

CHE

chemical engineering education

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CHEMICAL ENGINEERING DIVISION OF AMERICAN SOCIETY FOR ENGINEERING EDUCATION

JAMES J. CARBERRY
of Notre Dame



ChE at BERKELEY

1973 Award Lecture

DIFFUSION AND REACTION

A Chemical Engineering Symphony

Rutherford Aris

RHODES:
Waterloo Program for High Schools

ROSEN:
A Junior Course in ChE Computations

WILLIAMS:
Indirect Measurement of Reaction Rate

KRANICH, MA & ZWIEBEL:
The Project Approach to ChE Education

ODEN:
Test to Measure the Ability of Seniors in
the Practical Application of ChE Principles

SHAH:
An Undergraduate Course in Interfacial Phenomena



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James J. Carberry

OF NOTRE DAME

Prepared by the Faculty of the Department of Chemical Engineering

“WE ARE LIKE DWARFS seated on the shoulders of giants; we see more things than the ancients and things more distant, but this is due neither to the sharpness of our own sight, nor to the greatness of our own stature, but because we are raised and borne aloft on that giant mass.” So wrote Bernard of Chartres in the 12th century. Jim Carberry is rather fond of that quotation. How else could he have risen, in the words of his friend Rutherford Aris, “from the low tables of Morris to the high table of Trinity, Cambridge.”*

BROOKLYN BEGINNINGS

A NATIVE OF BROOKLYN, Jim managed to graduate from the famed Brooklyn Technical High School at which site he achieved absolute mediocrity as a single-wing halfback. “Brooklyn Tech” recalls Carberry “was somewhat more than absolutely competitive.” Several classmates invented radar some eleven months prior to Great Britain’s discovery of that toy. Carberry’s qualifications impressed President F. D. Roosevelt, who immediately appointed him an Apprentice Seaman in the U. S. Navy. Japanese intelligence learned of this and thus they assaulted Midway with supreme confidence. As Jim was at that moment interned at Torpedomen’s School at Great Lakes, Illinois, the Japanese lost the Battle of Midway.

Appropriately inspired by the quality of life aboard a U. S. Navy Light Cruiser, Carberry surrendered unconditionally in 1946 and, armed with the G. I. Bill, enrolled as a chemical engineering major at Notre Dame. He notes “there is nothing quite like sea duty amidst grunting ‘deck apes’ to inspire the lowliest of citizens to seek the highest

*Citation in U of Minn. “Semisesquiennial Wet Test Meter Award.” Carberry was first and last recipient of this noble award.



Now we must get on with our task—applied Chemistry.

of goals—outside the Navy.” At Notre Dame, he struggled with chemical engineering, played quarterback in its intramural tackle football program (said John Lujack, “a quarterback should hide the ball, but in Carberry’s case, it hides him”), helped classmate Leon Hart win the Heisman Trophy; while Leon tutored Jim in Physics I through IV. Somewhat less than inspired by the traditional chemical engineering program (“I haven’t been confronted with a plate and frame filter press since I burned my copy of Walker, Lewis, and McAdams at a cocktail party in 1949”), Jim minored in English Literature and, informally, Italian opera. “I was destined, I believed, to be a Literary-Musical critic for the now deceased Brooklyn Eagle—but John Treacy saved literature and music by introducing me to chemical kinetics in my senior year. My medieval mind prompts me to envision my ultimate paper “Nth-Order Adiabatic Reaction in a Plate & Frame Filter Press.”

INDUSTRIAL CONTACTS

JIM JOINED THE EXPLOSIVES Department of the du Pont Company in 1951 as a process engineer, at which post (Eastern Laboratory, Gibbstown) he labored happily under the mentorship of Bill Kirst, Bob Cavanaugh, Win Johnson, and John Vyverberg. Johnson, a former student of B. F. Dodge encouraged Jim to seek a Ph.D. at Yale. At Yale Jim worked under R. H. Bretton on

axial dispersion in fixed beds, talked endlessly with Jon Olson (now at University of Delaware) on topics ranging from Aquinas to Zeus, presented numerous impromptu seminars at Smith and Vassar Colleges, confounded B. F. Dodge by attending Barney's 8 a.m. class clad in p.j.'s, and worshipped R. Harding Bliss. "He, Harding, was a gentleman and a scholar." He feels he learned much from that Yale faculty—a logical consequence of his student days at Notre Dame under Treacy and Wilhelm, (then of the chemical engineering faculty) and Burton and Hamill of Notre Dame's Chemistry Department. "One likes to think that the Professor-Student relationship be mutually respectful yet informal, as it was between Wilhelm, Treacy (of Notre Dame), Dodge, Bliss, Bretton, Walker (of Yale) and me."

Jim returned to the Engineering Department of the du Pont Company as a research engineer at the Engineering Research Laboratory (ERL), a site famed by Chilton, Colburn, Drew, Pigford, Marshall, etc. Tom Chilton directed Carberry into catalysis: du Pont sent Jim to Johns Hopkins to take Paul Emmett's cosmic course "Catalysis" in 1959-60. "Between Paul's course and numerous discussions with Sir Hugh Taylor, I felt as would an altar-boy at the feet of Augustine and Aquinas." The four years at ERL proved most stimulating to Carberry. His mentors Von Wettberg, Rush, and Roberts, he notes "were most tolerant and therefore encouraging." His colleagues at ERL were most stimulating—humble Steve Whitaker, placid Forest Mixon. Marty Wendel shared his office and taught him all manner of things about wit and numerical analysis (namely there is a synergism there somewhere). In moments of scientific-technological terror, a fellow Brooklynite, Sheldon Isakoff, reminded Jim that "the sun never sets on Sheepshead Bay, Brooklyn."

RETURN TO ACADEMIA

TAKING THE CLOTH, as it were, Jim returned to Notre Dame in 1961 as Assistant

Professor of Chemical Engineering. Dr. J. T. Banchemo of Michigan had then assumed the Chairmanship of Chemical Engineering at Notre Dame and immediately set about the task of developing a graduate program in chemical engineering. Notre Dame's president, Father Heshburgh and then Dean of Engineering, Harry Saxe and later Norman Gay encouraged and sustained developments which created the chemical engineering Ph.D. program. "That indeed was a most fruitful period of maturation for our department. Without the energetic support of Father Heshburgh, Deans Saxe and Gay, Banky, Jim Kohn, and that wise man, Ernest Thiele, naught would



... he ... helped Leon Hart win the Heisman trophy.

have been reaped. We were, of course, not eligible for the first Carter Report rating since we had not granted a chemical engineering Ph.D. prior to '59. Yet in the second, our first, evaluation, we were judged as "Good"—a judgment both encouraging and challenging. I attribute this to the wise vitality of our administration, faculty, staff and students."

"Since those formative years, we've retained excellent people in Luks (Minn.) and Verhoff and Smith (Mich.). One can only hope that the present Engineering College administration will be cognizant of whose shoulders sustain us now."

"I was destined to be a literary- musical critic for the now deceased Brooklyn Eagle—but John Treacy saved literature and music by introducing me to chemical kinetics in my senior year. My medieval mind prompts me to envision my ultimate paper " 'Nth-Order Adiabatic Reaction in a Plate and Frame Filter Press'."

In his twelve years at Notre Dame, Jim has directed research in Chemical Reaction Engineering and Heterogeneous Catalysis. The now-universally employed "swirling basket catalytic reactor" or "Carberry Reactor," which Jim prefers to term the "Notre Dame CSTCR" was conceived and developed in 1964. The key experimental work was carried out by then Ph.D. candidate Dan Tajbl (now at Mobil Oil) who came to Notre Dame from Northwestern "a year before Ara made a move equally beneficial to Notre Dame" as Jim puts it.

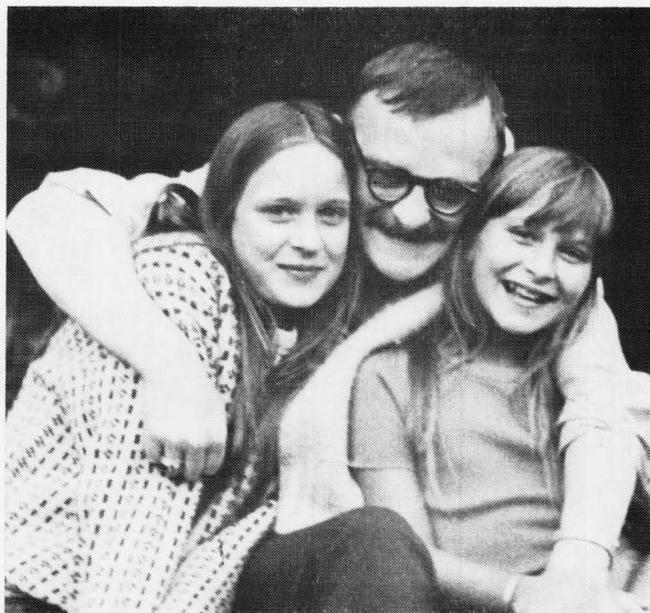
ACCLAIM AND ALLEGIANCE

IN 1965-66, CARBERRY was awarded an NSF Senior Postdoctoral Fellowship at Cambridge University, England where he thrived upon dialogues with Danckwerts, Pearson, Davidson, Turner, Bridgwater, et al. Between "teas" he managed to lecture at various posts between Warsaw and Haifa. Thus it was that he, the devotee of Verdi and Puccini, found Italy. "It is asserted that I am of Anglo-Irish derivation. So be it with respect to my blood chemistry, but I do declare that my heart is Italian," declares Giacomo Carberri. This Spring (1974) Commendatori Carberri will again be in Italy as a Senior Fulbright Scholar at the University of Rome.

In 1968, Jim received the Yale Engineering Association Award for Advancement of Basic and Applied Sciences, and he fondly hopes that in 1974 he will once again be recipient of the Interhall Football Coach Trophy at Notre Dame. For the "ole" Brooklyn Tech scrub halfback has been coaching intramural eleven man contact ("collision") football on the Notre Dame campus for over a decade. Says he, "oh, for the pre-Ara days when I could boast as being the only winning football coach on campus. But, alas, no threat to Ara am I."

Off-season, Carberry preoccupies himself with research in surface catalysis in association with his solid-state physicist colleague George Kuczyn-

"It is asserted that I am of Anglo-Irish derivation. So be it with respect to blood chemistry. But I do declare that my heart is Italian."



Carberry and his daughters.

ski and teaching both graduate and ("most importantly") undergraduate Reaction Engineering. He is now co-editor of *Catalysis Reviews* and a member of the U.S.-Soviet Working Group on Catalysis.

He harbors rather firm views regarding the future of Chemical Engineering and society in general. A Stevensonian Democrat, in typical eclectic fashion, Carberry is a devoted admirer of William F. Buckley, Jr. and his *National Review*. Given his studied dedication to Aquinas, Dante, and Maritain, the seeming paradox may be illusionary. He believes in civilized society, which signifies civilized discourse amongst civilized men, phrased in civilized form and spirit. "I am the enemy of the 'you know' generation, who are poised before bronze calves, mesmerized by a cacophony, miscoined by morons and idiotic soothsayers as meaningful, relevant, and true because it feels right."

Explaining how he views chemical engineering, Carberry relates "Olaf Hougen put it all in perspective—our roots reside in chemistry—at a particular stage the Hougen's, McAdam's, etc. put order into transport processes. Now we must get on with our true task—applied chemistry. This may well mean divorce with respect to general engineering. Che sara', sara'. Remember those shoulders which sustain us all." □



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BERKELEY

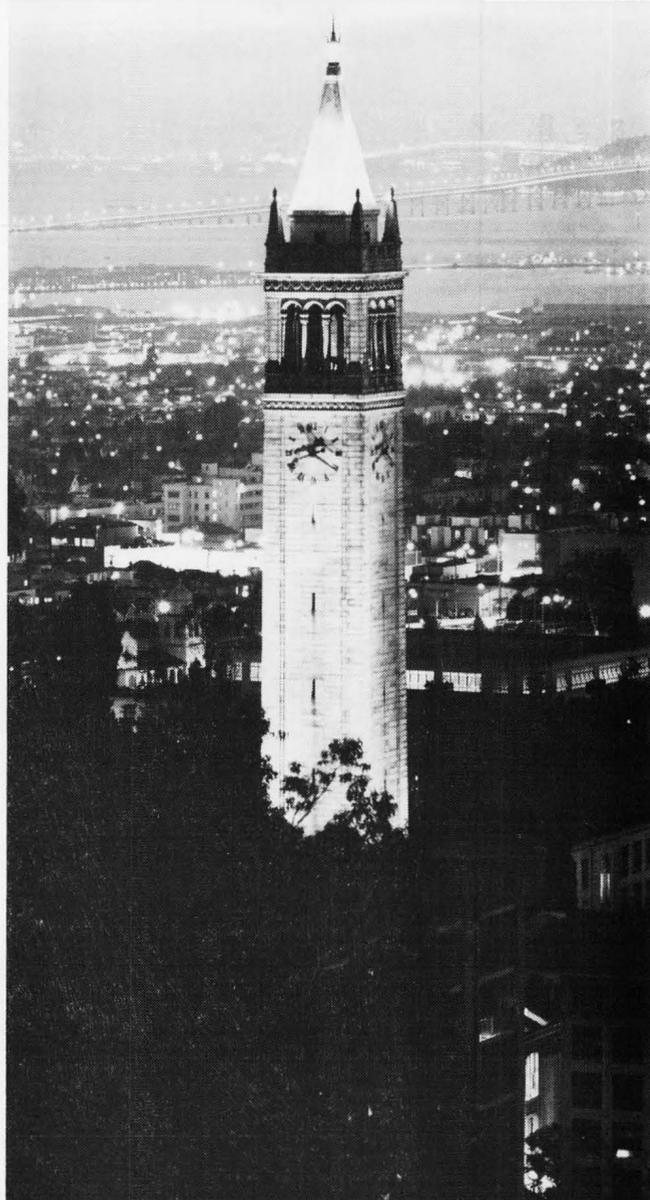
C. JUDSON KING, THEODORE VERMEULEN
and JOHN M. PRAUSNITZ
*University of California
Berkeley, California*

THE CHEMICAL ENGINEERING Department at the University of California's charter campus celebrated its 25th anniversary in 1971-72. Starting strong but small just after World War II, with both the M.S. and the Ph.D. programs preceding establishment of the B.S. degree, the department has grown to be one of the largest units among U.S. universities. Today there is a faculty of 20 full-time professors, a graduate student body numbering about 130, and 30 to 40 seniors graduating annually. The number of Ph.D.'s graduating in 1971-72 was 22, and in the same year there were 20 M.S. graduates.

Several distinctive features characterize Berkeley chemical engineering—beyond its relatively recent genesis and its physical location in the Athens of the West. One characteristic is its close affiliation with chemistry; in fact, the Departments of Chemical Engineering and Chemistry make up the College of Chemistry at Berkeley, one of very few such college structures. As another feature, Berkeley's department devotes a larger fraction of its effort to the graduate program than is possible in most schools. The M.S. shares center-stage with the Ph.D., and both degrees require a thesis. To a great extent graduate education is built around individual tutorial instruction, carried on for the most part through joint student-faculty research and design. The spectrum of topics of interest and investigation represented in the department is extremely wide, ranging from applied to fundamental. Chemical process design and engineering are emphasized equally with basic engineering science.

DEPARTMENTAL HISTORY

At Berkeley, chemical engineering by that name began in the 1940's but had been anticipated



Berkeley's Campanile dominates the campus skyline and overlooks San Francisco Bay—an Ivory Tower but not an academic refuge.

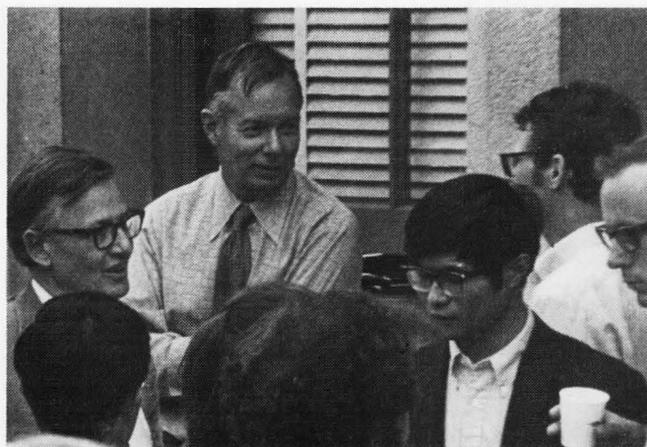
from the time the University was founded in 1868. Frederick Cottrell, Cal's first true chemical engineer, invented electrostatic precipitation here around 1906. In 1912, Gilbert N. Lewis, as incoming Dean of the College of Chemistry, instituted a chemical technology major, subsequently directed by Merle Randall. As of 1942 an interdepartmental Graduate Group offered the M.S. degree in chemical engineering. September 1946 marked the start of formal undergraduate instruction, offered in the College of Chemistry with complementary work in the College of Engineering. Philip Schutz, the program's first unofficial chairman, LeRoy Bromley and Charles Wilke formed the charter group. Succumbing soon to a tragic illness, Schutz was replaced by Theodore Vermeulen. This group was then joined by Donald Hanson and Charles Tobias in 1947, completing

the initial staff. The new program rapidly gained recognition, achieving formal approval of the Ph.D. program (1947) and B.S. program (1948), changing the departmental name to Chemistry and Chemical Engineering (1949), creating the sub-departmental Division (1952), creating a separate Department (1957), renovating and fully occupying Gilman Hall (1963), and subsequently expanding into a major portion of Lewis Hall (1965).

FACULTY GROWTH

WILKE SUCCEEDED Vermeulen as Chairman in 1953, and led a rapid expansion in numbers of graduate students and faculty, to serve the fast-growing needs of the State of California. Eugene Petersen (1953) and John Prausnitz (1955) were the next of the present professorial staff to arrive, and were followed by David Lyon who had been with the Low Temperature Laboratory of the College, Alan Foss (1961), Simon Goren (1962), Edward Grens (1963), Judson King (1963), John Newman (1963), Robert Merrill (1964), Michael Williams (1965), Robert Pigford (1966), Scott Lynn (1967), Alexis Bell (1967), Mitchel Shen (1969), and Lee Donaghey (1970). Thomas Sherwood, after two previous visiting appointments here, transferred permanently from M.I.T. in 1970. In 1963, Hanson succeeded Wilke as Chairman, followed by Tobias (1967-72) and King (1972-present).

Activities of the department are extended and supported by a number of other professionally active engineers, including Lecturers E. Morse Blue, Gerhard Klein, Arthur Morgan, Rolf Muller, Charles Oldershaw, and Otto Redlich. David Templeton, dean of the College of Chemistry, and Douglas Fuerstenau, Chairman of Materials Science and Engineering in the College of Engineering, participate often. Enrichment of the department's work also comes from strong ties with the Lawrence Berkeley Laboratory and the Sea Water Conversion Laboratory.



Students and faculty meet at the coffee hour preceding the department's weekly Colloquium.

