

CHE

chemical engineering education

VOLUME XIX

NUMBER 2

SPRING 1985



CHEMICAL ENGINEERING DIVISION OF AMERICAN SOCIETY FOR ENGINEERING EDUCATION

JOE HIGHTOWER

of Rice University



Award Lecture...

Semiconductor Chemical Reactor Engineering and Photovoltaic Unit Operations
T. W. F. RUSSELL

and...

Classical Solution Thermodynamics: A Retrospective View
VAN NESS, ABBOTT

An Improved Design of a Simple Tubular Reactor Experiment
ASF0UR

Use of Computer Graphics to Teach Thermodynamic Phase Diagrams
NAIK, CLANCY, GUBBINS

The Nature of Adjoint Variables and Their Role in Optimal Problems
CROSSER

The B.C. (Before Computers) and A.D. of Equilibrium-Stage Operations
SEADER

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CORNELL UNIVERSITY**

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Joe Hightower

of Rice University

JOYCE TABER
Rice University
Houston, TX 77251

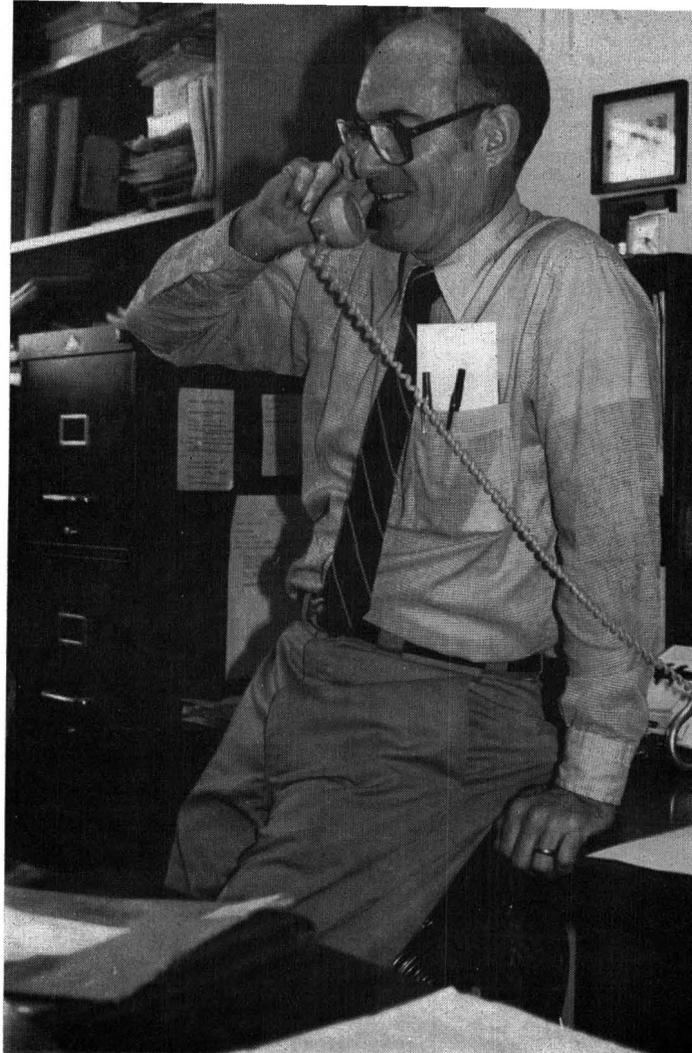
"I'VE BEEN DELIGHTED to be where I am," says Dr. Joe Hightower in regard to his decision 17 years ago to become a chemical engineer and an educator as well.

Joe Hightower, of the chemical engineering department at Rice University in Houston, says he started out like many other members of engineering faculties: "I started as a child by taking things apart—bicycles, motorcycles, clocks, everything!" As early as the fourth grade he proceeded to take his clarinet apart and to rebuild it shortly after he began taking music lessons. Then throughout high school, in addition to becoming an accomplished musician as a member of the all-state band, he made a veritable career out of repairing the instruments of the other band members.

While he was in high school Joe also decided to study chemistry. Later he obtained his masters and PhD in chemistry from Johns Hopkins but couldn't decide if he wanted to do industrial research or academic work. It was during a three-year stint at the Mellon Institute that he decided to teach. "I found that I enjoyed the interaction with the students, the stimulation of the faculty, and the flexibility of the job."

He found he had to make another decision, however—whether to go into a department of chemistry or chemical engineering. "All my educational background was in chemistry, but I had a philosophical desire to work on things that have very practical uses," he says.

However, chemistry departments were moving in the direction of quantum mechanics and other more esoteric areas while chemical engineering was moving from unit operations into engineering science. Thus, chemical engineering embraced catalysis, and Joe Hightower embraced engineering.



It happened at that time that heterogeneous catalysis, the research area in which Joe was interested, was a field that had been explored primarily in chemistry departments. However, chemistry departments were moving in the direction of quantum mechanics and other more esoteric areas while chemical engineering was moving from unit operations into engineering science. Thus, chemical engineering embraced catalysis, and Joe Hightower embraced engineering.

Since then, Joe's research philosophy has been directed toward providing new insights into how existing catalysts work as opposed to discovering new catalysts. "We try to ask the question 'Why?'" he says. Using his chemical training, Joe has worked at gaining information about the chemical nature and concentration of active sites, the influence of solid state parameters in determining activity and selectivity, and the mechanisms of reactions that occur over solids that are of interest to the petroleum and petrochemical industries. He and his students have extensively used isotopic

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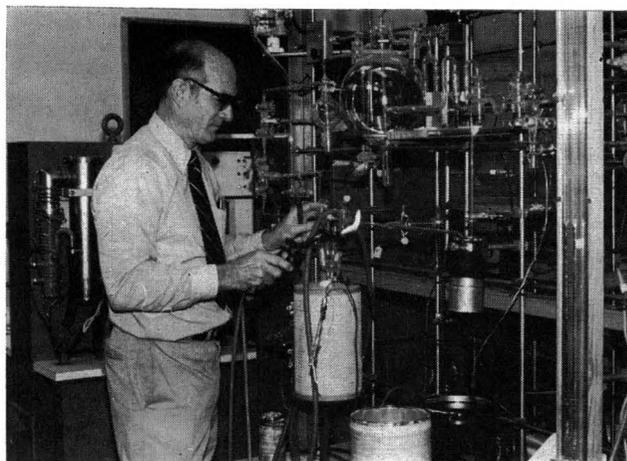
tracers (both stable and radioactive) to study the kinetics, reaction networks, rate limiting steps, and incorporation of surface species into product molecules. (Some of his work has been summarized in an earlier issue of this journal, Vol. XVI, No. 4, p. 148, Fall 1982). A few of the catalyst systems that his group has studied include cracking catalysts, auto emission control catalysts, partial oxidation catalysts, and zeolites.

