORATION OF PROCESS CONTROL COMPUTERS IN THE UNDERGRADUATE LABORATORY

A Case Study

WM. CURTIS CONNER, JR.
*University of Massachusetts
Amherst, MA 01003*

THE REBUILDING of our undergraduate unit operations laboratory was a substantial project and required the concerted effort of several individuals. To understand the process, it is first necessary to realize the state of our undergraduate laboratory before we began the conversion (*Background*). A plan for transforming the laboratory (incorporating state-of-the-art computers) was created, and a method for accomplishing the goals was developed (*Implementation*). The eventual capabilities were dictated by the choice of the computer systems to be used in the laboratory, and this will be briefly discussed (*Computer Capabilities*). A major aspect of the change was a realization that both the existing philosophy of the laboratory and the nature of the experiments needed to be modified; further, new experimental approaches would be available with the enhanced capabilities (*Course Content*). The next-to-last section will discuss the problems that occurred and our perception of the process (*Discussion*). We have continuing plans to modernize and update the laboratory to reflect current and developing "state of the art" in personal computers and their application to the measurement and control of chemical engineering processes. They will be discussed in the last section (*Future Plans*). The last two brief sections include an overview of the process (*Final Comments*) and *Acknowledgements* of the

A group of the faculty met and decided that the laboratory should be restructured. . . . Out-of-date experiments were dropped, and other experiments were combined into larger experimental projects

W. Curtis Conner, Jr., is an associate professor of chemical engineering at the University of Massachusetts at Amherst. He received his BES in chemical engineering and his PhD in catalytic chemistry from Johns Hopkins University. After postdoctoral positions at the University of Connecticut, the University of Wisconsin at Milwaukee, and Zelinski Institut in Moscow, he worked in catalytic research at Allied Chemical Corp. His major research is catalysis, and he is author of over eighty publications and patents.



myriad of people that made this whole process possible.

BACKGROUND

Seven years ago, when I came to the University of Massachusetts, the undergraduate laboratory was no more advanced than the ones I had been exposed to in my undergraduate education. It had been built in the 1950s and, without substantial state funds available for modernization, was essentially unaltered. The limited funding provided through the years had been used for maintenance of the existing equipment. At one time, our undergraduate chemical engineering laboratory course spanned three years and involved one credit hour each semester. A sequence of several small experiments was involved, *e.g.*, calibration of a thermocouple. Prior to that the laboratory had been run during several summer weeks between the junior and senior years, as a summer camp for chemical engineering undergraduates.

The laboratory can provide a method of testing and understanding the complexities of the concepts learned in class. This should occur after, or concurrent with, the class. Therefore, the laboratory was concentrated into two three-credit courses in the senior year. The focus in the fall semester was on thermodynamics and transport, and the focus in the spring semester

was on kinetics and control. We also had been conducting a "senior seminar" course that gave the students an opportunity to choose a general interest topic and present a talk to the other students.

A group of the faculty met and decided that the laboratory should be restructured. The first steps were organizational. Out-of-date experiments were dropped, and other experiments were combined into larger experimental projects. As an example, an experiment to measure the VLE diagram was combined with distillation to reflect the design of a separation based on a mixture of components for which the vapor liquid equilibria were "unknown." The "senior seminar" was incorporated into the course. The students were required to orally present a proposal of their intended experiments prior to going into the laboratory and then to orally report on the results after they had finished. Written expression was also emphasized as the students were required to write a one-page proposal and a concise (less than ten-page) report.

Our primary concern was that the laboratory did not reflect the "state-of-the-art" use of digital computers in the acquisition of experimental data and did not foster the ability to efficiently design experiments and control the processes. A program (discussed below) was developed by which this goal might be realized. Catalyzing this proposal was the donation of modern process control computers, MACSYM-350[®]s, from Analog Devices Corp., to the university. An undergraduate student, John Melanson, had used this system in our research in catalytic reaction engineering and found it was very easy to use and to interface with real experimental measurements.

IMPLEMENTATION

It was first necessary to plan the laboratory transformation. We initially proposed interfacing the computers over a three-year period. Two or three computers would be acquired each year and interfaced with two of the six or seven experiments conducted each semester in the laboratory. One or two computers would be set up in the student AIChE office to permit groups to write programs and to analyze data outside of the laboratory. Modest funding was requested for new experimental hardware (valves, transducers, *etc.*) which was to be augmented by funds from the university (generated by a new engineering school laboratory fee). The proposal was submitted to Analog Devices in the spring of 1983 and was accepted for the first year.

We had decided to directly involve the undergraduate students in the transformation of the laboratory. Two students, Ann-Marie Baker (a junior) and

The conversion . . . to computer data acquisition and process control involved . . . reorganization. Two and one-half weeks at the beginning of the fall semester are now set aside to introduce students to the computer systems.

John Dorgan (a sophomore), were given jobs in the Applications Group of Analog Devices during the summer of 1983. They returned to campus in August to begin the conversion. Other students were employed at the university during the summer (and on a continuing basis since then) to transform specific experiments and to develop new experiments.

We decided to make programming of the computers an integral part of the course. Teaching software was developed to instruct the students on the use of computers and on the specific version of BASIC (MACBASIC[®]) employed on these process control computers. Ten megabyte hard discs were acquired for each computer system, and the teaching and demonstration programs were loaded onto each system. The demonstration programs (described below) gave examples of all of the programming functions required for the course. A 25-inch color monitor (RGB input) was purchased for class instruction using on-screen display of the programs with color graphics. We found that classes of 25-30 could be conducted with the monitor.