Visiting professors have included Shinichi Aiba (Tokyo), Chandler Barkeley (Shell), Thomas Baron (Shell), Andre Bellemans (University of Brussels), Thomas Chilton (DuPont), Lewis Etherington (Esso), Ulrich Franck (Karlsruhe), Robert Finn (Cornell), Robert Greenkorn (Purdue), Norbert Ibl (ETH Zurich), Lewis Iscol (Chevron), Robert Johnk (San Jose State), Adriaan Klinkenberg (Royal Dutch), Herman Mark (Brooklyn Poly), John Ornea (Shell), Giuseppe Parravano (Michigan), Henrick Van Ness (Rensselaer), and Fumitake Yoshida (Kyoto).

The work of the department has been supported generously by the State of California, Federal agencies and several research foundations. Present industrial donors include the DuPont Company, General Electric Company, Shell Oil, Standard Oil of California, Exxon Companies, Union Carbide Corporation, Stauffer Chemical Corporation, Dow Chemical USA, Gulf Oil, Mobil Oil, and Union Oil.

Many members of the faculty have received awards from AIChE, ACS, ASEE or the Electrochemical Society. In addition, three are members of the National Academy of Sciences and two are members of the National Academy of Engineering.

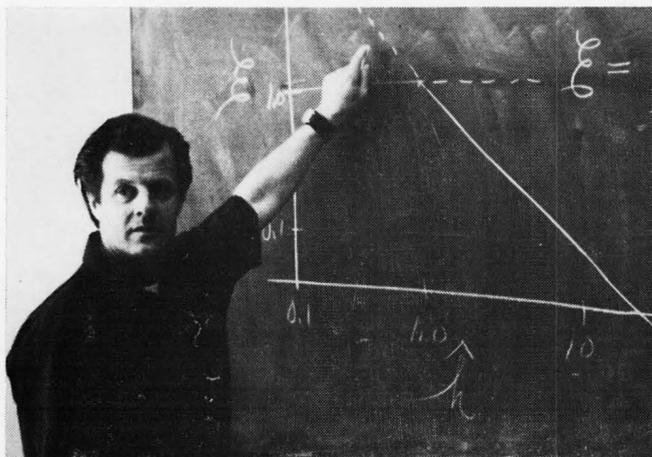
BERKELEY PHILOSOPHY

A STRONG TENET of the Berkeley faculty is that education in chemical engineering en-

Several distinctive features characterize Berkeley chemical engineering—its close affiliation with chemistry . . . it devotes a large fraction of its effort to the graduate program . . . and it puts the M.S. and the Ph.D. on center stage requiring theses for both degrees.

ables a graduate to undertake any of an extremely wide and steadily expanding range of endeavors. This is reflected in the broad scope of research and technical interests represented in the department, by the wide variety of courses and seminars, and by the diverse occupations filled by past graduates of the department: process engineers, electrochemical engineers, systems engineers, food engineers, biochemical engineers, extractive metallurgists, pharmaceutical-device engineers, environmental engineers, nuclear engineers, experts in pure sciences, and managers of technical enterprises. The program at Berkeley is designed to give the student extensive competence and understanding, with abilities to develop further knowledge and insight with minimal difficulty in whatever specialized area he may enter. In 1970, option areas were made available in the undergraduate program, offering supplementary study in chemistry, applied physics, systems analysis and applied mathematics, materials and molecular engineering, space systems, earth-ocean-atmospheric sciences, environmental balance, applied biology, food resources and processing, business enterprise, or science education.

Research and project engineering are the primary vehicles for tutorial instruction, which aims at developing the student's self-reliance, initiative, and technical maturity. The underlying principle is that a student learns best the things he does himself rather than those he hears second-hand. "Research" is interpreted in a broad sense. In recent years many theses have dealt with process synthesis, development, and design. The common thread of exploration in all these areas, as well as for research on more fundamental problems, is



Mysteries of catalysis are the focal point for research by professor Eugene Petersen and graduate student Daniel Kahn.

"Research" is interpreted in a broad sense . . .

In recent years many theses have dealt with process synthesis, development and design.

that the student undertakes a truly original problem—something clearly new, for which the answer has not already been determined. The department's attention to chemical process engineering as well as to fundamentals is reflected in several problem-oriented graduate courses, and in its focus upon chemical process engineering (together with transport phenomena and physico-chemical principles) in the comprehensive preliminary examination for Ph.D. candidates.

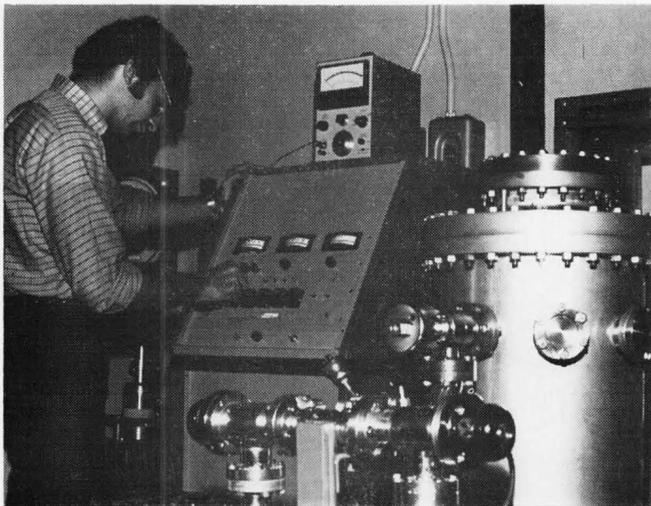
Emphasis upon developing the student's ability to work on his own is also reflected in the definitive Ph.D. oral qualifying examination. Here the student presents and defends a self-generated "proposition" for a significant research advance or process improvement. The proposition cannot be related to his thesis research; it is conceived on his own without faculty help, although advance criticisms may be made by his qualifying committee chairman. This examination provides a profoundly maturing experience, and when completed gives the student greatly increased self-confidence and independence of mind for further engineering studies which culminate his doctoral thesis.

The Berkeley Ph.D. program has proved to be a major supply of teachers for other universities. A recent count shows that 39 U.S. professors have received a Ph.D. in chemical engineering from Berkeley, most of them within the last 10 years. These include:

Richard Alkire (Illinois), Byron Anshus (Delaware), Douglas Bennion (UCLA), John Berg (Washington), Robert Blanks (Michigan State), David Bonner (Texas Tech), Ray Bowen (Wisconsin), Robert Chambers (Tulane), Thomas Chapman (Wisconsin), Winston Cheh (Columbia), Peter Clark (Virginia Poly), Milton Davis (South Carolina), John Duffin (Naval Postgraduate School), Charles Eckert (Illinois), John Friedly (Rochester), Joe Goddard (Michigan), Earl Gose (UI Chicago Circle), Robert Gunn (Wyoming), James Han (Michigan), Gordon Harris (Tulane), Thomas Hicks (UCLA), Jacob Jorne (Wayne State), William Krantz (Colorado), Robert Madix (Stanford), Thomas Massaro (Wisconsin), Robert Meredith (Oregon State), Reid Miller (Wyoming), Alan Myers (Pennsylvania), John O'Connell (Florida), John Powers (Michigan), Clayton Radke (Penn State), Peter Rony (Virginia Poly), Orville Sandall (UC, Santa Barbara), Fred Shair (Caltech), Lloyd Spielman (Harvard), Darsh Wasan (Illinois Institute of Technology), Henry Weinberg (Caltech), Douglass Wilde (Stanford), and William Wilcox (Southern California).

A corresponding list of Ph.D. graduates teaching at foreign universities would number another 15-20. Also a significant number of Cal's B.S. and M.S. graduates are serving on university faculties. These include, among others:

Philip Becker (Penn State), Robert Brodkey (Ohio State), Sunny Chan (Caltech), Bruce Gates (Delaware), K. R. Hall (Virginia), George Homsy (Stanford), Marc LeMaguer (Alberta), Octave Levenspiel (Oregon State), R. L. Merson (UC Davis), Zuhair Munir (UC Davis), Ken Nobe (UCLA), Channing Robertson (Stanford), Robert Sani (Illinois), L. E. Scriven (Minnesota), J. D. Seader (Utah), Oktay Sinanoglu (Yale) and Steven Whitaker (UC Davis).



Graduate student Daniel Kahn deals with the mysteries of catalysis in his research at Berkeley.

The department encourages its own bachelors to take their graduate work at other schools, based upon the principle that students should experience more than one approach to subject matter and to problem-solving techniques.

RESEARCH PROGRAMS

BERKELEY'S RESEARCH activity and capability encompass an ever-evolving range, as twenty full-time faculty and four of the part-timers in chemical engineering continually reassess the needs and opportunities for significant innovative work. The fields of research listed in the accompanying table include few surprises, as they almost all show a substantial relevance to eventual practical applications in physical preparation, separation, or chemical reaction, with respect to systems of multicomponent and/or multiphase character. Of the ten main areas, the first five are fields where Berkeley has an exceptional intensity

of effort, compared with the general average, and the second five can be considered as nearly universal.

What "master concepts" underlie this research activity? The goal already cited—intellectual growth by the student into the status of a fully independent professional—is implemented by a number of operational principles, proven by time and applied with flexibility.

First, when the interests of different staff members overlap or coincide, collaboration between them often occurs.

Second, the student's growth is measured by ever-increasing control over the research he (or she) conducts. A Ph.D. student in his first year typically does about 20% of the innovation and 80% of the physical and mental work involved in his research project, the faculty supervisor providing the remainder directly or indirectly. In his last year, the student does 80% of the innovation and 95% of the physical and mental work. A student engaged in research will typically spend two to four hours each week with his faculty supervisor. However in the period when the dissertation is being written, reviewed, and revised, many additional hours of intense discussion occur.

Third, graduate students consult widely with faculty members other than their immediate research supervisor, with enough opportunity to learn from all of them. They are expected in due time to become more expert than their mentors.

Fourth, although of course the professors are expected to provide the largest primary input into the communication chain, graduate students are likely to learn even more from one another than they learn directly from the faculty.

Fifth, the program emphasizes breadth as well as depth. Graduate students attend a variety of courses and seminars, including those in neighboring departments, and frequently carry out a second brief research project with a faculty member other than their thesis advisor.

Sixth, the student normally is spurred to complete his master's degree within 12 to 24 months, or his doctorate in 36 to 54 months, on the basis that graduate study is preparation for a career and not a career in itself.

WIDER AFIELD

Although the campus is most often identified by its 310-foot Campanile, Berkeley is no ivory tower but a bustling reflection of the world at large. Its scenic setting overlooking San Francisco

The department's attention to chemical process engineering as well as to fundamentals is reflected in several problem-oriented graduate courses, and in its focus upon chemical process engineering.

Bay provides a multitude of recreational and social opportunities for students and faculty. Besides the proximity of supportive industry and government laboratories, there are all the cultural attractions befitting this major urban center, as well as opportunities for hiking and mountaineering in the Sierra Nevada, sailing in the Bay, other participatory and spectator sports of all kinds, and finally a living laboratory of sociological, political, and philosophical "ferment" for which Berkeley has attracted international attention. □

RESEARCH ACTIVITIES AT BERKELEY

Process Development, Design, and Optimization

Calculation Techniques and General Strategy. Systematic procedures for synthesis, arrangement, and improvement of processes. Computation strategies to define optimum designs. Computer-implemented simulation of large process systems and their individual components. (Foss, Grens, King).

Process Engineering and Conceptual Design. Development and analysis of case problems for instruction. Desalination of sea water by processes involving evaporation, ion exchange, reverse osmosis, freezing and/or foam fractionation. Waste utilization through microbial processes and other techniques. Hydrogenation and extraction of coal and oil shale. Electro-refining of metals. Cryogenic separation, including isotope recovery. (Bromley, Grens, King, Klein, Lynn, Lyon, Sherwood, Tobias, Vermeulen, Wilke).

Pollution Control. Recovery of solvents from vent gases by adsorption. Catalytic treatment of automobile-exhaust components. Removal of SO_x and NO_x from stack gases. Water pollution abatement by solvent extraction, foaming, coalescence, process modification and other approaches. Radioactive waste disposal. (Bell, Bromley, Goren, King, Klein, Lynn, Petersen, Pigford, Prausnitz, Sherwood, Vermeulen).

Biochemical, Food and Biomedical Applications

Techniques for dense culture of bacterial cells, with applications to fermentation processes, vaccine production and solid-waste utilization. Reactions involving immobilized enzymes. Food processing by freeze-drying, freeze-concentration, and other dehydration methods. Polymers for biomedical applications, including synthesis by glow discharge. Fluid dynamics, structure, and susceptibility to damage of blood under flow conditions. (Bell, King, Shen, Wilke, Williams).

Polymeric and Inorganic Materials

Polymer Systems. Measurement and theory of viscoelasticity of solutions, melts, and multiphase polymer systems. Thermodynamics of block copolymers and polymer solutions. Polymerization kinetics. (Merrill, Prausnitz, Shen, Vermeulen, Williams).

Inorganic Solids. Determination of solid-surface lattice structure, composition, and reactivity. Crystal growth.

Of the ten main areas, the first five are fields where Berkeley has an exceptional intensity of effort, compared with the average, and the second five can be considered nearly universal.

Optical, electronic, and elastic properties of solids. Thin-film production and epitaxial growth. (Donaghey, Merrill).

Cryogenic Engineering

P-V-T behavior, separations, and heat exchange in the liquefaction of air, hydrogen, and helium. Adiabatic demagnetization with large-volume magnetic fields. Physical properties of fluids and solids at high pressure and low temperature. Low-temperature mechanical and dielectric relaxation and other physical properties of polymers. (Lyon, Prausnitz, Shen).

Electrochemical Engineering

Development and Design of Electrolytic Cells. Electrode processes—geometry, current distribution, limiting currents, gas evolution. Electro-chemical shaping and finishing of metals. Production of surfaces and fibers by electrolysis. (Lynn, Merrill, Muller, Tobias).

Energy Storage and Conversion. Batteries and fuel cells. Electrolysis in nonaqueous ionizing solvents. (Grens, Tobias).

General. Electrostatic gas-solid and liquid-solid separations. Continuous electrophoresis or electrochromatography in liquids. Electronic and ionic transport in inorganic solids. Corona- and glow-discharge devices for measurement of solid-aerosol areas and size distributions. (Bell, Donaghey, Hanson, Tobias, Vermeulen, Wilke).

Chemical Process Dynamics and Control

Control-systems development for industrial-scale reaction and separation systems. Dynamic models for large scale systems including fixed-bed reactors and distillation systems. Response mode-based synthesis methods for control system configurations. (Foss, Grens).

Kinetics and Catalysis

Heterogeneous Catalysis. Molecular-scale gas-solid behavior over extreme pressure ranges. Chromatographic reactors. Reactor dynamics and particle configuration. Process applications. (Bell, Merrill, Petersen).

Simultaneous Heat Transfer, Mass Transfer, and Chemical Reaction. Combustion. Particle deflagration. Reactor engineering. Kinetics of phase transitions. Photochemical reactor design. Plasma chemistry. Homogeneous catalysis. Kinetics and mass transfer in microbial growth. (Bell, Donaghey, Grens, Merrill, Petersen, Pigford, Sherwood, Vermeulen, Wilke).

(Continued on page 41.)



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THE PROJECT APPROACH TO CHEMICAL ENGINEERING EDUCATION UNDER THE WPI PLAN

W. L. KRANICH, I. ZWIEBEL, and Y. H. MA
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FOR MANY YEARS the faculty and students at Worcester Polytechnic Institute have been aware of the great educational value of independent projects. This awareness has been fostered by National Science Foundation Undergraduate Research Participation grants, senior theses (optional in many departments), use of undergraduates as assistants and participants in supported graduate research projects, and special programs such as the Clean Air Car race.

Projects have, in fact, become the cornerstone of the newly developed educational innovation, the WPI Plan. Unlike the usual experiments in education where one variable is altered at a time, this is a total commitment with changes in just about every aspect of the college. The central theme of the program is that the student is prepared for his professional life by an educational program which emphasizes his independence and develops confidence and self-reliance through a strong element of self-education. There is no formal curriculum and the criteria for graduation are intended to demonstrate the student's competence to enter his or her chosen profession. The basic criteria are given in Table 1.

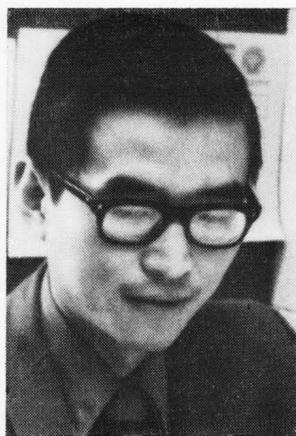
Table 1
GRADUATION REQUIREMENTS
UNDER THE WPI PLAN

1. Satisfactory completion of an independent project in the major field
2. Satisfactory completion of an independent project which relates society and technology
3. Successful performance on an examination which tests the competency of the student to enter his profession
4. Demonstration of sufficient competence in a secondary field

Students entering as freshmen during the first two years of operation were permitted to choose either this program or traditional departmental requirements (curriculum, minimum grade-point average, minimum credits). During the second year more than 95% of the entering freshmen elected the WPI Plan. This encouraged the faculty to eliminate the traditional option one year earlier than planned. As a result, during the current year the entire freshman class entered under the new program.

In addition to the new graduation requirements there are other innovative features of the Plan. During each of four or five seven-week terms the student concentrates on three subject areas (rather than studying five or six subjects for a 14-week semester). In the planning of a student's program the key roles are played by the student himself and by his academic advisor. Departments provide a home base for the faculty, but need not be of central importance to the student. So long as the student can find an advisor willing to work with him in his desired area, and that advisor can assemble a faculty committee willing to examine the student's competence, there are no constraints on the major area of the student. While we expect that for the next several years at least, most students will choose to major in the conventional fields of science and engineering, we expect to find some who will want a major in such areas as biomedical engineering with an

The central theme . . . is that the student is prepared for his professional life by an educational program which emphasizes his independence and develops confidence and self-reliance through . . . self education. There is no formal curriculum.



emphasis on the chemical point of view, or management engineering with concentration on the management of chemical plants. Naturally it will be one function of the advisor to discourage the student from too narrow specialization, but in the end it will be the student's choice.

PROJECT ORIENTED PROGRAM

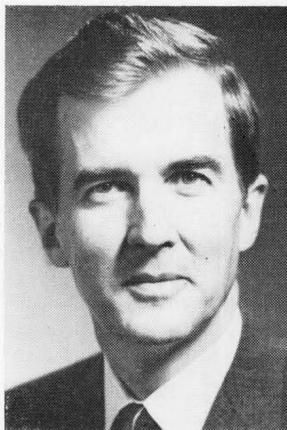
INDEPENDENT PROJECTS are at the heart of the new program. The projects may be carried out in groups or individually, as research or independent study. Up to about 25% of a student's activities at WPI will be taken up by such projects; some will be chosen to meet the degree requirements (i.e., qualifying type), while some will be exploratory or preparatory to the qualifying projects. They may be executed on campus or at an off-campus site, but still under full faculty supervision. Past experience shows that in chemical engineering, far more than half of these projects will be of experimental, research or development type as contrasted to design projects.