But Joe's research does not stop at the graduate level. Several years ago he incorporated some research techniques into a sophisticated undergraduate experiment. While taking his kinetics and reactor design course, junior level students now investigate all the kinetic parameters for cumene dealkylation over a silica-alumina cracking catalyst, explore the reaction mechanism with deuterium tracers and a mass spectrometer, and determine the surface area of the material. From their results the students are able to calculate the true surface reaction rate constant, the concentration of active sites, the turnover frequency, and the role of intraparticle diffusion on the kinetics (*Chem. Eng. Educ.*, p.118, Summer, 1969). This experiment allows the students to determine experimentally many of the parameters that are useful in scaling up such reactions from laboratory to plant size.

Joe's research has led him into other situations which he has especially enjoyed. In the early 70's, for example, he was chairman of several National Academy of Science panels which were assigned the task of assessing the feasibility of using catalytic converters to decrease pollutants from automobiles. "No one had ever applied catalysts in this way, and we were assigned the task of determining if these devices would in fact work," he says. "It was fascinating. There was a lot of secrecy. No company would tell us directly what they were doing, but they would tell us what they thought the other companies were doing, and we had to try to put together a clear picture. Once I was asked to testify before the House of Representatives Committee on Science and Technology which was chaired by Representative George Brown of California. The congressman from Detroit would say things like, 'I want you to know that people from my district are being put out of jobs because of government regulation and control.' Brown would respond, 'People in my district in California are dying because we don't have enough controls, and pollutants are killing people.' How can one give an objective testimony

in an atmosphere like that!"

Involvement in professional societies has been another rewarding part of Joe's career. He is currently chairman of the 24-member Petroleum Research Fund Advisory Board, a group that is responsible for a corpus of \$150 million. This year the foundation will donate \$11 million for university research in petroleum-related areas. In 1971 he received the National Award in Petroleum Chemistry from the American Chemical Society.



Joe finds time to enjoy simple, relaxing activities, such as blowing glass in his lab.

As a councilor for the American Chemical Society, he represents the southeastern Texas local section. He has been on the national research committee and is on the national awards committee of the American Institute of Chemical Engineers. He has also served as chairman of the petroleum chemistry division of the American Chemical Society.

Dr. Hightower has over 50 publications to his credit and is also very much involved in presenting short courses for industry. "Catalysis," he says, "is a field that is not taught in many universities as an area of specialization. Yet, 80 or 90% of all commercially important chemical reactions are catalytic reactions. People are trained as organic chemists, physical chemists, or chemical engineers and then learn about catalysis on the job. This creates a great demand for the types of short courses that we instituted at Rice years ago and that are being continued in cooperation with other schools such as the University of Houston."

It would appear that Joe's day would have to last more than 24 hours in order to accomplish his many activities. Yet, there is still another part of his life that is as important to him as his pro-

. . . there is still another part of his life that is as important to him as his professional work. In 1968 he was a leader in establishing the Human Resources Development Foundation . . . (which) provides free temporary housing for needy families who come for treatment to the Texas Medical Center hospitals.

fessional work. In 1968 he was a leader in establishing the Human Resources Development Foundation. The foundation provides free temporary housing for needy families who come for treatment to the Texas Medical Center hospitals. The foundation started as a project at Dr. Hightower's church and has expanded to serve over 700 families from over 38 states and 26 foreign countries in the last 16 years. Joe is president of the foundation whose facilities have grown from an old army barracks into 15 beautiful apartments. He heads a group of approximately 40 dedicated volunteers who minister daily to the needs of families who are under enormous stress.

"All a person needs to move in are pajamas and a toothbrush!" Joe laughs. But his statement



Human Resources Development Foundation apartments.

is very accurate. The apartments are furnished down to the pots and pans. A local church even provides meat once a week for the residents. Social workers, ministers, and even former residents refer potential patients. Selection is made on a first-come, first-served basis without regard to race, creed, sex, religion, age, or level of disability. Need is the sole criterion used to determine eligibility. Residents are allowed to stay for up to three months.

"The project is valued at over a half-million dollars, and most of it has been given because of something Joe has done," states Marge Norman, Vice-President of the foundation. "Joe never hesitates to go speak to a group if there is some chance that they might have an interest in the founda-

tion. His work takes him to the far reaches of the U.S. and overseas; on every airplane trip he takes he makes sure his seat partner is very well acquainted with his pet project, and it often leads to very good things for this foundation."

Senator Orrin Hatch was one of the latest people to hear about the foundation because of one of Joe's "airplane contacts." Joe sat next to a member of Senator Hatch's staff on one flight, and later he received a letter from the senator, who had been informed by the staff member about the foundation. The letter commended Dr. Hightower for his charitable work.

Continues Mrs. Norman, "Even though we have a foundation board which is functioning very well, without Joe I don't know if the Board would have been as effective or if this place would have become what it is today. He loves it so much, and he works so hard. A couple of times each year we have a work day when all our volunteers come to clean, repair, and paint. All kinds of people are represented in the workers. Joe is always the first here and the last to leave, working at anything that needs to be done. Even before he comes over, he gets up before dawn and bakes bread so that at 10 a.m. we can have hot bread and butter and coffee. We've been acquiring land to build more apartments next door, so you can be sure he's on the campaign trail again! We have parties for our residents, and again, Joe is always here with bread he has baked. He even brings his mandolin and plays and sings. There's not much Joe can't do!"