A technician and an instructor in our department also became involved in the conversion. Each had been involved in computer applications and readily volunteered their services and expertise. Graduate students who had used these computer systems were used as teaching assistants for the course.

The first year was so successful that we decided to complete the transformation in two years instead of the three years originally proposed. At the end of the first year, a renewal proposal for the completion of the conversion was submitted to Analog Devices and, in view of our progress, was accepted. The retail price was \$250,000 (\$200,000 in computer hardware and \$50,000 in experimental hardware).

COMPUTER CAPABILITIES

The capabilities of the computers used for the conversion are essential for transforming our undergraduate laboratory to primary computer data acquisition and control. We decided to take the "quantum leap" and use state-of-the-art process computers. The language used by the computers had to be easy to learn and readily adaptable to the measurement of

flow, force, temperature, and composition. We decided to incorporate dynamic control as well as data acquisition into the course curriculum; therefore, the ability to perform simultaneous tasks ("multi-tasking") was important. The MACSYM® line of computers produced by Analog Devices was ideally suited for this task. Analog Devices is a corporation based on the conversion of analog to digital and digital to analog signals.

MACBASIC® is a "compiled basic" language that is analyzed line by line as the program is written. Syntax errors are noted immediately. "On screen" editing is used. Analog to digital to analog conversions and high resolution graphics (including color) are inherent in the language. This system seemed to be designed specifically for the operations required in the monitoring and control of a chemical engineering process. Hence it was not necessary to adapt the computer system for communication with the world of real chemical processes. As an example, Table 1 illustrates a first attempt at proportional-integral control. It illustrates the ease of reading voltage inputs (line 30) and setting output voltages (line 100), in spite of the simplicity of the control scheme. Decisions regarding control and/or alarms are made in the program. On/off inputs such as valves and switches are controlled or recorded with comparable digital input (DIN) and digital output (DOT) command syntax. A number of commands are available to define simultaneous tasks and to activate or suspend the tasks. This permits the programming of simultaneous control, of gathering and storage of data, of printing, and/or of plotting.

We wanted to allow for expansion and the measurement and control of as many as forty variables on a single process (on a distillation column, for example).

TABLE 1
Program for PI Control

Command	Comment
10 INPUT "Setpoint, Gain, Integral Const. ?" SP,G,I	Choose setpoint, control gain and integral constant
20 zero timer, TOT = 0, PT = 0	Starts time clock, zero's integral
30 X = AIN(2,3,10)	Measures voltage on card 2, channel 3 with sensitivity 10
40 T = timer	Records time
50 ET = T - PT	Calculates elapsed time
60 E = SP - X	Calculates error
70 TOT = ET * E + TOT	The integral
80 If Abs(TOT) > 10 then TOT = 10 * TOT / Abs(TOT)	Preventing integral wind up
90 Y = G * (E + TOT / I)	Calculate new output voltage
100 AOT(3,1) = Y	Set channel 1 voltage on output card 3 at Y volts
110 PT = T	Saves time
120 GOTO 30	



Setting up the distillation column for a steady-state experiment. Distillation column is seen on the right as is the computer monitor depicting the schematic for the column with temperatures and flow rates being shown dramatically at the appropriate positions on the diagram.

There are eight card slots on the MACSYM® main-frame and each slot can take up to 16 differential or 32 single ended inputs, or four voltage outputs. Another twenty card slots are provided with the "200" front end.

A further consideration was the availability of service within twenty-four hours. Analog Devices is located in Norwood, Massachusetts, and their service hotline never failed to respond immediately.

COURSE CONTENT

The conversion of our laboratory to computer data acquisition and process control involved a reorganization of the course. Two and one-half weeks at the beginning of the fall semester are now set aside to introduce the students to the computer systems. Simple test benches are set up for each computer to provide voltage inputs and the display of voltage (analog) output signals. The students are divided into groups of two and are given three sets of homework during the period in order to demonstrate their mastery of the basic computer language. Five computer systems are set up and available each afternoon for the students. Teaching assistants are also available to assist in the programming.

Five or six experiments are required each semester. In the spring, the students are required to perform four experiments and to choose one from two additional experiments. The selection of experiments

TABLE 2
Laboratory Experiments

<i>Experiment</i>	<i>Equipment</i>	<i>3-Hr periods required</i>	<i>Computer Interfaced</i>
FALL SEMESTER			
Vapor/liquid equilibrium and distillation	Equilibrium still and gas chromatograph and 20', 13 plate, SS column	1+3	Temp. on each tray and 12 other points on the column; all flow rates; reboiler level
Concentric pipe heat exchangers	16' steam-water and 40' water-water co- or counter-current heat exch. network	3	Temperatures at 24 points in the network; all flow rates
Fluid flow through pipes and fittings	120' pipe network of different sizes with bends and fittings	3	Flow rate over a broad range; ΔP at 20 points; E & I for the water pump
Unsteady state heat transfer	Objects of different sizes and shapes immersed in water	2	None yet but all temperatures possible
Compressibility of gases and gas mixtures	Interconnected ballast volumes and pressure gages	2	None
SPRING SEMESTER			
Control of distillation	See above	3	As above with control of steam, reflux and feed flows
PID control of flow	Flow valve with transducer	2	Control valve and flow
Methanation	Catalytic PFR with on-line CO analysis	3	Control of all flows; reactor oven; analyzer
Water cooling tower	16' counter-current packed column	2	None
Saponification reactor	Liquid-liquid CSTR	3	Temperature; flow rates; up and down stream PH's
Diffusion	Capillary-column GC	3	Temperature; flow; concentration at 10Hz