While there has been considerable experience at WPI in project work of the on-campus, senior-thesis type, until recently we had little operating know-how on group projects, particularly those concerned with off-campus, real-world problems of government and industry. The chemical engineering department has participated in two major pilot projects of this type—one the Environmental Systems Study Program (ESSP) sponsored by the Sloan Foundation and the Environmental Protection Agency, and the other an off-campus internship center at the U.S. Army Natick Laboratories in Natick, Mass. One of the authors of this paper (I. Zwiebel) was instrumental in developing the former program and another

Y. H. Ma received his bachelor's degree from National Taiwan University, his master's degree from Notre Dame and his doctorate from M.I.T. (in 1967) all in Chemical Engineering. He has taught at WPI since 1967. His research areas include diffusion in porous solids and mathematical simulation. (left)

W. L. Kranich received his B.S. in Chemical Engineering from the University of Pennsylvania and his PhD. (in 1944) from Cornell University. He taught at Princeton University before coming to Worcester Polytechnic Institute in 1948, and has been Head of the Chemical Engineering Department since 1958. His current research interests are in reactions on molecular sieve zeolite catalysts and process development. (left below)

I. Zwiebel did his undergraduate work in Chemical Engineering at the University of Michigan and his graduate study at Yale, where he received his doctorate in 1961. He has had industrial experience with duPont and Esso, and has been on the WPI faculty since 1964. His research efforts are concentrated in the fields of adsorption and applied mathematics. (right below)



author (Y. H. Ma) played the key role in the development of the latter and serves as Internship Center Director.

PROJECT EXAMPLES

IN THE REMAINDER of this paper we present examples of student projects of the research type—associated with on-going sponsored research at WPI—and of the group, off-campus type under the ESSP program and the Natick Internship Center.

Both underclassmen and seniors have successfully joined teams of graduate students and carried out individual projects on a solid waste conversion program sponsored by EPA. The overall effort is concerned with conversion of cellulosic and other organic wastes to useful oil by hydrogenation. One undergraduate studied the effects of some of the process variables. Another developed an analytical technique for characterizing the product. A third, using computer-aided design techniques, developed a flow sheet and preliminary cost data for a projected large scale application.

A NASA-sponsored research program for long-duration space flight is concerned with conversion of human wastes into edible sugars via formose synthesis. One undergraduate looked into the effect of different catalysts. Another studied the fermentation of formose sugars with the objective of protein generation. A third attempted to explain and characterize the observed instabilities of the continuous stirred tank reactor in which the formose synthesis occurred.

The educational value of undergraduate projects cannot always be measured in terms of positive research results. In one instance an undergraduate study of the bonding between adsorbate species and adsorbent sites (associated with an EPA-sponsored air pollution control project) was not very productive. Infra-red absorption spectroscopic techniques with KBr pellets containing varying amounts of the adsorbent were used. The observed results were inconclusive. While the interpretation of I.R. spectra is a very complicated skill, the student in consultation with a faculty member of the chemistry department did a very fine job analyzing his meager spectra. However, the student exhibited a case of stubbornness. In the literature, only a very few instances were gas-solid interactions successfully investigated by KBr absorption techniques—most researchers prefer the reflectance methods. The student refused to

Past experience shows that in chemical engineering far more than half of these projects will be of experimental, research or development type as contrasted to design projects.

try out this technique, stubbornly insisting that a way *shall* be found to use the pellet technique. At the end, in light of the absence of results, he had to concede that research should not be a sledgehammer operation. The student enjoyed his experiments and was satisfied by his experiences; he went on to graduate school to pursue a career in biochemical engineering.

A more successful example of a research project is illustrated by a sophomore, who tried engineering research because he never had exposure to large scale facilities. He was facing a choice between a career in chemistry or chemical engineering. We teamed him up with a Ph.D. candidate who was studying the dynamics of adsorption

in fixed bed columns. This sophomore was to be in charge of the desorption experiments which had to be carried out before the next adsorption could be run. In part emulating the graduate student, the sophomore developed a comprehensive experimental schedule for the desorption runs, devoted many night-time hours to gather the data, analyzed his results, and developed sufficient results to warrant publication. In this case the learning and direction were very positive. He was gradually, through participation, introduced to chemical engineering. He has since graduated at the top of his class and gone on to graduate school in chemical engineering.

PROJECTS CONTRIBUTE TO SOLUTIONS

THE ENVIRONMENTAL SYSTEMS Study Program, sponsored by the Alfred P. Sloan Foundation, was designed to develop team interdisciplinary projects in conjunction with industrial/governmental sponsors. The intent was not to teach the subjects of the other disciplines represented on the team to the chemical engineers, or vice versa; it was hoped that students would learn to communicate with specialists from other areas. It was expected that each person working in his own field could contribute to the combined solution of complex real problems. We have had twelve such projects in the past two years. An example in which the chemical engineering contribution was quite significant was the Salem Harbor Project.

Salem Harbor power generating plant is located in the immediate vicinity of resort towns and is frequently influenced by local meteorological phenomena, i.e., strong but short range winds off the ocean. The growth of the plant has in recent years created an environmental concern. The environmental influences during transient peak-load operation of the plant were to be evaluated.

First the concepts of transient operations had to be brought across to the students. Then, familiarization with the power plant process had to be covered. This brought into focus the stoichiometric calculations.

Initial instinct was to measure SO₂ emissions. However, the student team quickly realized that SO₂ emissions are directly proportional to fuel feed rate, and in no way do they represent unique pollution problems during the transient operations.

While . . . most students will choose to major in the conventional fields of science and engineering, we expect to find some who will want a major in such areas as biomedical engineering with an emphasis on the chemical point of view, or management engineering with concentration on the management of chemical plants.

Next, they zeroed in on NO_x measurements. The various analytical procedures were evaluated; sampling and remote analyses were compared with continuous instrumental techniques. They selected instruments, chose sampling locations, and ran preliminary measurements under steady state operating conditions. Then the variation of NO_x concentration with operating load was observed.

A plot of air-to-fuel ratio versus time revealed that during the transient phase the plant operates in a fuel-rich regime. This prompted a switch to the measurement of CO, unburned hydrocarbons, and particulates.

The final in-depth design will focus upon improved precipitator operating conditions, the installation of some sort of scrubbing device to remove the NO_x which is in excess of emission standards, the establishment of an operating policy which will maintain reasonably uniform conditions in the combustion chamber, and the replacement of existing (old) control devices with equipment that will quickly respond to the primary variables.

The systems design will consider the power generation facilities of the entire plant, consisting of four units, and the entire New England Power System, and will attempt to establish a control policy so as not to burden the vicinity of the Salem area. Also the development of a regional simulation program, starting with one of EPA's air quality display models, is planned.

In industrially sponsored projects the lack of effective communications between the involved personnel may create some problems. Occasionally, the liaison-advisors assigned to work with the students are not involved in the project development stages. Then, if the educational objectives are not clearly specified, some of these supervisors may view the presence of the students with suspicion. In one instance when this happened, one meeting with the involved principals on an

ESSP project was sufficient to re-establish a favorable environment to continue the project. In another instance, however, on a project dealing with a sensitive water pollution problem, comments were made to the students by an uninformed engineer insinuating that the students were planted for espionage purposes. Rather than wasting the students' time while potentially extensive negotiations were being held to clear up a misunderstanding, we decided to terminate the project. The students were assigned to another problem.

One of the unique features of the Plan is the establishment of Internship Centers where WPI students can go for off-campus project experience. The WPI Internship Center is different from the commonly known cooperative program. While the industrial experience gained by the students through the co-op programs is undeniable, it must be recognized that one of the chief purposes is to extend financial aid to the student. The Colleges involved have little or no control of the students' on-site activity. On the other hand, the WPI Internship Center emphasizes the educational merit of the programs which are closely related to the student's technological interest. The students work on problems of their own choice at the off-campus Internship Center in cooperation with site personnel and under the overall supervision of WPI faculty as site directors.

CONTACT WITH GOVERNMENT RESEARCH

AN INTERNSHIP CENTER was established at the U.S. Army Natick Laboratories which accommodated six groups of students for the year 1971-72. The number of students in each group ranged from one to three. All were chemical engineering majors except one group of two mechanical engineers. Two typical projects are described in the following:

(Continued on page 40.)

Test to Measure the Ability of ChE Seniors In the Practical Application Of ChE Principles

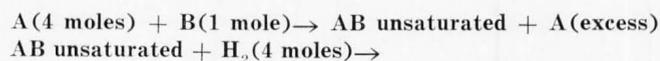
E. C. ODEN
*Mississippi State University
State College, Mississippi*

The following test was first given to our plant design students. It was meant to be part of a routine test toward the end of the semester in the practical application of ChE principles to the layout of a typical process flowsheet. When I reviewed the answers to the problem, it was very discouraging to have to accept the fact that our students had made so very many unexpected mistakes. It caused me to wonder how ChE seniors in other schools compared with ours in the practical application of chemical engineering principles. It occurred to me to ask other schools to give this same test, if their professors would cooperate.

Copies of the same test were submitted to several schools having ChE departments in hopes of making comparisons of our students with theirs. The professors were promised that I would not use school names or student names, if the test scores were analyzed and published. Thus, no effort is made to compare schools or individual students in this publication. The test presented below was given to the schools that agreed to the proposal.

OPEN BOOK PORTION OF TEST

Complete the process flowsheet that has been started having been given the following data: Compound A has physical properties comparable to isobutane. Compound B has properties comparable to hexane. The compound B is unsaturated but when combined with A and hydrogen over a nickel complex catalyst, a saturated compound AB is formed with traces of methane and about 2% tar based on total weight of A + B fed. Reactions may be represented:



*AB saturated + 3 moles H₂ + 2% tar
The tar boils at about 450°F and 35 to 40 psia.*

The reaction is exothermic having about 100,000 Btu/lb mole of AB formed. Compound AB has properties equivalent to decane.

Assume impurities in the hydrogen should not build up above 10% before being bled off and there is a constant supply of make up hydrogen available as well as A + B.

Assume product AB is to be 95% or greater purity. Show approximate temperatures, pressures and approximate compositions directly on vessels on the flowsheet you complete. Take advantage of utilities produced where possible. Reflux ratios on tower or towers may be taken as 1/1.

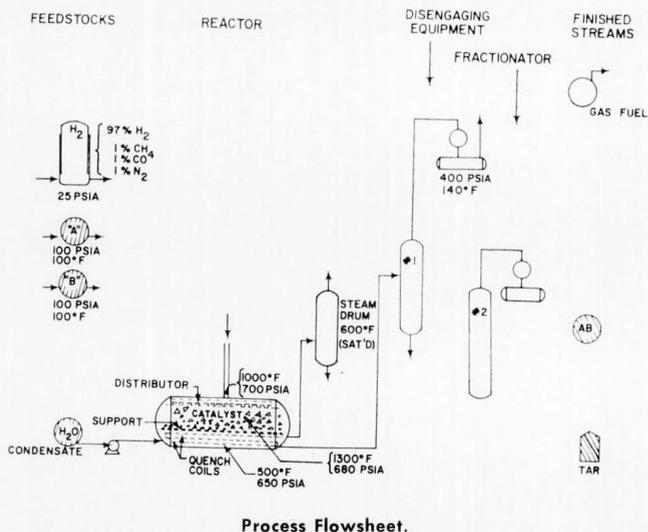
Approximately 100 students took the test, including all schools. The names of schools and names of students are not given to avoid embarrassing any schools or students. The test results are summarized below.

This was given as an open book test and equilibrium data or other needed data were available.

SUMMARY OF ANSWERS

1. 23% of the students used a pump to take the 25 psia gas from the holder and charge to the reactor at 700 psia.
2. Of those that used compressors to move the gas from

My analysis of the results reveals a very serious weakness on our part as professors in teaching our students to think.



22. 60% failed to place any type product coolers on product lines to storage vessels.
23. 90% failed to show any temperature or pressures recommended for storage vessels.
24. Only three students took into consideration that it would be better to store the tar at elevated temperature.
25. Only about 10% of the students established the correct design basis for the feed to the reactor—the moles H_2 should be in the ratio 9 moles per 1 mole of the sum of the inerts—10% inerts in the total Hydrogen feed.
26. Obviously, with the knowledge of the simple mistakes made as mentioned, it would be too much to expect them to know how to process the #1 column overhead in a manner to obtain the proper recycle compositions. Some students did select the correct type reboilers and similar considerations.

TEACHING OUR STUDENTS TO THINK

There were many other mistakes, too numerous to mention collectively, but it was extremely revealing just how little our students have learned to think. It was not a surprise to learn that many

Some of this weakness at our school may have started when we dropped the teaching of inorganic and organic technology.

would make mistakes on several of the above items, but the percentage that made these type mistakes and the grade point average (based on quality point averages in engineering courses) of some of the students that made mistakes was alarming. Professors will likely be surprised to learn their students will not do any better if they give this or a similar examination. It is believed other professors will have just as big a disappointment in the results as those of us that cooperated on this test, especially if they will not drill them on these specific type problems prior to giving the test.

My analysis of the results reveals a very serious weakness on our part as professors in teaching our students to think. It has uncovered a weakness in our teaching procedures or curriculum that I think is in need of correcting, if at all possible. Just where and how to undertake to do this, in the best possible manner, is the so-called "\$64 question". Some of this weakness at our school

- 25 psia to 700 psia, 69% failed to use a knockout drum ahead of the compressor.
3. 24% of the students used compressors to take liquid "A" at 100 psia and discharge to reactor at 700 psia. (Note: Equilibrium temperature and pressure relationships of "A" and "B" could have been consulted, if in doubt, as to being a liquid or a gas.)
4. 36% of the students used no pump to take liquid "A" at 100 psia to reactor at 700 psia.
5. 28% of the students used compressors for moving liquid "B" at 20 psia to reactor at 700 psia.
6. 26% took liquid "B" at 20 psia directly to reactor at 700 psia without any power mover.
7. 20% used no preheater of any type to go from the vessels as indicated to reactor at 1000°F.
8. 12% vaporized liquids then compressed to 700 psia with a compressor.
9. 46% preheated with 600°F steam only to reach 1000°F feed temperature entering the reactor.
10. 80% failed to recycle steam condensate to reactor.
11. 68% showed no recycle H_2 from flash vessel to reactor.
12. 82% showed no recycle of product "A".
13. Of those that did recycle hydrogen, only 10% took advantage of the pressure of gas off the flash vessel and returned it to one of the higher pressure stages of the compressor.
14. 80% failed to quote any temperature or pressure whatever as requested on the first tower.
15. 60% failed to show any reflux for tower #1.
16. 40% failed to take bottoms from tower #1 to tower #2.
17. 30% failed to use any reflux on tower #2.
18. Of those that had correct feed to the tower #2, 60% failed to select pressure and corresponding temperature correctly on reflux drum to #2.
19. 80% failed to give proper temperature and pressure for top of tower #2.
20. 42% failed to provide a reboiler of any type for tower #2.
21. 70% failed to use correct transfer equipment for tower #2 products where correct feed to tower was used.

may have started when we dropped the teaching of inorganic and organic technology. Any courses where flowsheets of various processes were rather thoroughly discussed emphasizing reasons for the various pieces of equipment, operating conditions, catalyst, etc., served to help the students apply engineering principles.

PROCESS FLOWSHEET DISCUSSION

TWO OR THREE PROCESS flowsheets involving various types of equipment are discussed in my plant design course. Then the students are required to lay out a process flowsheet. Apparently, they are able to find their particular process flowsheets illustrated fairly completely in the literature, but they do not receive enough practice in thinking out the reasons why all the specific equipment is used. There are many items that the students should have thoroughly fixed in their minds before they undertake a course in plant design. Some of these items are:

- Pumps are used to move liquids and compressors are only used to move gases.
- It costs a great deal more to elevate the pressure to some higher pressure by a compressor than it does a like weight of liquid by a pump.
- One does not vaporize material and then use a compressor to elevate it to some higher compression level if it can be elevated to the higher compression level first by a pump, then heated to the desired conditions to convert it to a vapor.
- One does not heat something to a higher temperature than the heating medium being used.
- Compounds having lower boiling points go out the top of an ordinary fractionator and the higher boiling compounds go out the bottom.
- All ordinary fractionating towers have a lower temperature and pressure at the top than at the bottom.
- All ordinary fractionating columns must have reflux and reboilers.

These and many other statements that could be listed should be fixed in the students' minds before starting plant design.

I have tried to analyze why this weakness exists with our present day students. Just about all graduates of 20 to 30 years ago were required to take courses in organic and inorganic technology. In those courses taught to me, process flowsheets were discussed thoroughly in class and students were required to give reasons why the type of equipment used was needed; why specific operating conditions were best, based on kinetic and thermodynamic relationships; the likely poisons for catalyst, considering the chemical reactions that were likely to occur, etc. These courses have

been dropped as required courses and in many curricula are not even offered. At least, I think those courses taught me to think and learn to apply fundamental chemical engineering principles. This causes me to wonder if we have not made a mistake in eliminating these courses. The other possibility is to utilize flowsheets in teaching some of the fundamental chemical engineering principles in such courses as mass and energy balances, unit operations, mass transfer phenomena, thermodynamics, kinetics, and plant design.

NOT ENOUGH PRACTICAL APPLICATION

IT HAS BEEN OBSERVED that the students are keen at memorizing fundamental principles, laws, rules, and derivations of equations, but when asked questions where these are to be used or could be applied to think out an answer or a solution, the students seem to fail to recognize the source of help. There appears to be too much emphasis placed on derivations of equations, theorems, etc., and not enough practical application. Perhaps the lack of industrial experience of faculty members or the tendency of faculty members to teach undergraduates like they were taught graduate courses, where derivations of equations were stressed, may have something to do with the weakness of students in the application of engineering principles.

At any rate, this test has convinced me that our ChE curricula have one serious weakness in the fact that so many of our graduates cannot do a better job of applying chemical engineering principles. □



E. C. Oden is a graduate of the University of Alabama and Brooklyn Polytechnic (M.S. '38) and has done graduate work at Cornell and the University of Michigan. He has many years experience in the chemical and petroleum industries and is presently teaching plant design.