On any given day the facility may house people from Florida, or from various towns in Texas, Columbia, or Indiana. There are no class distinctions. Last winter a brain surgeon from Mainland China was allowed to leave his country with only \$200 when he came to care for his quadriplegic daughter in the medical center. As a resident of the foundation's apartments, he scrubbed floors and took a lot of good-natured ribbing when he painted an outside door with interior paint. Something all residents share, however, is gratitude to Hightower, who personally greets each newcomer with a loaf of bread, and gratitude to the foundation he helped establish.

Wrote one resident, "What a tremendous help this facility has been to us. Each of us is faced with an extremely serious medical problem, and the expenses are staggering. To be sure, the financial savings are important, but even more, we have a place to call 'home' and people with whom we can talk as friends. I'm one of the lucky ones. Two weeks ago I had a kidney transplant, and now I am hoping and praying that my body will not reject it. I have been so impressed by the consistent care and visits that I've had from the jogger (Dr. Hightower) and his friends even during my recovery from surgery. I hope in some way I can repay the favors done for me. Right now, though, I'm going to sit back and enjoy another slice of the hot bread Joe Hightower has brought me before it has time to lose its flavor!"

In his professional life also, colleagues have only good things to say about Joe Hightower. Dr. T. W. Leland who was department chairman when Joe came to Rice says, "I was impressed with him right from the start, and I had a great interest in getting him to come to Rice. I think it's been a first-rate choice. He's done a remarkably good job over the years. He's an excellent teacher and has had an active research career. He is well thought of by his students and has perfected a graduate course in kinetics and catalysis to a high degree. He has been effective in giving short courses and he is outstanding in his volunteer public service. Personally, he is outgoing, friendly, and extremely well-organized. He has excellent rapport with people in all walks of life, from the top of the technical ladder in terms of ability to students not doing too well in their courses. He's a remarkable individual who has been a great addition to our department."

Joe is modest in describing his daily activities. "I just enjoy it all," he says. He gets up at 4:45 every morning to jog and share breakfast and a Bible reading with his wife Ann, a chemical engineer who works for the Exxon Chemical Company. By 6:30 a.m. he is at work, doing all the things he loves to do. "From the very beginning I couldn't make up my mind about what I wanted to do. I wanted something in both industry and the academic world. Now I have both, and I'm grateful for that. I probably border on getting involved in more things than I should . . . but they're all so interesting! I guess I just like being where I can interact with people and see them grow, whether it's at the university or whether it's with people who are hurting." □

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Olin Hall from the west.

ChE department

CHE AT CORNELL UNIVERSITY

JULIAN C. SMITH AND PAUL H. STEEN
Cornell University
Ithaca, NY 14853

FOUNDED IN 1868 AND with a long tradition in engineering, Cornell is almost unique in being both private and state-supported; about half the divisions, including engineering, are privately endowed while the other half are funded by the State of New York. An awkward arrangement, it would seem, but it works surprisingly well.

Cornell, a medium sized university with a total enrollment of some 18,000 students, is set on a hill overlooking the city of Ithaca, and the waters of Cayuga Lake, the largest of the Finger Lakes. Ithaca is small but strongly cosmopolitan. The setting is semi-rural; the scenery is beautiful; the air is clean. Almost the only drawbacks are a modicum of cold gray weather on occasion, and some possible difficulties in travelling in and out.

Ithaca has been called "the most centrally isolated city in the Northeast," but as a graduate student from Greece recently remarked, "If it wasn't for the weather, Ithaca would be Paradise!"

The School of Chemical Engineering has 18 faculty members, about 100 undergraduate students (3rd and 4th years only), and over 65 graduate students. During the past twelve years research activity and expenditures have greatly increased, and strong research programs have been established in fluid mechanics, polymers, surface science and catalysis, thermodynamics, and biochemical engineering. The number and quality of MS and PhD candidates (especially PhD's) have risen rapidly. The growth in research, however, has not reduced the traditional concern for undergraduate and professional graduate teaching. All faculty members are expected to teach undergraduate courses, and many participate in advanced design projects in the professional Master's program. The school occupies its own building (shared with a few other tenants) with

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a total area of some 90,000 square feet, 54,000 of which is exclusively chemical engineering.

A BRIEF HISTORY

At Cornell, as at many institutions, chemical engineering began in the Chemistry Department, but its development was somewhat unusual. Very early (before 1900) courses were offered in industrial chemistry which had a considerable practical flavor; as taught by Fred H. "Dusty" Rhodes in the 1920's they dealt with the principles and practice of chemical engineering. By 1930 Dusty had established both undergraduate and graduate programs in chemical engineering, but because of rivalries between Chemistry and the Engineering College the undergraduate program had to be a 5-year-long hybrid: four years in Arts and Sciences (leading to the degree Bachelor of Chemistry) followed by one year in engineering (for the degree Chemical Engineer).

In 1938 the department with its three faculty members became part of the Engineering College and the 5-year program led to the degree Bachelor of Chemical Engineering. In 1942 chemical engineering moved to Olin Hall, the first building on what was to become engineering's new quadrangle. It was at a considerable distance from chemistry and the old ties quickly weakened. After World War II all the undergraduate engineering programs at Cornell were lengthened to five years. This lasted until 1965, when the present 4-year BS programs, including that in chemical engineering, were established.

Dusty Rhodes was director of the school until he retired in 1957 and Charles C. "Chuck" Winding took over. Ken Bischoff, now at the University of Delaware, was director from 1970 to 1975; Julian Smith from 1975 to 1983; and Keith Gubbins from 1983 to date.

For many years chemical engineering at Cornell was known for its strong undergraduate program. Rhodes felt that good teaching was the most important thing required of a faculty member and while ability to do research should be considered in reviews for promotion or tenure, it should not be a major factor. This is not to say that there was no research or graduate work. Between 1932 and 1970 the school awarded 140 MS and 104 PhD degrees, and many of the recipients have had distinguished careers in industry and academia, including John Prausnitz (Berkeley), Ed Lightfoot (Wisconsin), and a string of past

or present heads of chemical engineering departments: Bob Coughlin (UCONN); Howard Greene (Akron); Deran Hanesian (NJIT); Will Kranich (Worcester Poly); Larry McIntire (Rice); Steve Rosen (Toledo); Julian Smith (Cornell); Tom Weber (SUNY Buffalo); and Jacques Zakin (Ohio State). Bob Finn's pioneering work in biochemical engineering was begun in the 1950's.