TABLE 3
Computer Programs Provided on Each System

<i>Name</i>	<i>Purpose</i>	<i>Description</i>
TempTest	Data Measurement	Conversion of a series of 16 thermocouples to a displayed list of temperatures (updated every second)
DTMX	Data Manipulation	Use of matrix to store data, to transfer to disc and to print out tables
Datman	Multi-tasked data handling	Simultaneous collection, storage, display, and printing of multiple analog inputs
Pltmx	On-Screen and 8 color plotting	Use of plotting graphics from data matrix "on screen" and, if chosen, with plotter (X vs Y or X vs time)
AIN-OUT	Setting outputs based on inputs	On/off decisions, alarms, and proportional control based on measured analog inputs
Condem	Demonstration of PID control	Setting of control constants and on-line screen plotting of set point, measured input and output
Conplot	Dynamic PID control	Multi-tasked control with data matrix storage and 8-color plotting...run dynamically
"LAB"	Specific	Basic programs for heat exchanger, distillation, methanation, saponification, and diffusion...includes flow diagrams

varies as the updating of the experiments is done on a continuing basis. During each break between semesters, groups of three students are involved in designing new experiments and in updating earlier experiments. This is a "modest" effort to keep the laboratory program dynamic.

The current list of experiments is shown in Table 2. Three experiments in the fall semester and five in the spring are interfaced with the computers. At least one experiment each semester does not involve computer data acquisition. The focus is on computer use as a tool to measure more variables more rapidly than was possible before. Further, the data can be stored instantaneously and decisions can be made to control the process variables and thereby the experiments. The emphasis of the laboratory performance is on chemical engineering principles and we are committed to retaining this perspective. The advantage is that computers are able to **dramatically** enhance the analyses on-line and thereby to permit changes and adjustments during the experiments.

The laboratory course is closely coordinated with the ongoing courses during the senior year. As an example, as the students learn PID control, Bode diagrams, cascade control, sensitivity analysis, or self-tuning regulators in their control course, these concepts are expected in their experimentation involving control. As mentioned above, each successive group performing experiments is required to go further than prior groups did. Oral reports from the groups are presented to the whole section (*i.e.*, those not in the laboratory conducting experiments). Students are encouraged to ask questions of other groups regarding experiments.

To facilitate the student's use of computers for data acquisition and control, a series of programs is provided which demonstrates all the techniques required for computer use. These are listed in Table 3. The programs are available on the 10MB Winchester disc attached to each system and they are discussed with the students in lecture sessions at the beginning of each semester. During the fall semester the emphasis is on proper techniques of data acquisition, management, and analysis. At the beginning of the spring semester this is augmented with lectures and demonstration programs on multi-tasking, on plotting, and on control. As the students become involved in the experimentation, they request assistance on programming at increasingly higher levels. The demonstration programs are employed (with encouragement and coaching) to develop the students' own approaches to their problems. The effect is synergistic. Basic data acquisition programs are provided for most

of the computer-interfaced experiments. This provides flow diagrams for the specific systems and starts the students in the right direction. However, the students are informed that the use of these programs without substantial modification is unacceptable. Finally, a copy of the program that they used is appended to their final reports.

With a total of only 33 three-hour laboratory periods each semester, it is obvious that a rotating plan for the laboratory is needed. Fridays are set aside for make-up. For each experiment, each group must provide a proposal and a report in addition to the time spent in the laboratory. The assignments rotate, and each student in a group of two is responsible for at least two reports and two proposals each semester.

DISCUSSION

As we expected, we experienced several difficulties during the conversion. The first semester was assembled "on the fly" since the computers and all the flow transducers and valves arrived just one week before the first class. Each computer system was configured identically (this is crucial) as we scrambled to install the valves and transducers. Each student was given a formatted disc, and then the format command was removed from the operating systems in the laboratory. This was done after it was (painfully) discovered that the hard disc could be inadvertently formatted and thereby erased in this manner.

We soon realized that homework needed to be assigned during these first weeks in order to focus the student's practice on the computers. There is an activation energy with the use of a new computer system; however, after the initial reluctance, the learning process is autocatalytic.

The manual was not explicit in describing our specific needs. Several phone calls to Analog Devices revealed that bleed resistors from voltage low to ground were needed, and all the inputs had to be on common ground. We included capacitors across the inputs to decrease spurious noise. All the Foxboro transducers required 20-24 volt DC power. A high capacity DC power supply was requisitioned and was set up to service all the needs from a single switchable source. This worked well. Temperature measurements were handled through a sixteen channel, zero compensating subsystem. The example use software in the manual needed to be consulted to determine the proper configuration.

The MACSYM® system is very fast, and a certain amount of signal averaging is desirable. The students

have to develop a perspective on the amount of data needed to perform each experiment; otherwise, they end up with reams of data and have difficulty extracting the pertinent portions. Proper experimental planning is essential, and this is emphasized.

Since we had obtained the computer system directly from Analog, there was no salesperson involved and the normal system-setup visit did not accompany the delivery. However, by learning to configure the systems "from scratch" and to set up the interfaces, we gained invaluable experience and insight. This has enabled us to correct problems and adjust the system parameters as needed. Almost all of our difficulties have occurred at the beginning of each semester when the computer systems are changed to new or different experiments.

The Macbasic® language runs on a CCPM operating system, although DOS can be partitioned into the MACSYM® 120 systems. We have kept DOS off all the systems and religiously excluded any word processing software (or games) from the systems. These are powerful minicomputers, but their exclusive use for the laboratory needs to be maintained.