The
Theory
of
Diffusion and Reaction

A Chemical Engineering Symphony

being the
Chemical Engineering Lecture
to the

American Society for Engineering Education

by

Rutherford Aris

Department of Chemical Engineering & Materials Science

University of Minnesota

1973

THE THEORY OF DIFFUSION AND REACTION

A Chemical Engineering Symphony

RUTHERFORD ARIS
University of Minnesota
Minneapolis, Mn. 55455

ALTHOUGH CHEMICAL ENGINEERS have been far from alone in their work towards a comprehensive theory of diffusion and reaction, their contributions have been so substantial and significant that it is only stretching the truth a little to claim the subject for our discipline. To claim that it is a symphony, an articulated and developed structure shot through with certain themes, held together by the relationships of its movements and breathing an inner life of its own—that is a claim of another sort. Yet, at the risk of being regarded as a shade fanciful or a mite precious, I will persist in offering the analogy for if, as Galileo held, “The book of nature is written in the language of mathematics” and if, in mathematics, structure is of the essence then we must always be concerned for structure. Indeed some have gone so far as to claim that a knowledge of structure is the “only articulate or communicable knowledge that we can attain”. Be that as it may, the emphasis on structure needs no justification to a society devoted to engineering education. But structures are not enjoyed entirely in isolation and it is tempting to employ that bright gift of our mediaeval brethren, the art of analogical thinking, to enliven this enjoyment. Nor am I alone in this predilection for I have heard one of the great men of our profession, R. B. Bird, subtitle his seminar “A sonata on rheology and kinetic theory”. Like all analogies, its tempo and timbre must be carefully controlled, but with this understood the orchestra can be allowed its head at least until we land in the ditch with a fine flourish of mixed metaphors.

I would like to begin by delineating the main outlines of the subject as I see it and to go on to some comments on its history which may serve to clothe the bare bones of abstraction with a few sinews and a little flesh.

THE STRUCTURE OF THE SUBJECT

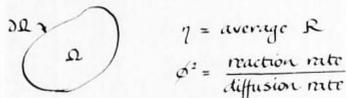
The theory of diffusion and reaction in permeable catalysts may be divided into four movements. The first, an allegro in sonata form, states and develops the partial differential equations from which all must depend. It is followed by a slow movement in sonata-rondo form, definitely andante for it deals with the steady-state solution of these equations and equally pedestrian, though important, matters. The tempo picks up a little (*allegretto*) in the third movement, a minuet and trio concerned with the question of uniqueness and its bearing on stability. This theme carries over to the fourth movement, a set of variations on the question of stability and transient behavior—*presto vivace*.

The distinction between the first half of the subject and the second is a clear one and the difficulties they present are those encountered by the great lexicographer. For if the results on steady state are, as Dr. Johnson said of the English tongue, “Copious without order”, the newer developments on uniqueness and stability are certainly “energetick without rules”. Indeed it will be some years before a comprehensive account of these developments can be given.

... if Galileo held, “The book of nature is written in the language of mathematics” and if, in mathematics structure is of the essence, then we must always be concerned for structure.

The theory of diffusion and reaction in permeable catalysts may be divided into four movements—allegro, andante, allegretto, and presto vivace.

I. The basic partial differential equations & their ramifications.



GENERALIZATION
SPECIALIZATION

$$\frac{\partial u}{\partial \tau} = \nabla^2 u - \phi^2 R(u, v) \quad \mathcal{L} \frac{\partial v}{\partial \tau} = \nabla^2 v + \beta \phi^2 R(u, v)$$

$$\frac{1}{\nu} \frac{\partial u}{\partial n} + u = 1 \quad \frac{1}{\mu} \frac{\partial v}{\partial n} + v = 1$$

Generalizations (more components) Specializations (Dirichlet problem)

DEVELOPMENT

Conservation Principles
Physics & chemistry of diffusion, adsorption, reaction
Diffusion in porous media

RECAPITULATION

Homogeneous and discrete models.
Reduction to a single equation.
Forms of the rate expression.

THE TWO SUBJECTS OF the first movement may be introduced without delay for they are the partial differential equations governing the concentrations and temperature in the catalytic region Ω and the appropriate boundary conditions to be applied on $\partial\Omega$. To take a case of fundamental importance for the exposition, an irreversible reaction whose rate $R(u, v)$ depends on the concentration, u , of a single reactant and on the temperature, v , will give rise to the equations

$$\frac{\partial u}{\partial \tau} = \nabla^2 u - \phi^2 R(u, v) \quad (1)$$

$$\mathcal{L} \frac{\partial v}{\partial \tau} = \nabla^2 v + \beta \phi^2 R(u, v) \quad (2)$$

where τ is the time (made dimensionless by the characteristic diffusion time), ∇^2 the Laplacian operator in the dimensionless space variables of the particle, β , the Prater temperature rise, \mathcal{L} , the Lewis number and ϕ the Thiele modulus or ratio of the diffusion time to the reaction time.

The concentration and temperature have been made dimensionless by dividing them by the concentration and temperature far from $\partial\Omega$. Hence the boundary conditions are

$$\frac{1}{\nu} \frac{\partial u}{\partial n} + u = 1 \quad \text{and} \quad \frac{1}{\mu} \frac{\partial v}{\partial n} + v = 1 \quad (3)$$

μ and ν being the Biot numbers for heat and mass transfer to $\partial\Omega$. The basic equations are thus seen to be a pair of parabolic, quasi-linear partial differential equations with Robin boundary conditions.

The exposition continues by showing the details of the reduction of the equations to this form and with the generalizations and specializations. The generalizations would include the forms of the equations when there are more chemical components, more than one reaction or for the case of volume change. The specializations include the isothermal case (for which v is fixed) and the Dirichlet problem (for which μ and ν tend to infinity). The exposition of these two subjects concludes with the definition of the characteristic functional of the solution, the effectiveness factor,

$$\eta = \frac{1}{V} \iiint R(u, v) dV \quad (4)$$

In the development section the physico-chemical basis of the equations may be examined. They rest of course on the principles of the conservation of mass and energy, but the constitutive relationships that go into these are based on the laws of diffusion and of reaction and on certain models and idealizations of the actual structures. Thus the concept of an effective diffusivity in a porous medium needs to be developed on the basis of the best available understanding of the structure of these materials.

In the recapitulation the justification for using a homogeneous model must be discussed. The catalytic reaction actually occurs at discrete sites on the walls of a network of pores and it is there that the transformation of matter and exchange of energy take place. The degree to which these are minuscule events happening very close together and uniformly dispersed throughout the particle is the degree to which an homogeneous set of equations will be justified. The case of a zeolitic catalyst, where a small proportion of sieves is sparsely distributed through an inert medium, calls the homogeneous model in question. Here also the circumstances in which the equations can be reduced to a single equation and the forms taken by the resulting nonlinearity may be considered.

The final transmogrification of the steady-state theme is to the question of multiple reactions. For first order reaction systems there are immediate analogies with the simplest theme of a single first-order reaction.

II. The solution of the equations for the steady state.

A¹. Steady-state: isothermal: first order.

B¹. Variational methods.

A². Steady-state: isothermal: not first order.

C. Unsymmetrical solutions: Singular perturbations

A³. Steady-state: non-isothermal: single reaction.

B². Approximations & numerical methods

A⁴. Steady-state: multiple reactions.

IN THE SECOND MOVEMENT the dominant subject, the steady-state solution, appears in four forms of increasing development and complexity. The basic features are found in its first exposition in the context of a first-order, isothermal reaction (A¹). Here the distinction between the Dirichlet and Robin problems, the effects of particle shape and the asymptotic behavior can be readily appreciated and these are themes that recur. After a section (B¹) on variational methods, whose validity though rooted in the linear situation yet reaches out to monotone non-linearities, we come to isothermal kinetics not of the first order (A²). This embraces the pth order reaction, Langmuir-Hinshelwood kinetics and such added features as surface diffusion and electrostatic effects. The possibility of unsymmetrical solutions, which arises as soon as there is more than one stable solution, and the utility of singular perturbation analysis provide a bridging section to A³, the discussion of the non-isothermal case. Here the question of uniqueness really comes to the fore and the problem of computing the effectiveness factor is an important one. It is therefore appropriate to consider the approximations and applicable numerical methods (B²). These have a certain affinity with variational methods though this connection is not to be over-emphasised.

The final transmogrification of the steady-state theme is to the question of multiple reactions. For first order reaction systems there are immediate analogies with the simplest theme of a single first-

order reaction. For in the one case we have

$$D \frac{d^2 u}{dr^2} = ku \quad (5)$$

with $u = u_s$ at $r = \pm a$ and this leads to the solution $u(r) = u_s \cosh\phi(r/a) / \cosh\phi$ and the effectiveness factor $\eta = (\tanh\phi) / \phi$ where $\phi^2 = a^2 k / D$. In the case of multiple reactions we have

$$D \frac{d^2 \underline{u}}{dr^2} = \underline{K} \underline{u} \quad (6)$$

where D and \underline{K} are matrices and \underline{u} a vector of concentrations that is specified as $\underline{u} = \underline{u}_s$ at $r = \pm a$. Let $\underline{\Phi}$ be the matrix defined by $\underline{\Phi}^2 = a^2 \underline{D}^{-1} \underline{K}$ and an effectiveness matrix \underline{H} be defined by setting $\underline{H} \underline{K} \underline{u}_s$ equal to the actual rate of reaction in the presence of diffusion. Then it can be shown that

$$\underline{D}^{-1} \underline{H} \underline{K} = \underline{\Phi} \tanh \underline{\Phi} \quad (7)$$

in close analogy to $\phi^2 \eta = \phi \tanh \phi$ for the single reactant.

III. Questions of uniqueness & stability

A. Data & desiderata.
Existence theorems.
Maximal & minimal solutions.

B. Sufficient conditions for uniqueness.
Bounds on the region of uniqueness.

A. Sufficient conditions for instability.
Liapounov methods.

THE THIRD MOVEMENT takes us into the question of uniqueness and the preliminary considerations of stability. The general feature of problems in diffusion and reaction is that for sufficiently small and sufficiently large systems the solution is unique. It is only for systems of intermediate size that multiple solutions can exist and then only if the kinetics are sufficiently nonlinear. Thus we can discern three groups of parameters: the kinetic group, such as the Prater temperature

β , the Arrhenius number γ and the order of reaction, p , as in the expression for a p^{th} -order irreversible reaction

$$R(u, v) = u^p \exp \gamma(v-1) / v; \quad (8)$$

the transfer group, namely the Biot numbers, μ and ν , and the parameters of the internal diffusion; finally there is the Thiele modulus which measures the size of the system in terms of the relative characteristic rates of reaction and diffusion and thus links the chemical and physical features of the problem. We can thus ask for sufficient conditions on the parameters of one class which will ensure uniqueness when the parameters of another class lie in a given range. For example if μ and ν are infinite (Dirichlet problem) we can ask for conditions on p, β, γ such that the solution is unique for all values of ϕ . Luss has shown that the monotonicity of $R(1-w, 1+\beta w)/w$ is sufficient for this. Jackson has extended this to the Robin problem by showing that the monotonicity of $R(1-w-\bar{w}, 1+\beta w+\alpha\beta\bar{w})/w$ ($\alpha = \nu/\mu$) with respect to both w and \bar{w} is a sufficient condition. Such conditions as these are "safe" but how proximate they may be to the exact condition has to be determined computationally; for example, Luss' condition for a first order reaction in a slab is extraordinarily close to the exact results.

Since uniqueness is to be expected for sufficiently large and sufficiently small values of the Thiele modulus (say, $\phi > \phi^b, \phi < \phi_n$), it is also of interest to try and obtain estimates of these so-called bifurcation values. In particular we would like a lower bound for ϕ_n and an upper for ϕ^b so that the region of multiplicity would be effectively delimited. Luss has obtained the former but the results on the latter are still only partial.

In the third movement it is appropriate also to raise the quasistatic questions of stability. Thus, it is often possible to give sufficient conditions for instability from an examination of the steady-state equations or to use Liapounov methods of the second kind which though involving the transient equations do not require anything approaching a solution of them. Jackson has given a very elegant geometrical interpretation to the analysis of stability which shows that for the Dirichlet problem only the maximal and minimal solutions can be stable. Specifically, he divides the η, ϕ curve up into segments at the points where $d\eta/d\phi$ becomes infinite. A segment such that $(d\eta/d\phi) \rightarrow -\infty$ at either or both of its ends must correspond to unstable steady states.

IV. Stability and transient behaviour

- a. The influence of L .
- b. Lumping
- c. Catalytic wires.
- d. Unsymmetrical solutions.
- e. Morphogenesis and chemotaxis
- f. Limit cycles.
- g. Limit cycles in lumped models.
- h. Weis' bound.
- i. Cyclic operation.
- j. Optimal control.
- k. The influence of adsorption capacity
- l. Diffusion waves

THE FOURTH MOVEMENT is a set of variations on the themes of stability and transient behavior. The key phrase is the introduction of the Lewis number whose value has no influence on the steady state as such but is critical in determining its stability. In particular there is evidence from many directions that a sufficiently small value of the Lewis number, the ratio of the material and the thermal diffusivities, will often render the steady-state unstable even when it is unique. This can give rise to limit cycles in which the concentration and temperature at each point oscillate and waves of concentration and temperature wax and wane within the particle. Cyclic operation, as a means of improving selectivity, has been deliberately cultivated in the work of Horn and Bailey and a recent investigation of Cresswell and El-nashie has shown that the influence of adsorption capacity may have to be considered.

Because the exact treatment of the parabolic equations is difficult various methods of approximation have been considered. These consist in some process of lumping or replacing the parabolic equations by sets of ordinary differential equations. This can be quite a crude analogy with the stirred tank obtained from the first term of a modal analysis or collocation method or a more precise development in a series of equations capable of giving as accurate a result as may be wished. Even the simplest of approximations betrays the same general features but the danger of an approximation of this sort is that its validity is almost unpredictable and at best one can hope to find qualitative and comparative results. The equations governing reaction on the surface of a catalytic wire are already in lumped form and this

... a symphony or any work of art may be completed and stands for better or worse, a whole to be praised and performed or disparaged and neglected. But the score of an area of natural philosophy cannot be so ended, but must constantly be revised and rewritten for each performance.

allows them to be discussed rather fully. In particular it is found that even when conditions around the wire are independent of position there can be periodic solutions to the equation. However only the uniform state is stable.

It is quite otherwise in the case of other solutions of the diffusion and reaction equations which lack the symmetry of the problem. The class of solutions discovered by Pismen, Kharkats, Marek, Jackson, Horn and others contains unsymmetrical members whose stability has been established with great care by Aronson and Peletier. Jackson and Patel have shown that the full diagram for the effectiveness factor as a function of Thiele modulus should contain branches corresponding to unsymmetrical solutions. Not only can unsymmetrical solutions be stable, but the symmetrical or uniform state may actually be unstable. Such is the case in certain models of morphogenesis that have developed from Turing's work and in a model

of chemotaxis considered by Keller and Segel. In the work of Nicolis and his colleagues it further appears that certain regions of a non-uniform steady state may become unstable and limit cycle behavior may be confined. The sophisticated use of group theory by Scriven and Gmitro to find solutions of varying degrees of symmetry has yet to be published, but this is another variation that adds colour and life to the finale.

Here the analogy certainly breaks down. For a symphony or any work of art may be completed and stands for better or worse, a whole, to be praised and performed or disparaged and neglected. But the score of an area of natural philosophy cannot be so ended, but must constantly be revised and rewritten for each performance. At least they have in common that, whether it bring relief or rapture, all such performances must be brought to a close.

Program Notes

REFLECTIONS ON HISTORY AND DEVELOPMENT

PROPHETIC AS WAS Mikhailo Vasilyevich Lomonosov's remark in 1745—"I saw not only from other authors, but am convinced by my own art, that chemical experiments combined with physical show peculiar effects" [1]—it is straining its context a little to apply it specifically to the question of diffusion and reaction. Yet it has interest as a dictum of the father of physical chemistry and an indication of the opinions far ahead of his time. After his boisterous student days in Marburg (1736-39 reading physics under Christian Wolf) and Freiburg (1739-40 reading metallurgy under Henckel), Lomonosov arrived back in St. Petersburg on July 8, 1741, just three days after Euler left for Berlin. He had had a hectic journey what with raising the money for it and escaping temporary impressment in the Prussian hussars and his early years at the Academy of Sciences were so disturbed by his own turbulence and that of his times that he does not seem to have

had time to write to the wife whom he had left behind in Marburg. Indeed he had barely made his peace with his colleagues in 1744 when, having made contact with her on her own initiative, she finally joined him in St. Petersburg. The chair of chemistry at the Russian Academy of Sciences had never adequately been filled for the first incumbent had injured himself fatally by tumbling out of his carriage in a drunken state when returning from a symposium only five months after he had arrived and for the next seventeen years it was held by a botanist who spent ten of them exploring Siberia. Lomonosov petitioned Elizabeth to be made professor of chemistry and, after he had written a satisfactory dissertation on metallurgy, an ukase on his promotion was published on July 25, 1745. With his promotion the petition for the building of a chemical laboratory, which he had been renewing year by year since 1742, was finally granted and it is from this proposal that Frank-Kamenetskii takes the quotation.

But it was his insistence on the combination of physical and chemical methods that gives him the claim to be one of the founders of physical chemistry. In his "Elementa Chymiae Mathematicae" (begun in 1741 but never completed) he conceives chemistry as a science of clearly defined chemical elements unified by mathematical methods and incorporated in a physical system based upon an atomic theory. Ten years later in a "Speech on the Uses of Chemistry" [2,3] he speaks of the relationships between mathematics, physics, and chemistry

"Eyes are useless to the man who wishes to see the interior of an object yet lacks a hand to open it. Hands are useless to the man who has no eyes to observe the objects once they have been disclosed. Chemistry may correctly be called the hands, and Mathematics the eyes of Physics. But as surely as each demands aid from the other, just as surely, notwithstanding, they often divert human minds into different paths. The Chemist, who sees in every experiment different and frequently unexpected phenomena and products and is thereby allured to gain a speedy advantage, laughs at the Mathematician as being involved only in certain vain cogitations about points and lines. The Mathematician, on the other hand, convinced of his propositions by exact proofs and evolving unknown properties of quantities through incontestable and uninterrupted deductions, scorns the Chemist as occupied only with practice and lost in many chaotic experiments; being himself accustomed to clean paper and shining geometric instruments, he abhors the smoke and dust of Chemistry. And thus up to this time these two sisters, closely associated for the common good, have for the most part given birth to sons of such different opinions. This is the reason why the complete study of Chemistry has not yet been combined with a profound knowledge of Mathematics."

If Lomonosov belongs to the prehistory of the exact analysis of the problem of diffusion and reaction, its early history and subsequent development are bound up with some of the great names of chemical engineering with those of Damköhler and Wicke in Germany, of Zeldowitsch and Frank-Kamenetskii in Russian and of Thiele, Weisz and Amundson in this country. Moreover we have some useful historical accounts in the recollections of Thiele [4] and the Murphree Award Address of Weisz [5]. Indeed it was commonly thought that the exact analysis flowered almost simultaneously in Germany, Russia and the U.S.A. in the late 1930's in the work of Damköhler, Zeldowitsch and Thiele until a paper of Ferencz Jüttner was discovered (as I understand it, by R. L. Goring of Mobil). This 1909 paper appears to have been almost totally overlooked for more than sixty years and was certainly unknown to the three who independently arrived at some of its results thirty years later. Jüttner (b. Feb. 28, 1878 Dr. phil.