Dusty's policies set a pattern for the school which persisted until the early 1970's. By then it was clear that the research effort had to be greatly



The Fred H. Rhodes Student Lounge, redecorated through a gift from Joseph Coors, '40.

expanded. Beginning in 1970, new faculty members were added who developed, or brought with them, strong research programs in several areas. This attracted additional research-minded faculty and increasingly stronger graduate students. During an 8-year period research expenditures increased by a factor of six. The number of graduate students has risen to 67; more significantly, a majority of them are now PhD candidates. And collaboration with Chemistry and other departments of the university is once again close and extensive.

RESEARCH GROWTH

From 1976 through 1982, the annual research expenditures, in dollars per faculty member, climbed at a rate that was second highest and reached a level that was fourth highest among all chemical engineering departments in the country.* Total sponsored research costs for 1983-84 were over 1.5 million dollars, for an average of \$94,000

**Journal of Engineering Education*, March issues, 1976-1983.

per full-time faculty member. This is especially striking since only about a third of the faculty was responsible for 75% of the total expenditures. As the current younger faculty develop their programs and additional research-minded faculty replace retiring senior professors, the overall research program should continue its strong expansion.

Biochemical Engineering

Biochemical engineering research has grown from **Bob Finn's** early studies of microbes and

... many of the PhD recipients have had distinguished careers in industry and academia, including **John Prausnitz (Berkeley)**, **Ed Lightfoot (Wisconsin)**, and a string of past or present heads of chemical engineering departments.

microbial populations. The goal was, and is, to develop new and more efficient biochemical conversions. One project seeks to find economical ways of producing ethanol from pentose sugars, a second to develop better treatment methods for wastes containing pentachlorophenol (PCP), and a third to exploit an unusual bacterium which can rapidly ferment arabinose.

Mike Shuler shares several specific interests with Bob Finn including the treatment of wastewater by specialized microorganisms. Mike's diverse interests are tied together by a view of the living cell as a "catalyst" waiting to be used in chemical reactors. His research embraces studies of plant-cell tissue culture, reactors with solid substrates (e.g. mold growth on solid surfaces), photobioreactors, biofilm formation, and the continuous protein production from bacteria with recombinant DNA. Particularly noteworthy have been his group's experimental demonstration of the feasibility of hollow-fiber membrane units for entrapment of microbial populations (necessary groundwork for the development of hollow-fiber reactors) and the construction of a mathematical model of the organism *Escherichia coli*.

Doug Clark, who joined the faculty in 1984, brings the point of view that enzymes rather than the whole cell can be the building blocks for biochemical reactors. He is studying how the immobilization, or attachment to a foreign matrix support, affects the structure and function of an enzyme. A related interest is the transport of bio-

logical macromolecules through porous media; this transport is an essential step in enzyme immobilization, gel permeation and affinity chromatography, and ultrafiltration. In collaboration with **Bill Streett**, Doug has initiated a study of methane-producing bacteria which live at extreme temperatures and pressures in deep-sea hydrothermal vents.

Polymers and Materials Science

For a million circuit elements to fit on a tiny silicon chip linewidths must be on the order of a tenth of a micron. In one technique for achieving such precision—electron-beam lithography—the silicon surface is covered with a polymer film (polymethyl methacrylate, for example), then irradiated by an electron beam creating a pattern of soluble polymer. The soluble polymer is washed away leaving a precision mask and the chip is ready for the final step, silicon modification. **Ferdinand (Rod) Rodriguez** is directing an interdepartmental program on polymers for advanced lithography, to improve the performance of the polymer "resist" used in the masking process. This is a good example of Rod's research on polymeric materials which has the broad goal of understanding the processes of polymerization and gelation (crosslinking) and degradation (chain scission) in order to produce better materials.

Claude Cohen uses macromolecular science to interpret the physical properties of polymer systems and to understand the structures that develop during industrial processing. On the fundamental level, predictions from models of macromolecules are used to understand rheological and light-scattering behavior, with experiments to complement the theoretical work and to test the adequacy of the models. On the applied level, the orientation of glass fibers in composite thermoplastics during the molding process is being investigated. This work is in conjunction with an interdepartmental program on injection molding.

Surface Chemistry, Catalysis and Reactor Engineering

The surface chemistry and physics of heterogeneous systems which have direct technological application is the central concern of **Bob Merrill's** studies. Examples are CO oxidation on noble metals (automobile exhaust converters), the decomposition of hydrazine (rocket monopropellant), the oxidation of aluminum (catalyst sup-

port technology, corrosion protection, and electronic insulators in microcircuitry) and hydrodesulfurization catalysis (sulfur removal from petroleum). On the one hand, Bob's group answers practical questions; on the other they are developing and sharpening several types of analytical tools. These include the use of lasers in surface chemistry, the use of synchrotron radiation (EXAFS) to study the dynamics of gas-solid reactions, and the use of spectroscopy in real catalyst systems (high-surface-area configurations and high pressures).

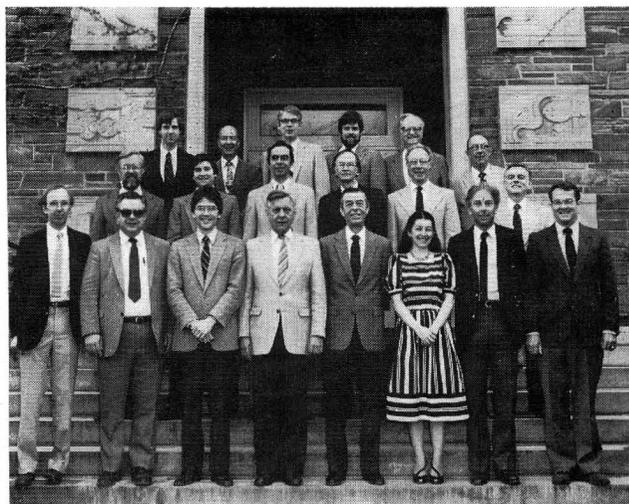
Peter Harriott studies the influence of mass transfer, heat transfer and mixing on the performance of chemical reactors as well as the kinetics of reactions in heterogeneous systems. One project concerns the regeneration of catalysts used in the pyrolysis and gasification of coal. Another examines the heat and mass transfer and the overall kinetics in lime-slurry droplets used in the "dry scrubbing" of SO_2 from flue gas; the goal is to pin down the rate-limiting step and improve the design of commercial units.