We initially attempted to prohibit students from sharing computer programs already developed for specific experiments, but this proved to be impractical. Subsequently, we encouraged the students to share their software, but required successive groups to do more and thereby improve on the prior experiments. We have found that at least four to five times as much data is gained by each group compared to our prior experience with the same experiment. As an example, prior running of the distillation column involved steady state measurements to compute plate-to-plate efficiencies. The students now start the system, investigate the dynamics, and develop elaborate control schemes to optimize the process.

The net results have been very dramatic. The technicians have developed programs to start up and check out the functions of each experiment. The students are stimulated to see how much they can extract from each laboratory. We noticed this soon after we started. Groups were asking to get into laboratory **an hour early** to get started! They often ask how to do various operations such as control, multi-tasking, or plotting before we instruct or require them to use these techniques. The most frequent questions start, "How can I . . .?" In addition to exercising their abilities in programming, they are developing a "feel" for chemical engineering processes and their state-of-the-art monitor and control. The whole process has been one of my most rewarding experiences in teaching.

FUTURE PLANS

The initial transformation of our undergraduate laboratory was first envisioned in 1983. Full implementation took several years. Since then we have continued to update and expand the available experiments. In particular, we realize the growing need for expertise in solids processing. A tray drier has been installed in the laboratory and is being interfaced with the computer systems. Further, we are expanding the separations/transport experimentation by adding a dynamic Taylor dispersion apparatus and a continuous membrane separation experiment. The first involves moment analysis of pulses in a capillary G.C. column. The second employs hollow fiber membranes to separate oxygen and nitrogen from the air. In both experiments temperature, flow rate, and composition are manipulated variables subject to monitor and control.

Since the availability and capabilities of computers has continued to change dramatically, we look at the latest state-of-the-art and the obvious directions in personal computers in order to plan for the next stage of development of our undergraduate chemical engineering laboratory. Further, Analog Devices has chosen to concentrate its effort on subsystems that are peripheral to the two major systems employed as personal computers (IBM and Apple). Indeed, this summer one of our students was employed at Analog Devices to develop the "drivers" for Macintosh SE® and MAC II® PC's to communicate with Analog's newest measurement and control systems (the 1050-1060 family of data acquisition subsystems). This seems to be the way to proceed with the abundance of PC's currently available. The computer driver would then be able to be changed and updated, retaining the A/D subsystems.

We look to the future and anticipate that we will begin a conversion to state-of-the-art personal computers with associated analog to digital to analog communication. This conversion will start next year and should be completed in three years. Ease of visualization (graphics) and a low activation energy for learning the specific system leads us to investigate the use of Apple Macintosh® II and SE systems for our future undergraduate chemical engineering laboratory. Multi-tasking has not yet become an integral part of either operating system; however, Apple seems to have recognized its significance in Multifinder®. For chemical engineering applications, **true multi-tasking** would be crucial as simultaneous monitor, display, and control of the processes are essential to a viable chemical engineering laboratory.

We have set up dedicated Apple Macintosh II and SE computers and the associated A/D and D/A sys-

tems. The use of these systems for the collection and control of analog inputs/outputs is being tested at this time in our reaction engineering laboratories. Our dialogue with Analog Devices continues as we and they investigate the use of their A/D/A based on Apple's Macintosh operating systems.

FINAL COMMENTS

Several aspects of the transformation might be discussed. The integration of computer based experimentation for one or two of the experiments, as compared with the transformation of the vast majority of the experiments at one time, is not recommended. There is an activation energy to learn and to teach a new computer language and the philosophy associated with digital acquisition and control. If the students gain this insight up front, they can focus on the actual experiments being conducted. Use of the computers becomes a tool by which they can function more efficiently in the laboratory. With only a few experiments, the computer and not the chemical engineering principles becomes the experiment.

It would be impossible to gain the same insight into experimentation by conducting "computer experiments" where all of the experiments are conducted against a "simulator" within a computer. I realize that this is a popular approach to teaching "experimental" work. However, this is not only naive, it is grossly unrealistic. If we are preparing our students to work in industry with real processes and materials, they must come to grips with the nature of experimentation. Throughout their education they are exposed to an idealization of real processes. The only place in our students' education where they are exposed to real, albeit simplified, engineering processes is in the laboratory. The real world is not dimensionless and represented by smooth curves. As they see the valves turn and the flow, pressure, temperature, and products change, they learn some of the limits to theory and the necessity of planning the experiments and making the appropriate measurements.

The undergraduate laboratory in chemical engineering can be a course that brings together the curriculum and allows the students to visualize the application of theories in their courses. If these experiments are interfaced with data acquisition and process control computers, and if they learn to use these to conduct the experiments, they can visualize the applications and learn to probe the more realistic aspects of real processes.

ACKNOWLEDGEMENTS

This whole process could not have been ac-
Continued on page 116.

TEMPERATURE EFFECTS IN HETEROGENEOUS CATALYSIS

CHARLES D. SCHAPER and C. O. BENNETT
*University of Connecticut
 Storrs, CT 06268*

IN THE STUDY of mass and heat transfer effects for a first-order irreversible gas-phase reaction occurring over a bed of catalyst pellets, it is interesting to analyze the effect of temperature on the observed rate of reaction. To a first approximation, it would seem that a graph of effectiveness factor, $\bar{\eta}$, versus Thiele modulus, m_0 , could be used to easily calculate the reaction rate, \bar{R} , as a function of temperature from the basic relation

$$\bar{R} = k_{vo} \bar{\eta} \quad (1)$$

where k_{vo} is the rate constant at the gas-phase temperature T_o . However, such charts (refer to [1], for example) are usually based on constant values of the Arrhenius parameter, $\bar{\gamma}$, the intraparticle thermal parameter, $\bar{\beta}$, and the Biot number for mass transfer, Bi_m . In reality, these three parameters vary appreciably with temperature for a given reaction system, so that the behavior of the system cannot be determined by following $\bar{\eta}$ versus m_0 on a single chart. Consequently, in order to analyze the effect of temperature, one must return to the model that was used to generate the charts, developed by Carberry and Kulkarni [2], and solve the model without holding $\bar{\gamma}$, $\bar{\beta}$ and Bi_m constant.