1901, Breslau) was a natural philosopher who published papers on thermodynamics, the theory of matter and relativity besides the three on chemical kinetics which we shall take note of. He is listed in Poggendorf as "Lehrer, Gymnas Brieg Schliesen, 1902", and was evidently a member of the "Schlesischen Gesellschaft für vaterländische Kultur" for he read one of these papers to its Mathematical Section on the 4th of May, 1909.

In his paper on "Reaktionskinetik und Diffusion" [6] Jüttner considers a general reaction $n_1A_1 + n_2A_2 + \dots \rightleftharpoons n'_1A'_1 + n'_2A'_2 + \dots$ and

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assumes mass action kinetics, setting up the time dependent equations for an arbitrary region and different diffusion coefficients for each species. In the stationary state and one space dimension he recognizes that certain combinations of any two concentrations will be at most linear functions of position and in the symmetric case will be constant. The equations can thus be reduced to a single equation of the form

$$\frac{d^2c}{dx^2} = g(x, c)$$

where g is a polynomial of degree $(n_1 + n_2 + \dots)$ or $(n'_1 + n'_2 + \dots)$, whichever is the greater. In the symmetrical case, when g is a function of concentration alone, Jüttner showed that the equation could be solved by an implicit function given in terms of an integral, while in the case of a reversible first order reaction he gives the explicit solution in terms of hyperbolic functions. In the general case he refers to the "new and important researches of Painlevé on algebraic differential equations of the second order" that had appeared in *Acta Mathematica* in 1902, but he again treats the reversible first order reaction in detail giving the solution under general boundary conditions. For the second order reaction he gives a series solution and remarks that the implicit solution for irreversible n th order dissociation gives elliptic functions for $n = 2$ and 3 . In discussing the transient case Jüttner gives a formal expansion of

(Continued on page 36.)

ENGINEERING

ENVIRONMENTAL SYSTEMS ENGINEERING

LINVIL G. RICH, Clemson University. *McGraw-Hill Series in Water Resources and Environmental Engineering*. 1973, 405 pages (tent.), \$16.50 (tent.)

In this quantitative introduction to the subject, Professor Rich uses a systems approach, in which the focus is on the system as a whole and how its components interact. Although water environment is considered in greatest detail, also included are air pollution and its control, solid waste management and radiological health. The mathematics of systems analysis and computer solutions is used extensively.

THERMODYNAMICS, Second Edition

JACK P. HOLMAN, Southern Methodist University. 1974, 608 pages (tent.), \$14.50 (tent.). *Solutions Manual*. Six audio-tutorial cassette tapes with an accompanying student workbook, \$50.00 (tent.)

All standard thermodynamics topics can be covered from either the classical or statistical viewpoint or from any desired integration of the two with this book. This revision includes a sixty per cent expansion of classical thermodynamics and applications, and many new examples and problems worked in both fps and SI units have been added.

MOMENTUM, HEAT AND MASS TRANSFER, Second Edition

C. O. BENNETT, University of Connecticut, Storrs and J. E. MYERS, University of California, Santa Barbara. 1974, 604 pages (tent.), \$16.50 (tent.). *Solutions Manual*

Combining a rigorous approach to fundamentals with an extended treatment of practical problems, this revision treats principles of transport phenomena as applied to simple geometries and then extends the discussion to analyze practical areas such as flow in pipes and equipment, filtration, heat exchangers and evaporators, gas absorption, liquid-liquid extraction and distillation.

THE INTERPRETATION AND USE OF RATE DATA

STUART W. CHURCHILL, University of Pennsylvania. 1974, 512 pages (tent.), \$17.50 (tent.)

Here is a completely new treatment of rate processes in which a generalized structure is used, greatly simplifying and reducing the number of concepts needed to study bulk transfer, momentum transfer, heat transfer and chemical relations. Emphasis is on the relationship between design and uncertainties in measurement, and these concepts are reinforced with over 300 problems based on raw experimental data from the literature.

SOLIDIFICATION PROCESSING

MERTON C. FLEMINGS, Massachusetts Institute of Technology. 1974, 580 pages (tent.), \$19.50 (tent.)

Here is the only significant book in the field in ten years. Building on the foundations of heat flow, mass transport and interface kinetics, the author presents the fundamentals and relates them to practice. Among the processes considered are crystal growing, shape casting, ingot casting, growth of composites and splat cooling.

INTRODUCTION TO METALLURGICAL THERMODYNAMICS

DAVID R. GASKELL, University of Pennsylvania. 1973, 550 pages, \$19.50

Treating in depth the thermodynamics of high temperature systems encountered in metallurgy, this book demonstrates the thermodynamic method through an extensive illustration program, using as examples real systems which have been carefully selected to illustrate the principles involved. The text introduces basic laws and necessary thermodynamic functions and makes applications that are numerous and thoughtful.

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MASS TRANSFER

THOMAS K. SHERWOOD, ROBERT L. PIGFORD, CHARLES R. WILKE, all of the University of California at Berkeley. 1974, 512 pages (tent.), \$18.50 (tent.)

Compared with the 1952 version, *Absorption and Extraction*, this volume is substantially more sophisticated, providing a much broader coverage of mass transfer. Emphasis is on the practical aspects and real problems that demand an understanding of theory. Yet theoretical derivations are minimized by explicit citation of over 1100 contemporary references.

SCIENTIFIC STREAM POLLUTION ANALYSIS

NELSON LEONARD NEMEROW, Syracuse University. 1974, 380 pages (tent.), \$16.50 (tent.)

A careful balance of the hydrological, chemical and mathematical concepts involved in the evaluation of stream quality is achieved in this comprehensive description of the analysis of water pollution. Practice problems are presented to demonstrate the difficulties surrounding stream analysis, and computation techniques for deoxygenation and reaeration rates are described and analyzed, as are all factors affecting oxygen concentration to give and overall oxygen sag curve in a stream.

AIR POLLUTION

H. C. PERKINS, University of Arizona. 1974, 480 pages (tent.), \$16.50 (tent.). *Solutions Manual*

To date, this is the only truly engineering-oriented text on the subject that draws on the student's background in analyzing and solving problems in air pollution. The treatment is sufficiently detailed to enable chemical, mechanical and sanitary engineering students to solve a variety of problems, and many applications-type problems are included.

ENVIRONMENTAL PROTECTION

EMIL T. Chanlett, University of North Carolina at Chapel Hill. 1973, 569 pages, \$15.50

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EXPERIMENTAL METHODS FOR ENGINEERS, Second Edition

JACK P. HOLMAN, Southern Methodist University. 1971, 448 pages, \$14.50. *Solutions Manual*

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INDIRECT MEASUREMENT OF REACTION RATE

R. D. WILLIAMS
University of Arizona
Tucson, Arizona

This paper describes an experiment which can be used to study the kinetics of chemical reactions which are accompanied by measurable heat effects. An indirect method of data collection takes advantage of the fact that the rate of reaction is proportional to the rate of energy release or absorption.

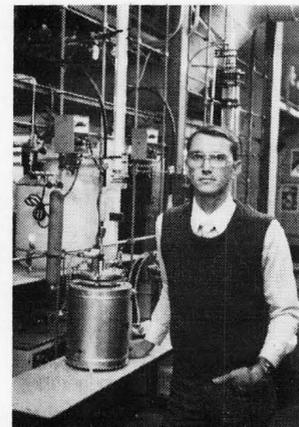
Laboratory experiments in chemical engineering curricula should be carefully selected according to the laboratory objective. Experiments which demonstrate several points are especially effective in the curriculum squeeze of today.

At the University of Arizona the undergraduate kinetics laboratory is used to give the student practical experience in the more important points covered theoretically in the lecture course the semester before.

The first three experiments of the lab are concerned with a demonstration of the differences in behavior of batch, continuous stirred and tubular reactors. The integral method of analysis is used in conjunction with isothermal batch kinetic data in order to determine the kinetics of the saponification reaction between ethyl acetate and sodium hydroxide. These kinetics are then used to predict behavior of the two continuous reactor types and these predictions are experimentally checked. The wet chemical method of data collection in these three experiments is tedious and by the end of the third the student is convinced that all kinetic determinations must be equally frustrating.

The fourth experiment was chosen in part for its comparative experimental simplicity. But more than this several important points from the theory course are well illustrated. These are enumerated below.

- An indirect data collection method is illustrated.
- An energy balance is required in addition to the material balance.
- The data cannot be conveniently analyzed by the integral method whereas the differential method can be used.
- Not only the kinetics, but also the stoichiometry and heat of reaction may be very simply determined.



Dick Williams received his undergraduate degree at Texas Tech University and his graduate degrees at Princeton University, all in Chemical Engineering. He has been at the University of Arizona since 1968 where his research has been involved primarily with chemical reaction engineering. Current research projects include design of a system to reduce automobile pollutants while increasing fuel economy and a study of hydrometallurgical leach recovery of minerals from their ores with emphasis on characterization of the underlying mechanisms involved.

This fourth experiment involves the determination, in an adiabatic-batch reactor, of the

TABLE 1: Possible Reactions between H_2O_2 and $Na_2S_2O_3$
 (From Reference 3)

Reaction	Reaction	v_A/v_B	theoretical $-dH_r/dt$ (cal/mole $Na_2S_2O_3$)
I	$2Na_2S_2O_3 + H_2O_2 \rightarrow Na_2S_2O_4 + 2NaOH$	0.5	39,000
II	$Na_2S_2O_3 + H_2O_2 \rightarrow Na_2S_2O_4 + H_2O$	1.00	41,400
III	$3Na_2S_2O_3 + 4H_2O_2 \rightarrow 2Na_2S_2O_6 + 2NaOH + 3H_2O$	1.33	122,500
IV	$Na_2S_2O_3 + 4H_2O_2 + 2NaOH \rightarrow 2Na_2SO_4 + 5H_2O$	4.00	210,000
V	$3Na_2S_2O_3 + 5H_2O_2 \rightarrow Na_2S_2O_6 + 2Na_2SO_4 + 5H_2O$	1.67	193,300
VI	$2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$	2.00	142,500
VII	$4NaOH + Na_2S_2O_6 + 4H_2O_2 \rightarrow 3Na_2SO_4 + 6H_2O$	----	-----

*stoichiometric ratio ($H_2O_2/Na_2S_2O_3$)

kinetics of the exothermic reaction between hydrogen peroxide and sodium thiosulfate. Glasser and Williams¹ have demonstrated a slightly more general technique using the acetic anhydride hydrolysis reaction. The former reaction has the pedagogical advantage of a non-obvious stoichiometry which can be experimentally determined. Several possible reactions between hydrogen peroxide and sodium thiosulfate are listed in Table 1.

Root and Schmitz² utilized this reaction in demonstrating reactor instability in an adiabatic loop reactor. Their analysis did not require a detailed knowledge of the kinetics. Cohen and Spencer³ have calorimetrically studied this system to obtain the kinetic details.

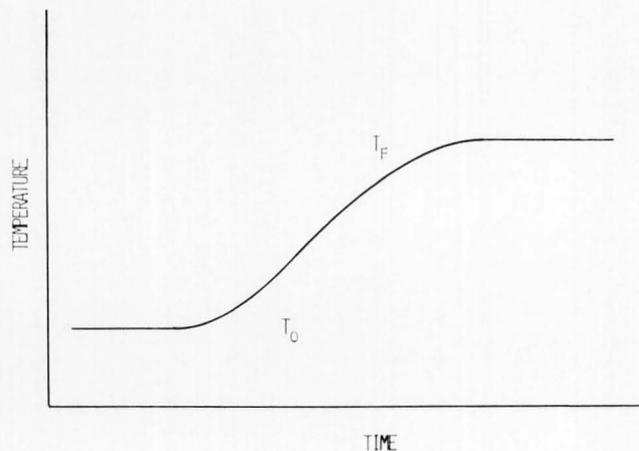


FIGURE 1: TYPICAL TEMPERATURE - TIME TRACE.

EXPERIMENTAL

The experimental apparatus consists of a 500 ml beaker, a magnetic stirrer, and a thermocouple-strip chart recorder arrangement. Volumes of two molar solutions of each of the reactants are mixed in the beaker and the temperature is recorded as the reaction progresses. An s-shaped curve such as shown in Figure 1 is obtained. If the total reaction mixture volume is held constant while varying the relative amounts of each reactant, then the temperature rise will go through a maximum when the reactants are mixed in their stoichiometric ratio. A graph of ΔT versus initial concentration ratio will exhibit this behavior. A typical result is shown in Figure 2. It can be seen

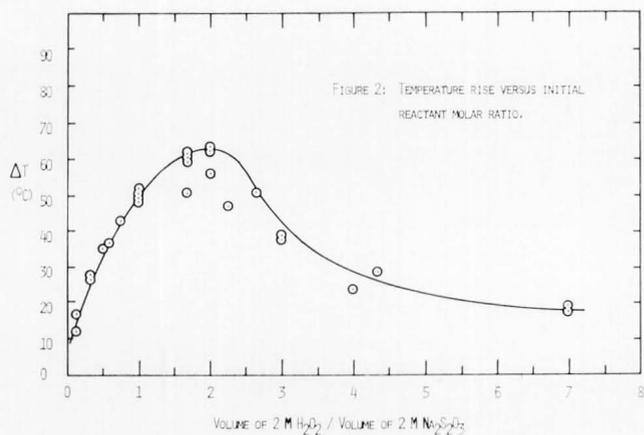


FIGURE 2: TEMPERATURE RISE VERSUS INITIAL REACTANT MOLAR RATIO.

An indirect method of data collection takes advantage of the fact that the rate of reaction is proportional to the rate of energy release or absorption.

that the maximum occurs near a reactant ratio of two implying that the major reaction occurring is VI in Table 1. A check on this result can be made by calculating the theoretical heat of reaction and comparing this value with values obtained from the experimental data using Equation 1. These results are given in Table 2.

$$\frac{\Delta H_R}{v_A} = \frac{\overline{\rho C} \Delta T}{a_0} \quad (1)$$

	v_A/v_B	$-\Delta H_r/v_B$ kcal/mole $\text{Na}_2\text{S}_2\text{O}_3$	E kcal/mole	k_0 liters/mole-sec
student	2	142 \pm 7	18.7	7.33×10^{11}
literature (ref. 3)	2	142.5	18.28 \pm .3	6.85×10^{11}

THEORETICAL

The kinetic data can be analyzed in light of the theoretical temperature-time relationship. The material and energy balances for an adiabatic, constant volume batch reactor are given below.

$$\frac{da}{dt} = v_A R \quad (2)$$

$$\overline{\rho C} \frac{dT}{dt} = (-\Delta H_R) R \quad (3)$$

These are subject to the initial conditions,

$$a(0) = a_0; T(0) = T_0.$$

Equation 2 can be divided by Equation 3 in order to eliminate the nonlinear rate term. Integration of this result gives a relationship between reactant concentration and temperature.

$$a = a_0 - \frac{\bar{\rho}C_p}{\Delta H_R / \nu_A} (T - T_0) \quad (4)$$

Assuming the reaction to be irreversible and first order with respect to each reactant the kinetic rate expression becomes,

$$R = k a b \quad (5)$$

where

$$b = b_0 + \frac{\nu_B}{\nu_A} (a - a_0) \quad (6)$$

or when reactants are initially present in the stoichiometric ratio,

$$b = \frac{\nu_B}{\nu_A} a. \quad (7)$$

Assuming Arrhenius temperature dependence for k , Equations 4, 5 and 7 can be inserted into Equation 3 to give a single nonlinear ordinary differential equation giving the temperature-time dependence,

$$\frac{dT}{dt} = \gamma (T_f - T)^2 e^{-E/R_g T} \quad (8)$$

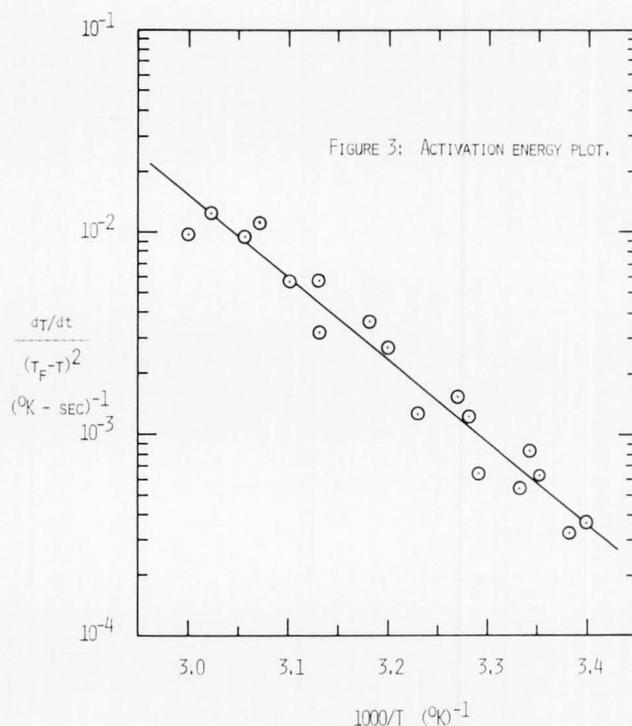
This suggests that a plot of $\log \left(\frac{dT/dt}{(T_f - T)^2} \right)$ versus

$1/T$ should give a straight line of slope $-E/R_g$ if the assumptions made with regard to the rate expression are correct. The pre-exponential factor can then be calculated from Equation 8. The temperature derivative is easy to determine in this experiment since a continuous temperature—time trace is obtained. Typical student results are plotted in Figure 3. As was the case in Figure 2 these data are from experiments run by several different groups on different days. Values of E and k_0 from Figure 3 are given in Table 2. □

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... the exothermic reaction between hydrogen peroxide and sodium thiosulfate has the pedagogical advantage of a non-obvious stoichiometry which can be experimentally determined.



NOMENCLATURE

a, b	reactant concentrations, moles/liter
C_p	solution mean heat capacity, calories/gm-°K
E	activation energy, kcal/mole
ΔH_R	heat of reaction for a given stoichiometry, kcal/mole
k	reaction rate constant, liter/mole-sec
k_0	pre-exponential factor, liter/mole-sec
R	reaction rate for a given stoichiometry, mole/liter-sec
R_g	gas constant, calories/mole-°K
t	time, sec
T	temperature, °K
ΔT	temperature rise, °K

Greek Letters

γ	a constant
ν	stoichiometric coefficient
ρ	solution density, gm/liter

Subscripts

A, B	denote different reactant species
0	denotes an initial condition
f	denotes a final value

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INTERFACIAL PHENOMENA FOR ENGINEERS

A Bridge Between Engineering and Life Sciences

DINESH O. SHAH
University of Florida
Gainesville, Florida

DURING RECENT YEARS it has become increasingly evident that the principles and techniques of chemistry and physics of surfaces are of considerable importance in chemical engineering. Theoretical and experimental research in this area have appeared in the chemical engineering journals under the general title of "Interfacial Phenomena." Therefore, it is not surprising that many chemical engineering departments have included in their curriculum courses on interfacial phenomena or surface and colloid chemistry. In the winter of 1972 I was asked to present three lectures on the principles and techniques of surface chemistry to undergraduate students in chemical engineering as a part of the course on "Materials of Chemical Engineering." I presented an introduction to surface tension, interfacial tension, miscibility of liquids, foams, emulsions and wettability of surfaces. Surprisingly, about 15 undergraduate chemical engineering students submitted a petition to the department requesting that an undergraduate course on interfacial phenomena be offered. At the suggestion of the department, I formulated a course to be given beginning the spring quarter of 1972.