Joe Cocchetto's recent work on catalytic reaction kinetics has concentrated on the fuel cell. By controlling the structure of a porous electrode, a better understanding of the interplay between transport and reaction has been gained and techniques for improving efficiency have emerged. Joe returned to industry in early 1985.

Bob Von Berg is interested in the use of gamma radiation in various chemical processes: ammonia synthesis and the reaction of hydrocarbons and liquid nitrogen. Bob has also collaborated with Herb Wiegandt on a long-term project involving the desalination of water by freezing, as described later.

Fluid Dynamics and Stability: Rheology

Bill Olbricht concentrates on problems in fluid mechanics and rheology with applications in enhanced oil recovery, biomedical fluid mechanics, and the production of semiconductor materials. He is studying the low-Reynolds-number motion and coalescence of immiscible drops in tubes of various geometries (characteristic of porous media) for critical evaluation of methods for enhanced oil recovery. In the biomedical area, in conjunction with the University of Rochester Medical School, he is modelling the motion of red blood cells in microcapillaries to predict the distribution of these cells within tissue. A third area



Cornell's Chemical Engineering Faculty, 1984. Back row: Shuler, Finn, Scheele, Steen, Smith, Winding. Middle row: Zollweg (Research Associate), Cocchetto, Harriott, Jolls (Visiting from Iowa State), Von Berg, Rodriguez. Front row: Olbricht, Merrill, Clark, Wiegandt, Thorpe, Clancy, Gubbins, Streett.

of research examines the momentum, heat, and mass transfer involved in silicon film growth by chemical vapor deposition with the aim of predicting rates of film growth in low-pressure deposition reactors.

Paul Steen, who joined the faculty in 1982, studies fluid motions and their stabilities. Buoyancy-driven convection patterns, generated in fluid-saturated porous media, are examined as prototypes of fluid motions susceptible to transitions in which strong nonlinear effects are dominant. This work involves the development of tools in applied mathematics. In another area, motions induced at fluid/fluid interfaces due to temperature gradients (thermocapillary effects) are being investigated by experiment, with relevance to the float-zone crystal-growth process and the break-up of thick films.

George Scheele's study of liquid-liquid immiscible systems focuses on the coalescence of droplets and the break-up of jets—both at relatively high Reynolds numbers. He also has interests in the computer simulation of chemical processes, particularly in computer graphics.

Molecular Thermodynamics and Computer Simulation

Keith Gubbins and **Bill Streett** have coordinated their efforts towards understanding, predicting,

Continued on page 103.

CLASSICAL SOLUTION THERMODYNAMICS

A Retrospective View

H. C. VAN NESS AND M. M. ABBOTT
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THE PRIMARY VARIABLES of classical thermodynamics for fluid systems are temperature T , pressure P , and the molar properties volume V , internal energy U , and entropy S . Temperature is a primitive, having no definition in terms of anything simpler. Pressure and molar volume are defined directly by three other primitives: force, mass, and length. These primitives—temperature, force, mass, and length—are subject to direct sensory perception, and we have little difficulty accepting them as meaningful. Internal energy and entropy, however, are primitives not associated with direct detection by the senses. Nor are they directly measurable; we have no energy meters, no entropy meters. Energy and entropy are mental constructs which have meaning only as mathematical functions. Accepting this, we then need to know what they are functions of.

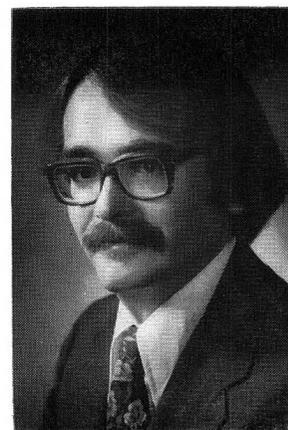
We find by experiment that the molar volume of a homogeneous phase is a function of its temperature, pressure, and composition. Generalizing, we postulate that the molar internal energy and entropy of a homogeneous phase are likewise functions of temperature, pressure, and composition. When this is true, the first and second laws lead to a fundamental property relation among the primary thermodynamic variables

$$d(nU) = Td(nS) - Pd(nV) + \sum \mu_i dn_i \quad (1)$$

The n_i are mole numbers of the species present,

Nor are they directly measurable; we have no energy meters, no entropy meters. Energy and entropy are mental constructs which have meaning only as mathematical functions.

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$n = \sum n_i$ is the total number of moles, and the μ_i are *chemical potentials*. Written for $n = 1$, Eq. (1) becomes

$$dU = TdS - PdV + \sum \mu_i dx_i$$

showing that

$$U = U(S, V, x)$$

Thus, in general, the natural independent (*canonical*) variables for U are entropy, volume, and composition.

New thermodynamic properties can be defined that are functions of alternative sets of independent variables. In particular, the enthalpy H and the Gibbs function G are defined as

$$H \equiv U + PV \quad (2)$$

and

$$G \equiv H - TS \quad (3)$$

Then

$$nG = nU + P(nV) - T(nS)$$

and

$$d(nG) = d(nU) + Pd(nV) + (nV)dP - Td(nS) - (nS)dT$$

Substitution for $d(nU)$ by Eq. (1) gives

$$d(nG) = - (nS)dT + (nV)dP + \sum \mu_i dn_i \quad (4)$$

This equation is equivalent to Eq. (1), and represents an alternative fundamental property relation. Written for one mole of material, it becomes

$$dG = - SdT + VdP + \sum \mu_i dx_i \quad (5)$$

whence

$$G = G(T, P, x)$$

Because temperature, pressure, and composition are subject to direct measurement and control, the Gibbs function is a defined thermodynamic property of great potential utility.