In this paper, we present an *analytic* solution of the heterogeneous reaction model for the effect of temperature on the system described earlier. Our analytic formulation utilizes a "reference state," or system characteristics at a single temperature, to explicitly determine the behavior of the system at any temperature.

The contribution which we want to make will be more accessible if the derivation of the basic equations of the heterogeneous reaction model is reviewed. We have incorporated the isothermal pellet assumption [2] into our model, realizing that a specific design problem may deserve a more rigorous approach and that our results do not apply to complex kinetics which may show autocatalytic behavior. Although it is the be-

havior of the system parameters with the bulk gas temperature T_o that is desired, we find that it is convenient to use the surface (*i.e.*, pellet) temperature T_s as the independent variable in our model. For any T_s we calculate the appropriate T_o , but in regions of multiplicity a value of T_o corresponds to three values of T_s at steady state, two of which are stable.

MASS TRANSFER EFFECTS

At steady state the rate of reaction in the pellet, \bar{r} , equals the rate of interphase mass transfer of reactant A towards the surface,

$$\bar{r} = k_c a (C_{Ao} - C_{As}) \quad (2)$$

where k_c is the mass transfer coefficient, a is the outside area of the pellet per unit volume, and C_{As} is the concentration of reactant A in the gas at the pellet surface.

Intraphase diffusion occurs with chemical reaction within the pellet and produces a concentration gradient, described in slab geometry by

$$\frac{C_A(z)}{C_{As}} = \frac{\cosh\left(z\sqrt{\frac{k_{vs}}{D_e}}\right)}{\cosh\left(L\sqrt{\frac{k_{vs}}{D_e}}\right)} \quad (3)$$

Charles Schaper received his BS in 1985 and his MS in 1986, both from the University of Connecticut. He is currently a PhD candidate in chemical engineering at the University of California, Santa Barbara. He plans to begin postdoctoral research in the Department of Electrical Engineering at Stanford University this summer. His current interests include robust control and probability theory with applications to IC manufacturing.



C. O. Bennett, presently professor emeritus at the University of Connecticut, received his PhD in chemical engineering from Yale University in 1950. He was on the faculty at Purdue University until 1959 when he left academia and went to work for the Lummus Company. He returned to teaching in 1964, joining the faculty at the University of Connecticut. His principle research interest is in heterogeneous catalysis.



where z is the distance from the center of the slab, L is the half thickness of the slab, k_{vs} is the rate constant at the pellet temperature T_s , and D_e is the effective Knudsen diffusivity. The Thiele modulus at T_s is

$$m_s = L \sqrt{\frac{k_{vs}}{D_e}} \quad (4)$$

The effectiveness factor associated with the pellet at T_s is

$$\eta_s = \frac{\bar{r}}{k_{vs} C_{As}} = \frac{D_e \frac{dC_A}{dz}(L)}{k_{vs} C_{As}} \quad (5)$$

so that one can obtain

$$\eta_s = \frac{\tanh m_s}{m_s} \quad (6)$$

For sufficiently high temperature, the rate increases so that the interphase temperature and concentration differences are important. Thus we need to consider the inter-intraphase (overall) effectiveness factor, $\bar{\eta}$, defined through Eq. (1). The rate \bar{R} , or the apparent rate constant \bar{k} , can be expressed in several ways, as follows; through Eqs. (1), (2), (5) and

$$\bar{R} = \frac{\bar{r}}{C_{Ao}} = \bar{\eta} \mathbf{Da} k_c a \quad (7)$$

The Damköhler number \mathbf{Da} is $k_{vo}/k_c a$, and it is convenient to consider together the product $\bar{\eta} \mathbf{Da}$. From Eq. (7) is clear that $\bar{\eta} \mathbf{Da}$ is an observable, as defined by Carberry [1]. This group measures the importance of the interphase concentration difference, as shown by combining Eqs. (2) and (7)

$$\bar{\eta} \mathbf{Da} = 1 - \frac{C_{As}}{C_{Ao}} \quad (0 \leq \bar{\eta} \mathbf{Da} \leq 1) \quad (8)$$

It is also useful to express $\bar{\eta} \mathbf{Da}$ in terms of m_s , at conditions in the pellet. By combining Eqs. (5), (6), and (7), we obtain

$$\bar{\eta} \mathbf{Da} = \frac{\tanh m_s}{m_s} \cdot \frac{k_{vs}}{k_c a} \cdot \frac{C_{As}}{C_{Ao}} \quad (9)$$

When C_{As}/C_{Ao} is replaced according to Eq. (8), the result is

$$\bar{\eta} \mathbf{Da} = \frac{m_s \tanh m_s}{m_s \tanh m_s + \frac{m_s^2 k_c a}{k_{vs}}} \quad (10)$$

Now $\mathbf{Bi}_m = d_p k_c / D_e$ and is used with Eq. (4), along with the relation for spherical pellets of diameter d_p , $L = 1/a = d_p/6$ following a common approximation [3], to replace the second term in the denominator of Eq. (10). The result is an equation for $\bar{\eta} \mathbf{Da}$ in terms of m_s and \mathbf{Bi}_m ,

$$\bar{\eta} \mathbf{Da} = \frac{m_s \tanh m_s}{m_s \tanh m_s + \frac{\mathbf{Bi}_m}{6}} \quad (11)$$

In this paper, we present an analytic solution of the heterogeneous reaction model for the effect of temperature on the system described earlier. Our analytic formulation utilizes a "reference state," or system characteristics at a single temperature . . .