My main objective in teaching this course was not to make every student an expert in surface and colloid science. Rather, the course would offer them a better understanding and appreciation of the principles and applications of surface-active molecules, the properties of surfactant solutions at various interfaces, and also a number of applications such as foams, emulsions, lubrication and flotation of minerals. Among the textbooks available, I suggested *Physical Chemistry of Sur-*

faces by A. W. Adamson. *Interfacial Phenomena* by J. T. Davis and E. K. Rideal was suggested as a reference book. However, it is important to mention that these books were not appreciated by most of the students. The fact that most of the material presented to the class was derived from a number of research papers, review articles, and other specialized books, contributed to their poor appreciation of these books. The course was designed for 3 credit hours and was taught three lectures per week. Instead of giving numerical examples as homework problems, I decided to provide them a number of reprints related to the topics being discussed in the class as required reading material.

TOPIC OUTLINE

The following is a brief outline of the topics followed during the quarter.

1. Introduction: surface-active molecules and five major interfaces; i.e., gas/liquid, liquid/liquid solid/liquid, solid/solid, solid/gas.

2. Properties of surfactant solutions: surface tension, CMC, Gibb's adsorption isotherms, surface excess concentration, solubilization, pH near a charged surface (i.e., surface pH *vs.* bulk pH), effect of salts, chain length, temperature and additives on CMC; cylindrical and lamellar liquid-crystalline structures of surfactants.

3. Spreading of a liquid on another liquid: spreading coefficient, effect of surfactants on spreading of oils, interfacial instability and interfacial tension, surface pressure, Marangoni effect.

4. Spreading of liquids on solids: work of cohesion and adhesion, contact angle and wettability, critical surface tension of solids.

5. Insoluble Monolayers: surface pressure-area curves, cross-sectional area of molecules, effect of temperature on phase-transitions in monolayers,



Dr. Shah received his undergraduate training at the University of Bombay and his doctoral degree in biophysics from Columbia University in 1965. He spent a year at NASA Ames Research Laboratory in California working on chemical evolution and the origin of life, and surface chemical aspects of the origin of membranes. Later he moved to the Biological Oceanography Division of Columbia University and worked on dispersion of oil spills, retardation of evaporation and wave damping by thin films of surface active agents and on surface chemical aspects of sea water. Since 1970, he has been at the University of Florida with a joint appointment in Anesthesiology, Biophysics and Chemical Engineering Departments. Dr. Shah has published in the areas of biological and model membranes, chemical evolution and the origin of membranes, foams, microemulsions, boundary lubrication and surface chemical aspects of vision, and anesthesia. He received the "Excellence in Teaching Award" of the University of Florida for 1972-73.

reactions in monolayers, surface potential, surface radioactivity, surface absorption spectra measurements, surface viscosity and two-dimensional Newtonian and Non-Newtonian liquids, equation of state for monolayers, electrical double layer and Gouy potential, effect of pH and salts on monolayers, surface p_k vs. bulk p_k for monolayers, mixed monolayers and molecular associations in 1:1, 1:2 and 1:3 molecular ratios. Monolayers of biological lipids and the correlations with membrane phenomena.

6. Foams: stability of soap bubbles, rate of drainage, surface viscosity and molecular packing, foam stabilizing and antifoaming agents, foam fractionation and other applications.

7. Macro- and Microemulsions: oil-water-surfactant systems, effect of structure, concentration and chain length of surfactant on emulsion properties, HLB values, spontaneous emulsification, phase-inversion, emulsion rheology and stability, various applications of emulsions.

8. Flotation of Minerals: collectors, frothers, activators, and depressors, selective flotation, absorption of collectors on minerals, contact angle

and flotability, use of oppositely charged collectors, ion-flotation.

9. Friction and Lubrication: Boundary and hydrodynamic lubrication, coefficient of friction, scuff load, percent metallic contact, wear rate, biolubrication, synovial fluid, structure of lubricant additives.

10. Gas/Solid Interface: Physical and chemical adsorption, catalysis, various types of adsorption isotherms, monolayer-multilayer adsorption and capillary condensation, pore volume, hysteresis.

11. Artificial Organs: Nonthrombogenic surfaces, blood-clotting, Heparin, biomaterials, transplants and implants, biological and model membranes, surface chemical aspects of lungs and cornea.

EXPLANATION BY DEMONSTRATION

On several occasions, I gave experimental demonstrations to make concepts clear and interesting. For example, two dimensional liquid and solid monolayers of stearic acid, respectively, on subsolutions of NaCl and CaCl_2 were distinguished by sprinkling talc particles and blowing air toward the particles. For monolayers in the liquid state, the particles move freely in the surface, whereas for solid monolayers, the particles do not move at all. In another experiment on the use of a wetting agent for wettability of surfaces, I dipped a polished teflon bar into aqueous KMnO_4 solution, and pulled it out. The teflon rod remained white because water did not wet the teflon. However, upon adding a few drops of soaps or detergents, when the same process was repeated the teflon became pink when removed from the KMnO_4 solution, suggesting that soap molecules caused water to wet the teflon surface. Many such demonstrations on foams and emulsions made students appreciate the importance of surface chemistry in many engineering applications.

There were two examinations, one mid-term examination and a comprehensive final examination. Here again, instead of giving numerical ex-

The course would offer . . . a better understanding and appreciation of the principles and applications of surface-active molecules, the properties of surfactant solutions at various interfaces and a number of applications . . .

... it was successful in giving a bird's eye view of a number of applications of surface chemistry in chemical engineering ... and ... balancing mathematically oriented courses, such as transport phenomena, process control, and kinetics, with a descriptive and application oriented course.

amples to solve, I submitted extensive multiple choice questions during both of these examinations. Each of the questions tested their thorough understanding of the principle involved rather than any memorization of equations. The questions were phrased in such a way that the possibility of guessing the answer was minimized. I should mention that often students took as much as two and one-half hours to answer 20 multiple choice questions. A few of these questions are mentioned as follows:

1. The contact angles of equimolar solutions of hexanoic acid (C_6-COOH) and decanoic acid ($C_{10}-COOH$) on a copper plate were found to be respectively _____ and _____. (0° , 70° , 110°)

2. An off-shore oil spill decreases the surface tension of air/sea interface to 40 dynes/cm. What should be the spreading pressure (π) of a surface-active agent to push the oil spill away from the shore line?

3. The surface viscosity of monolayers of stearic acid ($C_{17}COOH$) *cis*, oleic acid ($C_8-CH=CH-C_7-COOH$) and elaidic acid ($C_8-CH=CH-C_7-COOH$) *trans* were measured at a surface pressure 10 dynes/cm. The surface viscosities were found to be respectively _____, _____, and _____ centipoises. (3.7×10^{-3} , 4.1×10^{-4} , 9.7×10^{-4})

4. For two sliding surfaces the coefficient of friction was 0.02 and 0.07, respectively, at the load of 1,000 gm and 2,500 gm. Is this hydrodynamic or boundary lubrication?

5. The palmitic acid monolayers were studied at $25^\circ C$, $35^\circ C$, and $45^\circ C$. The average area per molecule at a surface pressure 10 dynes/cm were found to be respectively _____, _____, and _____ A^2 molecule. (28, 21, 35)

The numbers in parenthesis were not correct values, but simply indicated the trend or ordering of values. The first question is based on the effect of chain length on adsorption of surfactant on a solid surface. The second is based on the Marangoni effect; i.e., the surface flow occurs

from a high surface pressure region to a low surface pressure region. The third question is based on the effect of *cis* or *trans* double bonds on the area/molecule or molecular packing and hence on the surface viscosity of monolayers. The fourth is based on the definition of hydrodynamic and boundary lubrication from the variation of coefficient of friction with load. The fifth question illustrates the effect of temperature on the average area per molecule in monolayers.

STUDENT AND TEACHER EVALUATION

AMONG THE 15 STUDENTS who took this course, 12 made more than 85% points on both comprehensive examinations. This was particularly satisfying because more than 60 questions were asked from the materials presented throughout the course. The students were also asked to prepare a term paper on a topic in the general area of interfacial phenomena to be submitted at the end of the quarter. The process of preparing a detailed term paper exposed the students to most of the available sources of information in the area of interfacial phenomena. The quality of the term paper was taken into account in giving the final grade for the course.

I would like to add a note regarding the evaluation of this course by the students in the class. Again, to my great surprise, this undergraduate course on interfacial phenomena brought me the *Excellence in Teaching Award* sponsored by the Standard Oil of Indiana Foundation. The following are a few comments made by students in the teacher's evaluation forms about this course.

"Find a better textbook. . . It would be hard to make improvement in such an excellent course. . . I enjoyed it very much. Best course I ever had in chemical engineering. . . Excellent course and teacher; need better textbook. . . This is the most interesting course I have ever taken. . . One of the most interesting, well taught courses I have ever had. Greatly increased my interest and knowledge. . ."

The course, because of its extreme breadth, could not go into great depth in many of the topics discussed. However, it was successful in giving a bird's eye view of a number of applications of surface chemistry in chemical engineering. This course was successful in balancing a number of mathematically oriented courses, such as transport phenomena, process control, and kinetics, with a descriptive and application-oriented course. The course provided a brief introduction of detergents, foams, emulsions, lubrications, and other biomedical areas to chemical engineering students. I also repeated this course in the spring of 1973

with very similar responses by the students who took it. However, this time I used *Surface Chemistry* by L. I. Osipow (R. E. Krieger Publishing Company, Huntington, New York) as a textbook, which was better received by the students than the previous two books.

I believe a course on interfacial phenomena would be a very desirable part of the undergraduate chemical engineering curriculum, and would contribute greatly in exposing the students to the real systems which chemical engineers are more likely to encounter in their professional careers. □

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THEORY OF DIFFUSION & REACTION

(Continued from page 25.)

The concept of the effectiveness factor does not emerge from this work. The idea of a meaningful fudge factor is peculiarly characteristic of the engineer's need to wrap up the theory in an effective and practical parameter, the physically significant functional of an underlying function.

the solution for first order reversible reaction and comments on a reduction to Fourier's equation when the reaction is irreversible. He concludes with a correct formulation of the non-isothermal problem in which the diffusion coefficients are functions of temperature, remarking "Man erkennt, wie ausserordentlich gross die Schwierigkeiten für eine theoretische Behandlung der Gleichung sind". All in all it is a remarkable paper coming in the early summer of the classical period of kinetic studies and formulating, and where possible solving, equations that were not again taken up until nearly thirty years later. It is interesting to note that the concept of the effectiveness factor does not emerge from this early work. The idea of a meaningful fudge factor is peculiarly characteristic of the engineer's need to wrap up the theory in an effective and practical parameter, the physically significant functional of an underlying function.* When the biochemists examined the question of diffusional hindrance with immobilized enzymes their approach was not that of using a multiplicative effectiveness factor but of modifying the Michaelis constant for the reaction.

Jüttner's paper was followed by another in which he enlarged on the topic of Painlevé's transcendents [7] and a third on the general integrals of "ordinary chemical kinetics" [8], which need not concern us in the context of diffusion. Painlevé had been concerned to find out how transcendental functions were generated by differential equations of the form

$$y'' = R(y', y, x)$$

where R is rational in y' , algebraic in y and ana-

*The concept of the effectiveness factor for these equations probably arose first for the problem of convection from a thin fin. Indeed many of the solutions available for this problem (see, e.g. [100]) can be reinterpreted in terms of first order reaction and diffusion.

lytic in x [9]. In particular he found five canonical forms, the first two of which,

$$y'' = 6y^2 + x, y'' = 2y^3 + xy + \alpha$$

would be applicable to isothermal diffusion and second or third order reaction in the slab. Jüttner's paper is concerned with the conditions under which the equations for a second order reaction may be reduced to Painlevé's canonical form, and the essence of his result is that the quadratic terms in concentration and position must form a perfect square. This is always the case for the symmetrical solution but, in contrast to most writers since his time, Jüttner was concerned to have scope for general boundary conditions and hence allowed for the possibility of unsymmetrical solutions.

Thiele [4] notes that a German patent of 1899 has an implicit reference to the possibility of diffusion limitation in catalysis and that there are two experimental papers reporting the effect of catalyst particle size [10,11]. In one of these Juliard acknowledged that this result "s'explique par le fait que chaque grain constitue un système poreux présentant une surface interne incomparablement plus grande que sa surface apparente" but he was not able to assess this quantitatively. Wicke and Brötz in 1949 [12] were the first to use two sizes of catalyst and to compare their performance in the light of the theory that had by then been developed.

FOUR DIMENSIONLESS GROUPS

AT THE OUTSET OF his great series of papers on the influence of flow, diffusion and heat conduction on the yield of reactors [13,14,15,16,17] Damköhler recognized the importance of four dimensionless groups. The second of these is the ratio of the chemical rate to the diffusion rate and, though this is presented in the context of the tubular reactor, it was obvious that this would also be the key parameter in the study of the catalyst pellet. Indeed in his comprehensive article for the Eucken-Jacob handbook "Der Chemie-Ingenieur", Damköhler [18] expresses the condition for there to be no diffusion limitation in the form

$$\chi_p = \frac{\text{transport time}}{\text{reaction time}} = \frac{\ell_p^2}{2D_p} \frac{4v_j \bar{W}}{d_p \bar{c}_j} < 1.$$

This ratio, in which ℓ_p and d_p are the length and diameter of the pore, D_p the diffusion coefficient within it and $v_j \bar{W}/c_j$ ratio of a mean reaction rate to a mean concentration, is clearly of the same

form as his parameter II for the tubular reactor and the criterion is a valid one. However Damköhler does not appear to have published the solution to the full problem* which, in all cases except that of first order reaction, would be needed to relate the means \bar{W} and \bar{c}_j to observable concentrations.

Zeldowitsch came to "the theory of reactions on powders and porous substances", as he called his 1939 paper, by way of studies on adsorption and heterogeneous catalysis [19,20,21]. He recognized that the porous catalyst would present an intermediate region of internal diffusion limitation between the conditions of small reaction rate when transfer processes would be unimportant and the conditions under which mass transfer to the external surface would control. Without actually solving the differential equations he saw that the depth of penetration would be proportional to $\sqrt{D/kS}$, where D = diffusion coefficient, k = rate constant per unit area, S = internal area per unit volume, and hence the actual reaction rate to \sqrt{DkS} . He observed that an estimate of the activation energy from data in this region would give half the true value and that an n^{th} order dissociation would appear to be of order $(n + 1)/2$. [22]

Thiele [23] considered a straight pore of length

At the outset of his great series of papers on the influence of flow, diffusion and heat conduction on the yield of reactors . . . Damkohler recognized the importance of four dimensionless groups.

$2\ell_p$ opening to a concentration c of the reactant at either end. The concentration $c(x)$ at a distance x from the centre would then satisfy

$$D \frac{d^2c}{dx^2} = kSc^n$$

for the n^{th} order reaction in a slab or

$$\frac{D}{x^2} \frac{d}{dx} \left(x^2 \frac{dc}{dx} \right) = kSc^n$$

for the sphere. He obtained the solution for first

*The solutions are closely related to those given for a chain reaction in slab, cylinder and sphere earlier in Damköhler's article (p. 375).

order reaction in slab and sphere, for second order reaction in the slab and went on to consider the effect of volume change with first order reaction. The solutions and hence the mean reaction rates were functions of the parameter $\ell_p \sqrt{kS/D}$. This parameter is proportional to the square root of Damköhler's χ_D and is the ratio of ℓ_p to Zeldowitsch's penetration depth. The name "Thiele modulus" for this parameter has gained currency and the attribution is not unjust since Damköhler's II was defined in the context of the tubular reaction and the mention of χ_D , though prior to Thiele's work, is a passing one. Thiele presented the solution in the form of plots of the effectiveness factor versus this modulus and it is this concept of the effectiveness factor, or ratio of the actual reaction rate to the rate that would obtain if diffusion were infinitely rapid, that has proved so useful. By definition the effectiveness factor has the value 1 when the Thiele modulus is zero and its asymptotic properties as the modulus becomes large are of interest. It may be noted that Thiele assumed that the concentration of the reactant at the pore mouth would be known whereas Zeldowitsch, though not obtaining any solution of the differential equation, recognized that this concentration might be governed by external mass transfer limitations.

DIFFUSION IN POROUS BODIES

AT THE SAME TIME as these developments were taking place the whole question of diffusion in porous bodies was being opened up by the work of Wicke [24,25] and Wicke and Kallenbach [26], who developed the notion of an effective diffusion coefficient, recognized that surface diffusion could have an important role and did many of the pioneer determinations. Mention should also be made of the work of Wagner of Darmstadt both for its general influence on the work in Germany and for his papers [27,28], the last of which discusses the question of multiplicity of steady states. Damköhler had also been concerned with the temperature rise within a catalyst particle and showed that this could not exceed $(-\Delta H) D_e c_s / \nu \lambda_e$, where ΔH is the heat of reaction, D_e the effective diffusivity, c_s the surface concentration of the reactant with stoichiometry coefficient ν and λ_e the effective thermal conductivity of the pellet. His demonstration for a sphere, repeated later by Wheeler [29], was generalized for any shape by Prater [30], who found that the max-

... "diffusion and chemical transformation" are interdisciplinary considerations. In fact until recently the physiologists' contributions have been almost entirely overlooked by the engineer and vice-versa.

imum possible temperature rise for the dehydrogenation of cyclohexane was some 53°C, considerably in excess of the highest figure of 3°C among Damköhler's examples.

Aside from these references to the internal temperature the non-isothermal equations received little attention until the late 50's, as Wheeler's two reviews [31,29] and the incorporation of the problem in its isothermal form into the pioneer text of Hougen and Watson [32] show. Schilson, working under Amundson's direction, showed how to solve the equations both for single and complex reactions, but the method of iteration that they used did not lend itself to calculating a large number of particular cases and they did not calculate effectiveness factor curves, though they were the first to report effectiveness factors greater than 1. When their work was published [33] it appeared only a short time before two papers giving effectiveness factor curves, but using the positive exponential approximation to the Arrhenius temperature dependence [34,35] and a perturbation solution by Tinkler and Pigford [36]. A year later the comprehensive calculations of Weisz and Hicks [37], which used the Arrhenius temperature dependence of the rate constant, appeared.