An equation such as Eq. (4) is too general for direct practical application. Its value is in storing much information. Thus, we write by inspection

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, x} \quad (6)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, x} \quad (7)$$

and

$$\mu_i = \left(\frac{\partial (nG)}{\partial n_i} \right)_{T, P, n_j} \quad (8)$$

where the subscript n_j indicates that all mole numbers are held constant except n_i . Application of Eqs. (6) through (8) presumes knowledge of G as a function of T , P , and x ; given this, then Eqs. (6) and (7) yield S and V as functions of T , P , and x . Other properties come from defining equations; for example, by Eq. (3)

$$H = G + TS \quad (9)$$

Thus, if we know how G is related to its canonical variables, we can by simple mathematical operations evaluate all the other thermodynamic properties; given $G = G(T, P, x)$, we can also find S , V , μ_i , H , C_p , etc. as functions of temperature, pressure, and composition.

All this is the legacy of J. W. Gibbs and in principle nothing more is needed. An expression giving $G = G(T, P, x)$ is an example of a *canonical equation of state*. Such an equation serves as a generating function for the other thermodynamic properties, and implicitly represents complete property information.

For real-fluid mixtures, canonical equations of state are unknown. The problem is that such an equation must be based on experimental data. Unfortunately, there are no G meters and no convenient experimental measurements that lead easily to values of G . Without a canonical equation of state, we can make no direct practical use of a fundamental property relation. The slow evolution of solution thermodynamics since Gibbs' time has led to new formulations that relate much more directly to experiment. Our purpose here is

The slow evolution of solution thermodynamics . . . has led to new formulations that relate much more directly to experiment. Our purpose is to rationalize the structure of modern solution thermodynamics.

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In the early years of this century, G. N. Lewis introduced several concepts basic to all subsequent developments: the partial property, the fugacity, and the ideal solution.

A *partial property* is defined by the equation

$$\bar{M}_i \equiv \left(\frac{\partial (nM)}{\partial n_i} \right)_{T, P, n_j} \quad (10)$$

where M is the molar value of any extensive property. The simplest interpretation of Eq. (10) is that it apportions a mixture property among the constituent chemical species. Thus, \bar{M}_i has the characteristics of the property of species i in the mixture. Indeed, a mathematical consequence of Eq. (10) is the relation

$$M = \sum x_i \bar{M}_i \quad (11)$$

which shows that the partial properties combine in the simplest rational way to yield the mixture property. We see by comparison of Eq. (8) with Eq. (10) that

$$\mu_i = \bar{G}_i \quad (12)$$

Thus, the chemical potential is identified with the partial Gibbs function.

The *fugacity* is an auxiliary thermodynamic property related to the Gibbs function. Thus, for a mixture, the fugacity f is defined by the equations

$$dG = RT d \ln f \quad (\text{const } T, x) \quad (13)$$

and

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (14)$$

For the special case of pure species i , these become

$$dG_i = RT d \ln f_i \quad (\text{const } T) \quad (15)$$

and

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1 \quad (16)$$

For species i as a constituent of a mixture, the fugacity \hat{f}_i is defined by the equations

$$d\bar{G}_i = RT d \ln \hat{f}_i \quad (\text{const } T) \quad (17)$$

and

$$\lim_{x_i P \rightarrow 0} \frac{\hat{f}_i}{x_i P} = 1 \quad (18)$$

For an ideal-gas mixture one replaces V in Eq. (5) by RT/P ; then

$$dG' = RT d \ln P \quad (\text{const } T, x) \quad (19)$$

where the prime ($'$) denotes an ideal-gas property. From Gibbs' theorem for such mixtures, we have

$$G' = \sum x_i G'_i + RT \sum x_i \ln x_i \quad (20)$$

By Eqs. (6), (7), and (9), we get

$$S' = \sum x_i S'_i - R \sum x_i \ln x_i \quad (21)$$

$$V' = \sum x_i V'_i \quad (22)$$

and

$$H' = \sum x_i H'_i \quad (23)$$

Each of these is implicit in Eq. (20). Moreover, Eq. (8) yields

$$\mu'_i = \bar{G}'_i = G'_i + RT \ln x_i$$

whence

$$d\bar{G}'_i = dG'_i + RT d \ln x_i \quad (\text{const } T)$$

By Eq. (19) written for pure species i , this becomes

$$d\bar{G}'_i = RT d \ln (x_i P) \quad (\text{const } T) \quad (24)$$

The actual properties of a fluid may be compared with the properties the fluid would have as an ideal gas at the same temperature, pressure, and composition. The comparison by subtraction gives rise to *residual properties*. Thus, by definition

$$M^R \equiv M - M'$$

and

$$\bar{M}_i^R \equiv \bar{M}_i - \bar{M}'_i \quad (26)$$

Applying this concept to the Gibbs function, we subtract Eq. (19) from Eq. (13)

$$d(G - G') = RT d \ln \frac{f}{P} \quad (\text{const } T, x)$$

or

$$dG^R = RT d \ln \phi \quad (\text{const } T, x) \quad (27)$$

where ϕ is the *fugacity coefficient*, defined as

$$\phi \equiv \frac{f}{P} \quad (28)$$

Integration of Eq. (27) gives

$$G^R = RT \ln \phi \quad (29)$$

The integration constant vanishes, because for $P = 0$, $G^R = 0$ by assumption and $\ln \phi = 0$ by Eq. (14). For the special case of pure species i , this becomes

$$G_i^R = RT \ln \phi_i \quad (30)$$

For species i as a constituent of a mixture, we subtract Eq. (24) from Eq. (17)

$$d(\bar{G}_i - \bar{G}'_i) = RT d \ln \frac{\hat{f}_i}{x_i P} \quad (\text{const } T)$$

or

$$d\bar{G}_i^R = RT d \ln \hat{\phi}_i \quad (\text{const } T) \quad (31)$$

where $\hat{\phi}_i$ is the fugacity coefficient of species i in the mixture, defined as

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{x_i P} \quad (32)$$

Integration of Eq. (31) gives

$$\bar{G}_i^R = RT \ln \hat{\phi}_i \quad (33)$$

Unlike a formulation based on a canonical equation of state, the residual-property formulation cannot provide complete property information. One needs in addition the heat capacities necessary for evaluation of properties for the ideal-gas state.

where again the integration constant vanishes.