Although this equation permits the calculation of $\bar{\eta} \mathbf{Da}$ for a given T_s , we still need to find the corresponding T_o and k_{vo} in order to calculate $\bar{\eta}$.

HEAT TRANSFER EFFECTS

The interphase temperature difference is determined by equating the rates of heat generation and removal for the pellet.

$$\bar{r}(-\Delta H) = ha(T_o - T_s) \quad (12)$$

where $(-\Delta H)$ is the reaction enthalpy difference and h is the heat transfer coefficient. Substituting Eq. (7) into Eq. (12) gives

$$\bar{\eta} \mathbf{Da} (-\Delta H) k_c C_{Ao} = h(T_o - T_s) \quad (13)$$

This equation can be rearranged to

$$\frac{T_s}{T_o} = 1 + \frac{k_c (-\Delta H) C_{Ao}}{h T_o} \bar{\eta} \mathbf{Da} \quad (14)$$

According to the Chilton-Colburn analogy [4], $j_M = j_H$, so that we can derive

$$\frac{h}{k_c} = (\mathbf{Le})^{2/3} \rho C_p \quad (15)$$

where $\mathbf{Le} = \mathbf{Sc}/\mathbf{Pr}$ and write the temperature-effect equation as

$$T_s - T_o = \bar{\beta} \bar{\eta} \mathbf{Da} T_o \quad (16)$$

where

$$\bar{\beta} = \frac{(-\Delta H) C_{Ao}}{(\mathbf{Le})^{2/3} \rho C_p T_o} \quad (17)$$

REFERENCE STATE

In order to follow the effect of temperature easily, a reference temperature T_r is defined at which the rate constant k_{vr} is known. Usually T_r would be a suitable low temperature. In the example we shall give, T_r is 600 K. The appropriate k_{vs} can then be calculated by

$$k_{vs} = k_{vr} \exp \left[-\gamma_r \left(\frac{T_r}{T_s} - 1 \right) \right] \quad (18)$$

where the Arrhenius parameter $\gamma_r = E/RT_r$ is a constant.

Clearly Eq. (18) can be used to calculate k_{vo} at T_o . We also need D_e at T_s . We assume Knudsen diffusion, so that

$$D_e = D_{er} \left(\frac{T_s}{T_r} \right)^{\frac{1}{2}} \quad (19)$$

Now m_s can be computed at the chosen T_s . In Eq. (11), which we need to calculate $\bar{\eta}Da$, the parameter Bi_m must be found. We write

$$Bi_m = Sh \frac{D_{AB}}{D_e} = j_M Re Sc^{\frac{1}{3}} \frac{D_{AB}}{D_e} \quad (20)$$

where $Re = d_p G / \mu$, G is the gas mass velocity, μ is the viscosity of gas, and D_{AB} is the diffusivity of gas A thru B. Among many possibilities, we choose the following correlation for j_M in a packed bed [4]:

$$j_M = 2.25 Re^{-\frac{1}{2}} \quad (21)$$

so that

$$Bi_m = 2.25 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \frac{D_{AB}}{D_e} \quad (22)$$

As a first approximation we evaluate Bi_m at T_s ; after T_o is estimated, the solution could be iterated with an average of T_o and T_s used for the estimation of μ and D_{AB} . Sc is little affected by temperature. If D_{AB} is proportional to $T_s^{3/2}$, and μ to $T_s^{1/2}$, then there results

$$Bi_m = Bi_{mr} \left(\frac{T_s}{T_r} \right)^{\frac{3}{4}} \quad (23)$$

For a chosen T_s we now calculate Bi_m from Eq. (23), m_s from Eq. (4) with Eqs. (18) and (19), and then use Eq. (11) to find $\bar{\eta}Da$. Before using Eq. (16) to find T_o , it is convenient to define

$$\bar{\beta}_r = \frac{(-\Delta H) C_{A0}}{(Le)^{\frac{2}{3}} \rho C_p T_r} \quad (24)$$

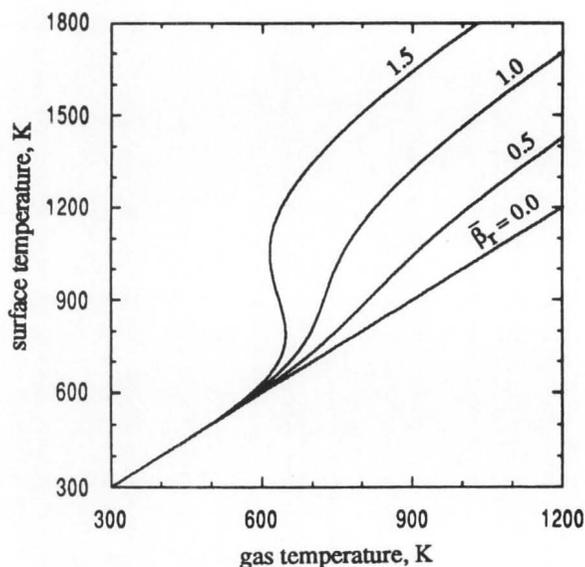


FIGURE 1: Surface temperature as a function of gas temperature for the example pellet-reaction system.

so that

$$T_s - T_o = \bar{\beta}_r \bar{\eta} Da T_r \quad (25)$$

For a given mole fraction X_{A0} , $\bar{\beta}_r$ defined by Eq. (24) is approximately constant; C_{A0}/ρ is constant, and usually the effects of temperature on $(-\Delta H)/C_p$ and Le are small.