The independent and almost simultaneous efflorescence of interest in a particular aspect of the problem was to occur again in the mid-60's when Bischoff [38], Petersen [39] and Aris [40] all called attention to a normalization of the Thiele modulus made possible by the implicit form of the solution for the slab. Aris [41] had earlier (1957) given a normalization with respect to shape and this allowed the solutions for all problems with Dirichlet boundary conditions to be presented as effectiveness factor versus Thiele modulus curves with the same asymptotes at both zero and infinity. The same insensitivity to shape was discovered independently by Roughton in a physiological context [42] but both were ignorant of the fact that Wheeler had stated a similar result without proof as early as 1951 [31].

In the last decade the subject has broken wide open and a rough count of the number of papers published per year has jumped from an average of

3 in the 50's to 12 in the first half of the 60's to 35, 48, 59, 80, 70, 82, 60, 78 for the years 1965 to 1972. Aside from filling in some of the gaps in the steady-state picture the most stimulating activity has been on the question of the uniqueness of the steady state solution, its stability and the form of the transient solution that may arise. The monograph of Gavalas [43] was a pioneering effort in this direction but many other names distinguished in chemical engineering circles—Amundson [44], Denn [45], Hlaváček and Marek [46], Horn and Bailey [47], Jackson [48,49], Lapidus [50], Levich [51], Luss [52,53], McGreavy [54], Schmitz [55], Varma [56], Villadsen [57], Wei [58], are to be found. Mathematicians, such as Cohen and Keller [59], Aronson and Peletier [60], Fujita [61], Kastenbergh [62], Sattinger [63,64] to mention but a handful. Meanwhile results on the steady state solution have continued to accumulate and have been obtained and examined by Bischoff [65], Butt [66], Carberry [67], Chu [68], Finlayson [69], Gunn [70], McGreavy and Cresswell [71], Petersen [72], Ray [73], Rony [74], Satterfield [75], Smith [76], Stewart [77], and Ostergaard [78] and many others. Nothing approaching a comprehensive overview can be attempted here but it is hoped that some sort of picture emerges from the account that I have endeavoured to give elsewhere [79].

But this story has been told from a chemical engineering viewpoint and, as Weisz has pointed out [5], "diffusion and chemical transformation" are interdisciplinary considerations. In fact until recently the physiologists' contributions have been almost entirely overlooked by the engineer and vice-versa. Yet as early as 1928 Hill and Roughton were considering the absorption of oxygen into tissue [80-82] and Roughton's 1932 paper contains solutions of the diffusion reaction equations more detailed than any the chemical engineers were to derive for many years.

PATTERN AND RHYTHM

MORE RECENTLY THE pioneering paper of Turing [83] on morphogenesis has borne fruit

in the effort to show how pattern and rhythm may arise from the interaction of diffusion and reaction as for example in Scriven's work with Othmer [84,85] or with Gmitro [86]. Nicolis [87] has given an excellent review of the work of the Brussels school on dissipative structures and limit cycles [88]. These indeed show some similarities of behaviour to the limit cycles found in non-isothermal catalyst particles [89] but depend for their existence on an autocatalytic step in an isothermal reaction scheme. Allied to this is the current interest in the Belousov-Zhabotinskii reaction [90-93] and other forms of diffusion wave. The simplest wavelike solution of the diffusion equation arising in the one-dimensional propagation of an isothermal autocatalytic reaction

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \kappa c(1 - c)$$

arose as a problem in genetics [94] and was considered in 1937 by no lesser mathematicians than Petrovsky and Kolmogoroff. The development of this theory has been couched in terms of combustion theory [95,96]. Another biological problem that has had a significant input is the stability theory of chemotaxis [97,98,99] in which it is found that a uniform distribution of organisms is unstable and that their aggregation may be accounted for as a transient tending toward a stable non-uniform steady-state.

This by no means exhausts the contributions and interactions with biological problems, but hopefully it will suffice to make us aware of the need to pay attention to what our colleagues in other branches of natural philosophy are concerned with. □

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THE PROJECT APPROACH TO CHEMICAL ENGINEERING-WPI PLAN (Continued from page 15.)

• **Engineering Studies on an Enzymatic Process for Converting Cellulose to Sugars.** This process was developed by scientists in the U.S. Army Natick Laboratories. However, no engineering studies had been performed to obtain data necessary for design purposes. Two groups of Chemical Engineering students (one group of three sophomores and one group of two seniors) worked on the project to obtain some data which would be useful in the design of a process to convert cellulosic wastes to useful food.

Students worked closely with the Natick Laboratory scientists under the direct supervision of the WPI Center Director. They performed experimental studies to obtain rate data in a batch process. They also studied the effects of mechanical stirring, particle size of the ground waste and grinding time on the reactivity of the enzymatic reactions.

In addition to performing experimental work, students also were required to have some specific background in mathematics, biology and engineering for successful analysis of their data. They obtained some of this background from their course work, but had to learn a major portion of the material on their own in order to satisfy their specific needs.

While close supervision was maintained in the Center,

the students were provided with the opportunity to try out some new ideas. For example, one group tried to use ultrasonic equipment to treat the suspension of shredded newspaper and to test its reactivity.

Both groups performed very well in their work. The sophomore group wrote an excellent report detailing their findings and their interpretation of the experimental results. The work performed by the senior group was reported in the student paper session of the ACS meeting in Boston, Mass.

• **Determination of the Effects of *Gymnema Sylvestre* on the Taste Receptors in Hamsters.** This project, which is entirely different from the usual chemical engineering projects, involved one sophomore. She worked closely with a scientist from the U.S. Army Laboratories. As this is a highly specialized field outside that of chemical engineering, a major portion of the supervision was provided by the Army personnel. However, the Center Director still maintained his control of the project by regularly discussing her progress with her. The final evaluation of her report was done by the Director in consultation with the Army personnel.

Hamsters were used as test subjects in this case. The student had to spend a large portion of her time under

close supervision getting familiar with the testing procedures and the handling of the animals. These were done in a closely supervised manner.

After two years' experience, we find the operation of the Center very encouraging. Excellent cooperation has been provided by Natick Laboratories personnel. They have highly praised our students in terms of their working habits as well as their intelligence. The experience was viewed by the students as very valuable.

As the WPI Plan moves into full operation at the upperclass level, project work is expected to consume about half of the total time of the faculty devoted to undergraduate education. The experiences to date in involving chemical engineering students in a wide variety of activities suggest that the transition, though not simple, will be successful. □

CHEMICAL ENGINEERING AT BERKELEY

(Continued from page 10)

Thermodynamics

Experimental and statistical thermodynamic analysis of fluid mixtures. Liquid crystalline behavior and other phase equilibria. Interfacial phenomena. Equations of state based on molecular properties. Electrolyte dissociation and activity-coefficient behavior. Adsorbed state of diatomic molecules. (Bromley, Lyon, Newman, Pigford, Prausnitz, Redlich).

Transport Phenomena

Fluid Mechanics. Laminar-flow systems. Rheology of polymeric systems. Flow of molten alloys. Mechanics of suspended particles. Properties of liquid films. Wave propagation in dispersive media. Mixing and dispersion phenomena in liquids. Drag reduction. (Donaghey, Goren, Newman, Shen, Vermeulen, Wilke, Williams).

Heat Transfer. Nucleate boiling. Promotion of dropwise condensation. Boiling enhancement by additives. Direct-contact heat transfer between immiscible liquids. Thermal conduction of solids. (Bromley, Donaghey, Goren, King, Lyon, Wilke, Williams).

Mass-Transfer Fundamentals. Transport properties of concentrated electrolytes. Absorption with chemical reaction. Atmospheric spread of pollutants. (Grens, Newman, Pigford, Vermeulen).

Separations and Mass Transfer

Gas-liquid mass transfer and accompanying interfacial effects. Computation methods for distillation, extraction, and absorption. Separations of fine-particle systems. Absorption and ion exchange. Oscillatory processes. Foam fractionation. Membrane separations. Separations by freezing. (Goren, Grens, Hanson, King, Klein, Lynn, Merrill, Pigford, Sherwood, Vermeulen, Wilke).

ChE book reviews

Chemical Engineering Thermodynamics: The Study of Energy, Entropy and Equilibrium, R. E. Balzhiser, M. R. Samuels, and J. D. Eliassen, 696 pp. Prentice-Hall, Inc., (1972).

Reviewed by T.S. Storvick, University of Missouri-Columbia

The significant flux of thermodynamics textbooks into the technical literature suggests that there is a general dissatisfaction between authors of these books and those who use them. This book appears to have been conceived in this atmosphere.

The evolution of thermodynamics textbooks indicates that they must now contain the classical material and some new elements:

- It must be written for readers from more than one discipline.
- The particle theory matter must be used in the logical development of the subject.
- The use of electronic computers must be demonstrated.
- Thermodynamics of irreversible processes must be introduced.

The authors have written for Mechanical and Chemical Engineering students (the title is unfortunate in this sense), they have used combinatorial and probability arguments to introduce the entropy function, provided computer codes for several of the calculations in the worked examples and concluded with a short chapter introducing irreversible thermodynamics.

To this reviewer, the relationship that exists between the authors of thermodynamics textbooks and their readers is similar to that of a chef and the clientele of his restaurant. The basic ingredients are always the same but the menu, the division into courses, the spicing and flavoring, and the service and atmosphere are all designed to enhance the practical experience of eating. A satisfactory relationship is established when there is a match between cuisine and palate. It is the same with textbooks.

Most undergraduate engineering students should learn to use classical thermodynamics in their first course on the subject. This book is written for that audience and the authors provide over 90 worked examples and 225 exercises for the student. Some of the exercises will require considerable time to complete. The text is clearly written, the illustrations are generally useful and

there appears to be very few troublesome typographical errors.

The order of presentation is conventional in nearly all respects (except for the introduction of the entropy function discussed below). The thermodynamic functions are introduced in the early chapters, the sections on work producing cycles and fluid flow are expanded to accommodate the needs of the mechanical engineering student. The final 215 pages are devoted to physical and chemical equilibrium of mixtures. A 20 page introduction to the currently important electrochemical processes is also included.

There are some features of the book that may be related to matters of "taste" that this reviewer feels should be discussed in more detail. The mathematical structure of classical thermodynamics is disarmingly simple to undergraduate students who have completed much of their formal work in mathematics. Their concurrent experience with dynamical mechanical systems and the rate processes that are described by more complex mathematical formalism adds to this confusion. The authors never clearly state what experiments establish the relationship of internal energy, volume and composition to the equilibrium state of a system. The mathematical form of the internal energy function as it passes through successive equilibrium states as work is done by the system and heat is added to it is left implicit. This may cause the student more trouble as he seeks to find the relationships between physical systems and the thermodynamic functions.

It is an open question whether statistical thermodynamics should be taught to undergraduate engineering students in their first thermodynamics course. The authors use the mathematics of permutations and combinations to compute the number of distinguishable configurations of a macroscopic thermodynamic system. They then compute the probability p_i that a particular configuration will be found and say, after Boltzmann, that the entropy of that configuration is given by

$$S_i = k \ln p_i.$$

The equilibrium state is then proclaimed to be the one with the maximum probability, $p_{i,\max}$ (and therefore the maximum entropy S_i) consistent with the constraining conditions that there be N particles in volume V with total energy E . None of the statistical thermodynamics formalism is developed and therefore, all of the real compu-

tational power of statistical thermodynamics is lost. The Carnot cycle is used to establish the relationship between reversible heat flow, the thermodynamic temperature and the entropy. It is never clearly established that the total entropy change for all spontaneous processes must be positive and that this is the criteria for all the equilibrium considerations used in later chapters. This presentation does not appear to be a useful way to introduce the entropy function and it cannot be called an introduction to statistical thermodynamics.

One can ask, would it not have been better to use the postulatory approach of Cullen? (*Thermodynamics*, H. B. Cullen, John Wiley, New York, 1960, p. 24-25). This approach establishes the central role of the state function in the mathematical formalism of thermodynamics. It then yields the processes (work and heat flows, mass flows, etc.) by differentiation of the state functions. On page 52, the authors have listed nearly all of the necessary equations to implement this approach. It is still necessary to make the identifications between the mathematical functions and the physical systems that an engineer must make. But, as the authors say, "The utility of the entropy concept depends on relating it to the changes with which we as engineers are involved. Since our concerns are generally macroscopic in nature, it is necessary to associate entropy with macroscopic phenomena, such as heat and work, so that it can be used in the analysis of processes involving these energy flows and interconversions" (page 129). Since the authors follow the phenomenological approach everywhere in their book except for the introduction of the entropy function in Chapter 3, the postulatory approach would be consistent with the presentation they have made. It is also true that the macroscopic descriptions of statistical thermodynamics must be inferred from macroscopic experience whether it is taught before or after a course in applied macroscopic thermodynamics.

There are some specific comments about the presentation that should also be made. The authors have chosen to use the general energy balance for an open system to introduce the relationships between heat and work and the other terms in that balance. The discussion that follows does not establish the important and startling mathematical fact that a conservative or state function, or exact differential of the internal energy written in terms of the physical parame-

ters (for instance, temperature, volume, and composition) is always equal to the heat added to and the work done by the system! Both the heat and work terms are path dependent functions. Once this has been established and is clearly understood by the student, the addition of potential and kinetic energy terms to obtain the general energy balance should cause little difficulty because the students have studied Newtonian mechanics.

The treatment of the entropy function proceeds by writing an entropy balance. It is inferred, but never clearly shown or stated that the entropy is a state function of the same thermodynamic coordinates as the internal energy. The authors use the "lost work" term to account for irreversibilities in a process and therefore do not state the powerful mathematical relationship for all spontaneous processes.

$$\sum_{\text{Subsystems}} \left(\frac{dQ}{T} \right)_{\text{rev}} = dS_{\text{Total}} \geq 0.$$

The authors then write (page 161) "... the third basic equation of thermodynamics (the energy balance and the entropy balance are the other two)"

$$dU_{\text{sys}} = T_{\text{sys}} ds_{\text{sys}} - P_{\text{sys}} dV_{\text{sys}}.$$

This is *not* a third basic equation but rather the combined first and second law equations.

The authors incorrectly state (page 362) that

$$\sum_{i=1}^c n_i d\bar{G}_i = 0$$

is the Gibbs-Duhem equation rather than the previous equation

$$\sum_{i=1}^c n_i d\bar{G}_i = v dP - S dT.$$

The development of the procedures to compute the fugacity coefficient (page 373) does not explicitly state that the integration must proceed on an isotherm (although the original partial derivative that is integrated is clearly marked as taken at constant temperature). Further "... to eliminate computational difficulties in the limit $P^* \rightarrow 0$, we subtract the equation

$$\text{from } \ln(P/P^*) = \int_{P^*}^P \frac{1}{P} dP$$

$$\ln(f/P) = \int_{P^*}^P \frac{v}{RT} dP$$

$$\ln f/P = \int_{P^*}^P \left(\frac{v}{RT} - \frac{1}{P} \right) dP."$$

This is a mathematical problem and the integrand in this final equation still appears to diverge at $P \rightarrow P^* \rightarrow 0$ even with the reassuring statement "we anticipate no further problems arising in the limit $P^* \rightarrow 0$ because the right-hand side remains bounded as P becomes small." This statement could have been made explicit by substituting the compressibility factor $z/P = v/RT$ and using L'Hopital's rule to obtain

$$\lim_{P \rightarrow 0} \left(\frac{\partial z}{\partial P} \right)_T = \frac{B(T)}{RT}$$

where $B(T)$ is the second virial coefficient, a well defined experimental quantity. This procedure not only provides a satisfactory mathematical answer to the problem but provides an analytical method for making the extrapolation.

It is clearly much easier to criticize a book than to write one. The authors have presented their method for presenting thermodynamics to engineering students. They have found this treatment to be successful and this success can only be judged by allowing students to read the book. Their tastes and appetites are nearly always different than those who grew up a decade or two ago.

DEPARTMENT CHAIRMEN

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WATERLOO PROGRAM FOR HIGH SCHOOLS

E. RHODES

*University of Waterloo
Waterloo, Ontario*

“WHAT’S THE DIFFERENCE between Chemistry and Chemical Engineering?” That’s a question often asked by high school students (and teachers and guidance counselors) when they are seeking out a career with a chemistry bias. We have even been asked the question by students who have already chosen to study chemical engineering. The question is no doubt symptomatic of the lack of communication between schools and chemical engineering departments which, to my mind, has arisen because traditionally we could attract all the students we wished to enroll and we were definitely blasé about recruiting. Times have changed however, and now departments are worried about falling enrolments and the solid decline in the overall number of students wishing to study engineering in general and chemical engineering in particular. We must communicate with the schools and somehow we must get across to students and teachers the attractiveness of chemical engineering as a study discipline and career opportunity. In return we need to be educated in the changing patterns of high school curricula so that we are flexible and agile enough to adjust our courses to accommodate the needs and abilities of the new Freshmen. How can we open up this line of communication. No doubt there are many ways tried by many departments across North America and the world.

The Waterloo programme was inspired by my sabbatical experience at the University of Queensland, Australia, where I was called upon to take part in the Chemical Engineering High School Day Programme. This kind of educational programme is aimed at challenging small numbers of interested students to seriously learn about chemical engineering and consider the profession as a career opportunity. In our High School Programme we do not invite busload after busload of uninterested students to the campus and deliver a pep talk, a movie, and a donut in the hope of catching a few. Instead, we send out a limited number of invitations to those students who have

We must communicate with the schools and somehow we must get across to students and teachers the attractiveness of chemical engineering as a study discipline and career opportunity.

a curiosity (be it mild or strong) about chemical engineering.

On a typical High School Day we can entertain about 33 students from outside the university. To these we add 11 of our own volunteer first-year undergraduates, several professors and some graduate student demonstrators. Small groups consisting of three high school students and one undergraduate, tackle four experiments selected from a total offering of eleven. Each experiment takes about one hour to complete and the students have to do the work themselves, although Professors are close at hand to introduce the basic principles of the experiments and answer questions. The experiments have been developed by the Professors of the department and strongly reflect their own interests, thus illustrating the breadth of the Waterloo degree programme and the scope of Chemical Engineering.

EXPERIMENTS TO CHALLENGE HIGH SCHOOL STUDENTS

1. Expansion of the Kitchener waste treatment plant (P.L. Silveston).

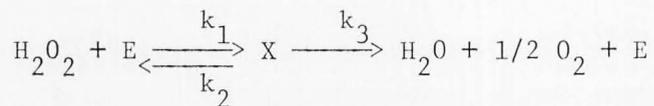
The object of the experiment is to illustrate what goes into process design and how one sets about it. The experiment gives the student a brief introduction to pollution control, computers and computer-aided design. In the explanation of the experiment (we have a High School Programme Manual) the concept of a process system is explained by reference to the present Kitchener (Ontario) Sewage Treatment Plant. It is then shown how the plant can be simulated by use of a digital computer programme. At this stage the

existing programme is handed over to the students and they are requested to find out:

- If the present plant is capable of handling 95% of the Biological Oxygen Demand and Suspended Solids expected in 1985;
- What will be the effect of adding cylindrical tanks in the settlers or rows of square tanks to the aerators;
- What will be the cost to expand the city of Kitchener Plant to meet the 95% target.