An alternative form of Eq. (4) derives from the mathematical identity

$$d \left(\frac{nG}{RT} \right) \equiv \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT$$

Substituting for $d(nG)$ by Eq. (4) and for G by Eq. (3) gives

$$d \left(\frac{nG}{RT} \right) = \frac{-nH}{RT^2} dT + \frac{nV}{RT} dP + \sum \frac{\mu_i}{RT} dn_i \quad (34)$$

For the ideal-gas state, Eq. (34) becomes

$$d \left(\frac{nG'}{RT} \right) = \frac{-nH'}{RT^2} dT + \frac{nV'}{RT} dP + \sum \frac{\mu_i'}{RT} dn_i \quad (35)$$

With μ_i replaced by \bar{G}_i in Eq. (34) and μ_i' replaced by \bar{G}_i' in Eq. (35), we subtract these two equations:

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \frac{\bar{G}_i^R}{RT} dn_i \quad (36)$$

where the definitions of Eqs. (25) and (26) have been invoked. This is the fundamental property relation for residual properties. In view of Eq. (33), it may also be written

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \ln \hat{\phi}_i dn_i \quad (37)$$

Working relations for the residual properties can now be written by inspection

$$\frac{H^R}{RT} = -T \left(\frac{\partial (G^R/RT)}{\partial T} \right)_{P,x} = -T \left(\frac{\partial \ln \phi}{\partial T} \right)_{P,x} \quad (38)$$

$$\frac{V^R}{RT} = \left(\frac{\partial (G^R/RT)}{\partial P} \right)_{T,x} = \left(\frac{\partial \ln \phi}{\partial P} \right)_{T,x} \quad (39)$$

and

$$\ln \hat{\phi}_i = \left(\frac{\partial (nG^R/RT)}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial (n \ln \phi)}{\partial n_i} \right)_{T,P,n_j} \quad (40)$$

where the second form in each case follows from Eq. (29).

Equation (39) may be written

$$d \ln \phi = \frac{V^R}{RT} dP \quad (\text{const } T, x) \quad (41)$$

where by definition

$$V^R \equiv V - V' = V - \frac{RT}{P}$$

Values of V^R come directly from experimental PVTx data, and Eq. (41) then allows calculation of $\ln \phi$; Eqs. (38) through (40) yield other properties of interest. This close link to experiment is the major reason for a residual-property formulation of solution thermodynamics. Given a PVT equation of state

$$V = V(T, P, x)$$

we can evaluate all residual properties. Because of its direct relation to experiment, a PVT equation of state is far more easily developed than is a canonical equation of state. Furthermore, the principle of corresponding states allows the generalization of PVT data and the development of generalized correlations for the residual properties, thus greatly extending the usefulness of available experimental data. Unlike a formulation based on a canonical equation of state, the residual-property formulation cannot provide complete property information. One needs in addition the heat capacities necessary for evaluation of properties for the ideal-gas state.

In principle, PVT equations of state apply equally to gases and to liquids. In practice, however, the accurate representation of liquid properties proves much more difficult. Thus, an alternative formulation of solution thermodynamics has developed for liquids. The key idea is that of an *ideal solution*. By definition

$$\hat{f}_i^{\text{id}} \equiv x_i f_i \quad (42)$$

where the superscript id denotes an ideal-solution property. Expressions for all of the properties of an ideal solution follow from this equation.

Integration of Eq. (17) from the state of pure i to the state of i in solution at the same T and P gives

$$\bar{G}_i - G_i = RT \ln \frac{\hat{f}_i}{f_i} \quad (43)$$

For an ideal solution, this becomes

$$\bar{G}_i^{\text{id}} = G_i + RT \ln x_i \quad (44)$$

and by Eq. (11)

$$G^{\text{id}} = \sum x_i G_i + RT \sum x_i \ln x_i \quad (45)$$

Equations (6), (7), and (9) in this case yield

$$S^{\text{id}} = \sum x_i S_i - R \sum x_i \ln x_i \quad (46)$$

$$V^{\text{id}} = \sum x_i V_i \quad (47)$$

and

$$H^{\text{id}} = \sum x_i H_i \quad (48)$$

Just as we may compare the actual properties of a fluid with its ideal-gas-state properties, so may we compare the actual properties of a fluid mixture with its ideal-solution properties at the same temperature, pressure, and composition. Thus, we have definitions of *excess properties* quite analogous to those for residual properties

$$M^E = M - M^{\text{id}} \quad (49)$$

and

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{\text{id}} \quad (50)$$

Equation (49) applied in turn to the properties whose ideal-solution expressions are given by Eqs. (45) through (48) becomes

$$G^E = G - \sum x_i G_i - RT \sum x_i \ln x_i \quad (51)$$

$$S^E = S - \sum x_i S_i + R \sum x_i \ln x_i \quad (52)$$

$$V^E = V - \sum x_i V_i \quad (53)$$

$$H^E = H - \sum x_i H_i \quad (54)$$

The excess properties are closely related to *property changes of mixing*

$$\Delta M \equiv M - \sum x_i M_i \quad (55)$$

These quantities measure the changes that occur when one mole of mixture is formed from the pure constituent species by a mixing process at constant T and P. The definition of Eq. (55) allows Eqs. (51) through (54) to be written

$$G^E = \Delta G - RT \sum x_i \ln x_i \quad (56)$$

$$S^E = \Delta S + R \sum x_i \ln x_i \quad (57)$$

$$V^E = \Delta V \quad (58)$$

$$H^E = \Delta H \quad (59)$$

Thus, the excess properties are readily calculated from property changes of mixing and vice versa. Interest in property changes of mixing is focused on ΔV and ΔH , because these quantities can be experimentally determined by direct measurement.

Unfortunately, measurements of $\Delta V = V^E$ and of $\Delta H = H^E$ for liquid mixtures do not allow calculation of G^E . For this, we need vapor/liquid-equilibrium data, which are related to G^E as follows. Subtraction of Eq. (44) from Eq. (43) gives

$$\bar{G}_i^E = \bar{G}_i - \bar{G}_i^{\text{id}} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

or

$$\ln \gamma_i = \frac{\bar{G}_i^E}{RT} \quad (60)$$

where the *activity coefficient* γ_i is defined by

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i} \quad (61)$$

In accord with Eq. (11)

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT}$$

and by Eq. (60) this becomes

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (62)$$

Values of γ_i are calculated from experimental vapor/liquid-equilibrium measurements by the equation

$$\gamma_i = \frac{y_i P \Phi_i}{x_i P_i^{\text{sat}}} \quad (63)$$

Here, Φ_i is a secondary factor of order unity that can be readily evaluated from volumetric data for the equilibrium phases or from correlations of such data.