For a chosen T_s , we now know $\bar{\eta}Da$ and T_o . Equation (24) can be used to find k_{v0} at T_o , and m_o is defined by Eq. (3) with k_{v0} replacing k_{vs} . It is interesting to

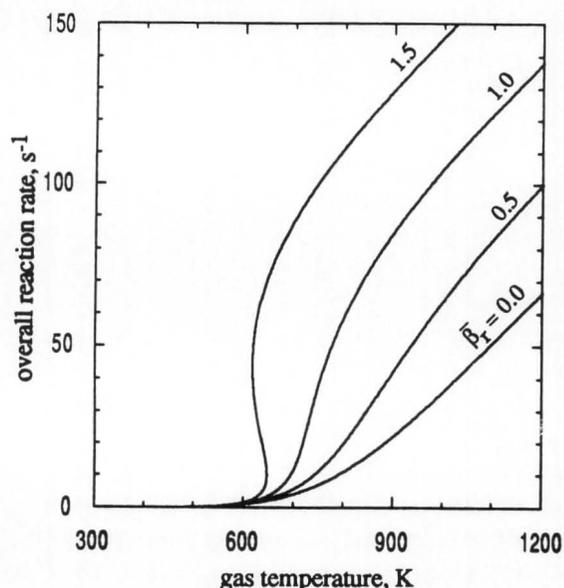


FIGURE 2: Overall reaction rate as a function of gas temperature for the example.

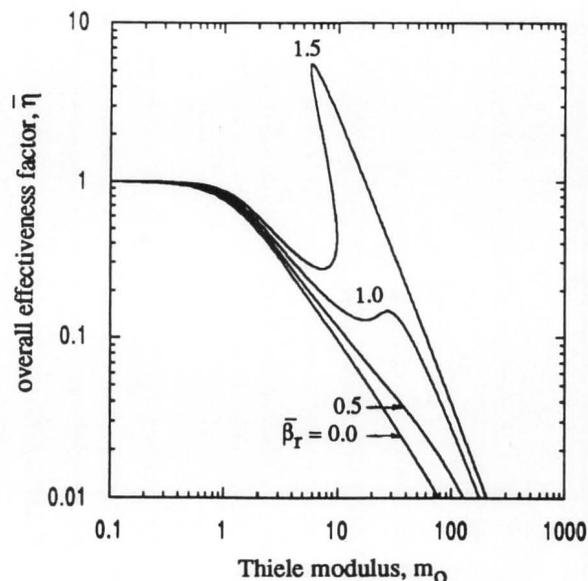


FIGURE 3: Variation of the overall effectiveness factor with the Thiele modulus m_o , for the example.

calculate the rate R , and Eq. (12) gives this quantity once we evaluate $k_c a$. The \mathbf{Bi}_m can be written as

$$k_c a = \frac{\mathbf{Bi}_m D_e}{d_p} \cdot \frac{6}{d_p} \quad (26)$$

Then Eqs. (19) and (23) are used so that

$$k_c a = \frac{6 \mathbf{Bi}_m D_{er}}{d_p^2} \cdot \left(\frac{T_s}{T_r} \right)^{\frac{5}{4}} \quad (27)$$

This completes the calculation procedure; for a chosen T_s , we can now calculate $\bar{\eta} \mathbf{Da}$, T_o , m_o , \bar{R} and then $\bar{\eta}$ by Eq. (1).

EXAMPLE

Let us consider the behavior of spherical pellets of 6 mm diameter. Experiments using a powder of 0.3 mm diameter, made by crushing the pellets, give a value for $\bar{k} = \bar{R}$ of 5 s^{-1} at 1 bar and 600 K. For these conditions $\bar{\eta}$ is unity, and $k_v = k_{vs} = k_{vo}$, since $T_s = T_o$. This reaction is first-order and irreversible. Considering T_r to be 600 K, we establish for the 6 mm pellets the values $\gamma_r = 20$, $D_{er} = 2.0 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, and $\mathbf{Bi}_{mr} = 1300$, corresponding to $\mathbf{Re} = 50$, $\mathbf{Sc} = 0.6$ and $D_{ABr} = 0.2 \text{ cm}^2 \text{ s}^{-1}$. Now we can follow the procedure described in the previous section to find the values of interest for this example. A simple computer program with graphics gives the curves discussed below.

Figure 1 shows the surface temperature corresponding to various bulk (gas) temperatures T_o . As T_o is increased, for a large enough $\bar{\beta}_r$, hysteresis loops with multiple steady states are found. Recall that in

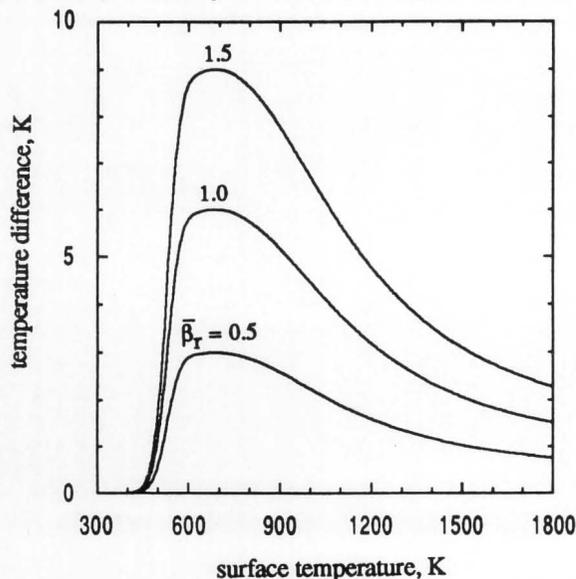


FIGURE 4: Estimation of the difference between the temperatures at the center and at the surface of the example pellet, as a function of surface temperature.