2. Enzyme Catalysis (J.M. Scharer)*.

Intended to illustrate the involvement of biochemical applications of chemical engineering, the student is asked to determine the Michaelis—Menten constant for a particular enzyme reaction and the maximum reaction rate for a given enzyme concentration. The reaction studied is



in which E represents catalase, and X an enzyme— H_2O_2 complex. The catalase is synthesized by use of bacteria such as *E. coli*, *B. subtilis*, *S. Faecalis* and *S. Aureus*, while the evolution of oxygen indicates the presence of the enzyme. Having determined the two constants from the system the students are asked:

- To explain why most aerobic organisms can synthesize catalase;
- How a change in enzyme concentration would affect the experimental results.

3. Analog Computation in Chemical Engineering (K.S. Chang).

A short presentation is given to the students in which the general purpose analog computer is described as an orderly collection of amplifiers, potentiometers, resistors, capacities etc. The patch board is introduced and the students are asked to patch up the circuit to be used for generating the $4 \sin t$ and $4 \cos t$ functions. The signals are displayed on an oscilloscope and an X-Y recorder. Among other questions, the students are asked:

- Why the signals produced by the circuit are $4 \sin t$ and $4 \cos t$.
- To develop a circuit diagram which would generate $4 \sin(10t)$ and $4 \cos(10t)$.

*Gorber, D.M. and Scharer, J., CEE 5 (2), 141 (1971).

4. An Advanced Analog Computation Problem (T.Z. Fahidy).

Following on from experiment (3) the students investigate the oscillatory behaviour of the Van der Pol Equation. Having done this the students then go on to:

- Sketch the shape of the limit cycle at various potentiometer settings and describe the findings.
- Discuss the practical use (if any) of such an electronic circuit.

5. Elastomers—A Fourth State of Matter? (B.M.E. Van der Hoff).

After a general introduction to the concept of viscoelasticity and the chemistry of rubber, the students use an Instron tester to investigate the properties of natural rubber and polyvinylchloride softened by the addition of oil. For example an elastic band is elongated in the machine and the force acting on the band is measured against time at constant elongation. The sample is then heated

We sent out a limited number of invitations to those students who have a curiosity about chemical engineering.

and the experiment repeated. Hysteresis is measured in the form of a force-elongation curve. Typical questions asked of the students are:

- What is the value of the initial modulus at small elongation and the modulus just before break?
- Why is the area of the hysteresis loop larger for the polyvinylchloride than for the natural rubber?
- Why does a sample not return to its original length?

6. Experiments Demonstrating some Industrial Electro-Chemical Processes (K. Enns).

The objects of this experiment are to demonstrate a) the electrowinning of copper, b) electro-etching and c) brass electroplating. It is explained that all electrochemical processes found in extractive metallurgical, metals refining and finishing industries involve cells containing anodes and cathodes. The students find out by experimentation the amount of copper won per kilowatt hour and calculate the energy cost per ton of copper. Then by building a cell using graphite for the anode and a partially covered copper sheet for the cathode, electroetching is discovered, and the

amount of copper removed during the etching process is calculated. Finally another cell using a sheet steel cathode and a brass anode is built to enable the plating of the steel. Cu-Zn-cyanide solution is used in this experiment. Typical of the questions posed to the students at the end of this session are:

- Why is brass plated from a Cu-Zn cyanide solution?
- Why not plate brass from a much less poisonous CuSO_4 - ZnSO_4 solution?

7. Waste Water Renovation by Ion Exchange and Adsorption (K. Enns).

This experiment is designed to demonstrate the demineralization of water by cation/anion exchange and colour removal by adsorption. A "waste water" sample is renovated firstly by exchanging all positively charged ions in the waste by H^+ using a cation exchanger. After testing for metals by atomic absorption, the solution is treated with an anion exchanger and then activated charcoal. By now the original murky solution is quite clean. The students are asked typically:

- Is it economically feasible to use ion exchangers to treat concentrated solutions?
- Can you suggest a reason why ion exchangers generally prefer (are selective for) bivalent and trivalent species over univalent species?

8. Determination of Lead in Gasoline by Polarographic Analysis (K. Enns).

Here the students find out what is meant by the polarographic method of analysis and determine the concentration of lead in a typical sample of gasoline. The significance of the typical 'S' shaped polarogram is explained and the students firstly calibrate a machine by making up a known sample containing lead nitrate, and secondly, investigate the unknown gasoline sample previously extracted into an aqueous solution. Typical questions to round off the session are:

- In what form is lead usually present in gasoline?
- Why can't we carry out polarographic analysis directly on the gasoline sample?

9. Determination of a Chemical Reaction Rate Constant By Thermal Analysis (K. Enns).

By a simple thermal analysis method the reaction rate constant of the catalyzed reaction between n-butanol and phenyl isocyanate is deter-

mined. The principles of heat of reaction and reaction kinetics are explained, and the students after being presented with an adiabatic reactor (thermos flask), magnetic stirrer, thermometer and automatic delivery syringe are put to work. The students are asked typically:

- Is it reasonable to assume that the thermos flask approximates an adiabatic reaction?
- Is the rate constant data obtained in this way useful? Or is it just an academic exercise?

10. Measurement of Liquid Flow (J. D. Ford).

It is explained that an important problem frequently encountered by engineers is that of measuring the rate of flow of a liquid. Whether it is the flow of a river or the flow of water into a kitchen sink, a few simple principles enable such measurements to be accurately made. The students are asked to investigate the use of an orifice for

One student presented the enzyme experiment in the form of a series of cartoons of whale-like bugs gobbling up molecules and burping up the new ones all over the place.

measuring the flow from a large variable head tank. The students discover the relationship between mean velocity in the orifice and head of fluid and are finally asked the following:

- A one pound ball falls to the ground from a height of 2 ft. At what velocity does it hit the ground?
- Considering the above question is related to our graph of $\log(\text{velocity})$ versus $\log(\text{head})$, what is the theoretical value of the exponent n in the relationship $(\text{velocity}) \propto (\text{head})^n$.

11. Flow Through Porous Media (F.A.L. Dullien).

In part one of the experiment the students are set the task of measuring the permeability of a porous material consisting of a packed bed of glass beads or sand by establishing the relationship between pressure drop and flow rate across the sample. In the second part of the experiment the students observe the phenomenon of dispersion by use of a dye tracer injected into the flow of a packed bed. Typical questions are:

- What is the permeability of a non-porous substance?
- What factors may influence dispersion in porous media?

BULL SESSION

When each group has completed four experiments it must prepare a two minute verbal report on the final experiment. This report is presented at the closing session of the day. Half an hour is allotted for report preparation and the usual visual aid materials are provided for the assistance of the students. The reports have been remarkable for several reasons. For example, the students have been seen to respond amazingly well to the challenge and have quickly learned the principles on which the experiments are based. Secondly, it has been worth noting how interesting and often amusing the students have made their two-minute presentations. One student presented the enzyme experiment in the form of a series of cartoons of whale-like bugs gobbling up molecules and burping out new ones all over the place.

Each group having made one report, the whole programme of eleven experiments is covered and the final half hour is devoted to informal open discussion. It has been our experience that at this stage, most of the barrier of shyness has been broken down and everyone is anxious to get a word in. Our own undergraduates make a big contribution to the discussion. Marilyn was a very glamorous first-year chemical engineer in 1971 and she came to all our High School Days in flaming hot pants. When one High School threw out the question "What was it really like to be a chemical engineering student?", it was answered by Marilyn with a very eye-catching gesture and one word "Fabulous." Despite the fact that from then on, the Professors thought Marilyn was our best advertisement, she left us at the end of the year for academic reasons, a very sad departure for one and all.

EFFECTIVENESS OF THE PROGRAMME

So far the only method of measuring the effectiveness of the programme has been to ask the students for their opinions at the end of the day and to observe the reactions of both students and professors in the laboratory and in the culminating group discussion.

Nearly all the students responding to a questionnaire say the programme is suitable for

One fellow suggested we insert a steak dinner into the program and another felt the program would be helpful for his school teachers.

Grades 12 and 13 High School Students but *not* for Grade 11. Most of the experiments were judged to be correct level of difficulty, although most problems were caused by the analog computer experiments and least difficulty was experienced in the waste water treatment and fluid flow experiments. Many students would have liked an extra day to do *all* the experiments and most felt they had learned a lot. Several students indicated that the opportunity for discussion was a very important factor contributing to the success of the programme. One fellow suggested we insert a *steak* dinner into the programme and another felt that it would be very beneficial for his school teachers. This last comment prompted us to invite the local School Teachers' Federation to include an evening of working in our laboratories on their Professional Development Programme. One such evening has now been held with enormous success. The format was the same for the teachers as it was for the students and the closing discussion provided a real opportunity for the exchange of ideas on education.

It has been mentioned that first year undergraduates were also used in the programme. Their reaction has also been very positive and we are considering offering the programme to all the Freshmen during registration week. Its purpose here will be to break down the barriers between Faculty and students almost before they have time to be erected, and to motivate the students by providing them with a broad view of the department at the very beginning of their university career.

Does our programme answer the question "What is the difference etc. . . .". At least it illustrates the breadth of interest of chemical engineering, which we believe is one of its most attractive features. It also provides a forum where all kinds of people by working together, find communicating questions, answers and ideas to be very easy.

The High School Programme Manual can be obtained by writing to Professor E. Rhodes, Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada. Please enclose a cheque for \$2.00 to cover the printing and postage costs. The cheque should be made payable to Chemical Engineering, University of Waterloo. □

A JUNIOR COURSE IN CHEMICAL ENGINEERING COMPUTATIONS

E. M. ROSEN
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IN THE SPRING of 1973 the author was asked to develop a three unit course in chemical engineering computations based on the text "Material and Energy Balance Computations" by E. J. Henley and E. M. Rosen.¹ This was to be the second semester course in the two semester Elements of Chemical Engineering sequence for third year chemical engineering students at Washington University, St. Louis. It was a listed prerequisite for the senior Systems Analysis and Design course.

Typically at this stage, students have had a course in thermodynamics, and a course in the use of mathematics and the methods of engineering in the analysis of chemical and physical processes. In addition, they have had a course in basic chemical process principles including stoichiometry, ideal gas law and gas mixtures, vapor pressure, solubilities and energy balances. Only those interested (about 1/3 to 1/2 of the students) had taken the optional one unit digital computer programming course. In general, the student had not used the computer as an integral part of his previous course work. The traditional unit operations courses covering such topics as distillation, absorption and heat transfer were no longer offered, though a two semester junior sequence in transport phenomena was a listed requirement.

The basic approach to the material in the text has been described previously.² Major emphasis was given to the machine methods chapters in the text, chapters 5, 8 and 9. Table 1 gives the general outline of the course and the number of sessions devoted to each topic. Each session was scheduled for 75 minutes twice a week in the evening hours. Almost one third of the course was devoted to graphical methods in distillation and absorption. This was done in part to fill the lack of exposure to the unit operations. Outside reading^{3,4} was used in support of this portion of the course in addition to the use of a secondary text.⁵



Edward M. Rosen received his BS and MS from the Illinois Institute of Technology and his PhD from the University of Illinois. Currently he is a Science Fellow and Manager, Systems Technology at the Monsanto Co. where he has been since 1959, except for a postdoctoral academic leave at Stanford University in 1962-3. With E. J. Henley, he is co-author of the text "Material and Energy Balance Computations". (John Wiley, 1969)

CONDUCT OF THE COURSE

THE COURSE WAS A traditional lecture type with homework (which was not graded) assigned from the text or specially designed and handed out. In addition the class was divided into teams of three persons each for the purpose of doing the five computer problems that were assigned and which formed 20% of the course grade. The reason for the teams was two-fold:

- Some members of the class did not know FORTRAN programming.
- It was desired to hold the computing bill down.

Eight one hour exams, of which only the highest six were counted, (60% of grade) were given, plus a final (20% of grade). The comparatively large number of exams was designed to prevent members of the class from falling behind and to provide them a means of gaining new insights to the topic areas. The number of exams received little class criticism though not grading the homework (though it was always discussed) apparently gave the students little motivation for doing it.

THE COMPUTER PROBLEMS

THOUGH THE COMPUTER problems were intended to be a major portion of the course they were weighted comparatively lightly since knowledge of F ϕ RTRAN was not a course prerequisite. It was intended that every member of each team would participate equally in the computer problem analysis and that those members knowledgeable in coding would teach the un-knowledgeable ones. This, it was felt, closely

TABLE 1—COURSE OUTLINE

Session Numbers	Topics
Part A. Chemical Process Calculations	
1-2	Course Conduct Review of General Energy and Material Balance Equations
3	Matrices and Vectors
4-5	Independence, Orthogonalization and Rank. Solution of Linear Equations and Material Balances
6-7	The One Dimensional Nonlinear Equation and Flash Calculations
8-9	Chemical Reactions and Their Independence. The Extent of Reaction.
10	Chemical Equilibrium
11-12	Energy Balances: Adiabatic Flash and Adiabatic Flame Temperatures.
Part B. Distillation and Absorption	
13-14	Binary Distillation—The McCabe-Thiele Method.
15-16	Minimum Stages and Minimum Reflux. Analytical Shortcut Methods.
17	Multicomponent Methods—Tridiagonal Equations
18-19	Absorption—Graphical and Analytical Methods
Part C. Plant Simulation	
20	Streams and Building Blocks
21	The Split Fraction Concept
22-23	Partitioning and Tearing Equations. The Convergence Block Concept
24	Direct Substitution and Wegstein's Method
25	Information Feedback
26	Comprehensive Flow Sheet Calculations

The intent was for the student to formulate the problem, code the main program but let the subroutine do the tedious work of computation.

paralleled the environment found in industrial organizations. Each member of the team was required to hand in a problem analysis though only one computer output per team was required. However, this did not turn out satisfactorily, since the knowledgeable F ϕ RTRAN students spent a disproportionate amount of time coding and debugging the computer problems while the others spent comparatively little time.

At the start of the course source decks for the four F ϕ RTRAN subroutines listed in the rear of the text¹ were handed out to each team. (This was necessary since only the WAT IV compiler which required all source coding could supply adequate turnaround). The four subroutines supplied to each team were:

GSMT	Gram Schmidt Orthogonalization
GELG	Simultaneous Linear Equation Solver
ROOT	One dimensional Root Finder
BS ϕ LVE	Simultaneous Nonlinear Equation Solver

The intent was for the student to formulate the problem, code the main program but let the subroutine do the tedious routine work of computation. The five problems were either formulated by the author or adapted from the recently released CACHE committee volume of computer programs on Stoichiometry.⁶ Table 2 lists the titles of the problems for the course and the subroutines which were to be used.

COURSE EVALUATION

A TOTAL OF ELEVEN students enrolled in the course and were asked to fill out a questionnaire at the conclusion of the course. The questionnaire asked the student to rate each of the computer problems for instructive value and interest. Other questions relating to the usefulness of the computer problems and course organization were then asked. Finally the student's response to specific topics was queried. Table 3 lists the raw responses of the class to the questionnaire. Overall the course elicited a broad range of

rather strong responses. Students with an adequate computer background appeared to respond favorably while those without the background appeared to be much less satisfied. There appears little question that a prerequisite for the course should be coding proficiency in FORTRAN by all participants.

TABLE 2—COMPUTER PROBLEMS

Problem	Description	Use of Subroutine
1. A.	Inconsistent and Incomplete Material Balances ¹	GSMT
B.	Linear Material Balances ¹	GELG
2.	Flash Vaporization	ROOT
3.	Simultaneous Gas Phase Equilibrium Reactions	BS ϕ LVE
4.	Theoretical Maximum Flame Temperature ²	ROOT
5.	Recycle Calculations Using Split Fractions	GELG

1. Taken from Reference (6), p. 85, 147.
2. Adapted from (6), p. 198.
3. Copies of the problems may be obtained from the author on request.

The use of teams seems to be little justified. Students complained that only one person on the team did all the work and were not sufficiently credited for their effort. There seemed little basic difficulty with the level of the course material in the text though some complaints were recorded about its clarity in places.

Efforts were made continuously to relate the numerical methods portion of the course to direct applications though it should be noted that the text separates these functions for ease of reference and development. This meant considerable jumping around in the text and required carefully planned reading assignments.

Rather strong interest was displayed in the unit operations section of the course as evidenced by the desire for more time to be spent in this area. No time was spent on heat transfer calculations and this would certainly be an area for course expansion. Whether or not the course was best separated into its three distinct parts or could better be integrated into a single topic called process simulation is unclear at this time. □

Efforts were made continuously to relate the numerical methods portion of the course to direct application.

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TABLE 3—RESPONSE TO QUESTIONNAIRE

Questions 1-5: Computer Problems

	Material Balance	Flash	Equilibrium	Max. Temp.	Split Fraction
Very Instructive	1	3	2	1	
Instructive	8	5	6	5	3
Adequately Instructive	2	3	2	1	4
Not Instructive					1
Very Interesting			3	1	1
Interesting	5	6	1	3	4
Fairly Interesting	3	2	4	6	3
Dull, Dull	1	1	1		

6. The computer problems

Added substantially to the course.	4
Added to the course	4
Added marginally to the course	3
Detracted from the course	—

7. Supplying the subprograms

Was very useful and did not detract from the problems	10
Was useful but made the problems less instructive	—
Marginally useful	1
Was a poor idea	—

8. The course was				
Well organized				5
Fairly well organized				5
Adequately organized				1
Poorly organized				—
9. Topic				

	Should be Ex- panded	Re- duced	About Right	Dropped
A. Phase equilibrium	3		8	
B. Inconsistent material balances	2	1	7	1
C. Chemical reactions	7		4	
D. Distillation	5		6	
E. Absorption	7		4	
F. One dimensional equation solving	2	2	7	
G. Multi-dimensional equation solving	4		7	
H. Plant simulation	5	1	4	1
I. Matrices and vectors		1	10	
J. Energy balances	6	1	4	
K. Independence and orthogonalization		5	6	

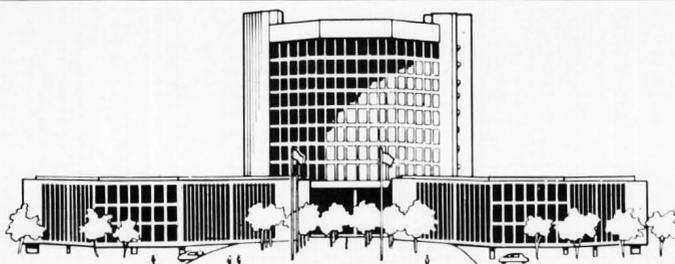
CHEMICAL ENGINEERING DIVISION ACTIVITIES



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The suggestion for the new visitation program was made by Prof. L. E. Scriven of the University of Minnesota, a former award winner and transmitted to 3M by Prof. Leonard Baker when he served as Division Chairman. Announcement of the increased support was made by W. W. Burton of 3M to Dr. George Burnet of Iowa State University, who participated in the discussion with 3M and was instrumental in obtaining the original grant from that company.



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