the actual calculations, T_o is found from T_s . The variation of $\bar{\beta}_r$ can be thought of as arising from changes in C_{Ao} . If $(-\Delta H)$ were varied, this would imply a different reaction with a different γ_r and other parameters. Figure 2 demonstrates how the overall reaction rate (or \bar{k}) varies with T_o for the given example.

Curves can also be presented in terms of the usual dimensionless parameters, $\bar{\eta} \mathbf{Da}$ or m_o ; the variation of $\bar{\eta}$ with m_o is presented in Figure 3. These diagrams have the same general appearance as those of Carberry's text, for example [1]. However, they apply to the chosen particle and reacting system with the parameters already enumerated. Because of the dependence on temperature of k_{vo} , \mathbf{Bi}_m , and D_e which are built into the model, somewhat different results for $\bar{\eta}$ would be obtained for a different set of parameters which might lead to the same values of m_o .

It is worth noting that the assumption of a constant pellet temperature is equivalent to choosing a Carberry number [5] of infinity, where

$$\mathbf{Ca} = \frac{\bar{\beta}_r}{\beta_r} = \frac{\mathbf{Bi}_{mr}}{\mathbf{Bi}_{hr}} \quad (28)$$

As the thermal conductivity λ_p of the pellet goes to infinity, $\bar{\beta}_r$ and \mathbf{Bi}_{hr} go to zero and \mathbf{Ca} is infinite, corresponding to an isothermal pellet. If we retain the results already calculated with $\mathbf{Ca} = \infty$, we can set $\mathbf{Ca} = 100$, a reasonable value [1], and estimate the temperature rise inside the pellet. The result for our example is shown in Figure 4. The ΔT 's found are low enough so that the isothermal pellet model seems justified.

In the design of a fixed-bed catalytic reactor, the mass and energy balances written in terms of T_o and C_{Ao} are integrated along the bed. The present simple model for heterogeneous effects can easily be incorporated into an algorithm for the simulation of such a reactor. Thus a realistic result can be obtained by simple methods.

ACKNOWLEDGEMENT

The authors wish to thank Professor Robert Rinker for a helpful discussion of the paper.

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STUDENT-DESIGNED LAB

Continued from page 79.

block under water, calculate h for the top and sides, and subtract to find h for the bottom. (Hopeless!)

• Did they measure the thickness at more than one point, and did they plot all their points? Or did they just average all their readings?

• Did they state that they tried to make their measurements with as little disturbance as possible (agitation will greatly increase h)? Did they discuss this and verify this with calculations?

• Did they choose a large enough reservoir of water so that the water temperature did not change significantly during the experiment?

• Did they choose to weigh the ice? (Not such a good method because the edges of the slab melt faster than the center.)

• In the weighing approach, if that was used, did they remove the slab for weighing? (Poor, because the extra agitation increases h drastically.) Or did they figure out how to weigh the slab in place? (Better.)

Variations and Extensions

Many variations and extensions of this simple experiment can be used by the teacher throughout the years. For example:

- Find h for vertical surfaces in water at different water temperatures.
- Find h for horizontal upfacing surfaces in water. (This is more difficult experimentally and is not recommended.)
- Repeat all the above for ice in air.
- Find the effect of fluid motion relative to the ice surface. For air, all one needs is a regular household fan and a pitot tube to study this.

For the teacher, there is the inescapable temptation to ask the student to study a number of these factors, all in one experiment: upfacing, downfacing, vertical, effect of velocity and of ΔT , etc. Try to resist this as the lesson of this experiment can be learned just as well by studying one factor alone.

FINAL COMMENTS

What do students learn from this type of experiment?

- They have to use their ingenuity and come up with their own way to answer the question.
- The best way of approaching the problem will not come to them right away, but only after they have thought up a number of

schemes. This sort of exercise may give them an appreciation of the value of group discussion.

• They had to develop their own analysis and equations—no copying from books. This should give them a taste for doing original work.

• The laboratory course can be challenging, surprising, and interesting.

We feel that there is a place for this type of laboratory experiment in the undergraduate program.

AWARD LECTURE

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PROCESS CONTROL COMPUTERS

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accomplished without the effort of several dedicated people. Professors R. L. Laurence and B. E. Ydstie helped with the initial proposal. Dr. Graham Sterling, Alan Ryan, Michael Hajjar, and the whole educational support committee from Analog Devices supported and assisted in our development of this laboratory. Their faith and vision were crucial to this project. Paul Grabin and Frank Pulaski were central to the setting up of the laboratory. We also acknowledge our undergraduate classes of 1985 and 1986. With their patience, assistance, and feedback, this major transformation was completed with a minimum of problems and an enhancement of the results.

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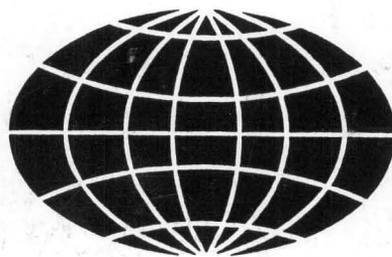
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