The fundamental property relation for the excess properties follows from Eq. (34). For an ideal solution, this equation is written

TABLE 1
Summary of key equations

$$d \left(\frac{nG}{RT} \right) = \frac{-nH}{RT^2} dT + \frac{nV}{RT} dP + \sum \frac{\mu_i}{RT} dn_i \quad (34)$$

$$d \left(\frac{nG^R}{RT} \right) = \frac{-nH^R}{RT^2} dT + \frac{nV^R}{RT} dP + \sum \ln \hat{\phi}_i dn_i \quad (37)$$

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \ln \gamma_i dn_i \quad (66)$$

$$\frac{G}{RT} = \sum x_i \frac{\bar{G}_i}{RT} = \sum x_i \frac{\mu_i}{RT}$$

$$\frac{G^R}{RT} = \sum x_i \frac{\bar{G}_i^R}{RT} = \sum x_i \ln \hat{\phi}_i$$

$$\frac{G^E}{RT} = \sum x_i \frac{\bar{G}_i^E}{RT} = \sum x_i \ln \gamma_i$$

$$d \left(\frac{nG^{id}}{RT} \right) = \frac{-nH^{id}}{RT^2} dT + \frac{nV^{id}}{RT} dP + \sum \frac{\mu_i^{id}}{RT} dn_i \quad (64)$$

With μ_i replaced by \bar{G}_i in Eq. (34) and μ_i^{id} replaced by \bar{G}_i^{id} in Eq. (64), we subtract these two equa-

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \frac{\bar{G}_i^E}{RT} dn_i \quad (65)$$

tions where the definitions of Eqs. (49) and (50) have been invoked. In view of Eq. (60), this equation may also be written

$$d \left(\frac{nG^E}{RT} \right) = \frac{-nH^E}{RT^2} dT + \frac{nV^E}{RT} dP + \sum \ln \gamma_i dn_i \quad (66)$$

Equation (66) is analogous to both Eqs. (34) and (37); analogous to Eqs. (38) through (40), we have

$$\frac{H^E}{RT} = -T \left(\frac{\partial (G^E/RT)}{\partial T} \right)_{P,x} \quad (67)$$

$$\frac{V^E}{RT} = \left(\frac{\partial (G^E/RT)}{\partial P} \right)_{T,x} \quad (68)$$

$$\ln \gamma_i = \left(\frac{\partial (nG^E/RT)}{\partial n_i} \right)_{T,P,n_j} \quad (69)$$

The formulation of solution thermodynamics through excess properties derives its usefulness from the fact that H^E , V^E , and γ_i can all be found by experiment. This relative abundance of experimental entries provides alternative measurements that yield property data. However, the excess-property formulation provides even less-complete property information than the residual-property formulation, because it tells us nothing about the properties of the pure chemical species.

In Table 1, we bring together for comparison the parent fundamental property relation for the Gibbs function and the two analogous property relations which follow from it for the residual and excess Gibbs functions. Included as well are the equations which relate the three mixture Gibbs functions to their respective partial properties. These are particular applications of Eq. (11). □

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THE NATURE OF ADJOINT VARIABLES AND THEIR ROLE IN OPTIMAL PROBLEMS

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ADJOINT VARIABLES ARE frequently arbitrarily introduced into the textbook discussion of optimal or extremal theory. For example, Bryson and Ho [1] "adjoin" them to the optimization problem, Denn [2] introduces them as a "convenience," and Leitman [11] regards them as a transformation to a "useful" vector space basis. Only Jackson [10] has shown that they are desirable as a general transformation from one set of variables which appear naturally during the formulation of the problem to the set of interest in the solution search problems. Adjoint variables are the sensitivity coefficients in optimal search problems. Adjoint variables exist because the coefficient matrix of every system (of describing equations) has a transpose, and there are, therefore, two independent solutions to the homogeneous form of the system.

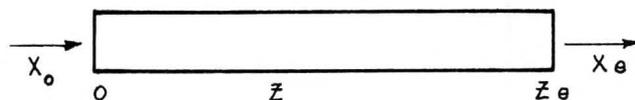
However, it was the late Professor F. M. J. Horn who in 1958 most directly presented the fundamental nature of the adjoint variables and their role in optimal reactors in chemical engi-



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neering [5]. The original papers [6, 7, 8] and the more complete elaboration in his thesis were in German, with results published in English [9] by 1967. Publications about Pontryagin's Principle [8, 10] became the standard literature reference, and the directness of Horn's approach became less available for the beginning student to appreciate. Furthermore, this appreciation or understanding of adjoint variables makes much of Horn's later work in optimal chemical reactors—effect of bypassing, cyclical operation of non-linear processes—much easier to follow.

This demonstration makes use of the example presented in detail in appendix I.11 of his Thesis [5]. One asks for the optimal temperature profile for a plug flow reactor with several independent chemical reactions. The set of independent chemical reactions is any set of the smallest number of time dependent stoichiometric equations sufficient to define all reaction compositions uniquely in time. The proper interpretation of independent is also clearly discussed in this thesis, although a more formidable presentation is now available [12]. We suppose a tubular plug flow reactor with several chemical reactions and arbitrary kinetics (Arrhenius)



$$dx_i/dz = v_i(x^1, x^2, \dots, x^m, T), \quad (i = 1 \text{ to } m) \quad (1)$$

and presume that the objective function has the form

$$M = M(x^{1e}, x^{2e}, \dots, x^{me}) = M(x_e) \quad (2)$$

M depends only upon the exit composition (extents) x_e and a straightforward solution to the problem would be to assume a temperature profile, calculate the exit composition vector to give

M, then presume another temperature profile and continue to adapt the profile in some beneficial way until an extreme in M was obtained. Suppose we had two such solutions (we use x for the vector of extents of the independent reactions and V for the vector of reaction rates, and the super dot to imply differentiation with respect to z)

$$x_1 \rightarrow \dot{x}_1 = V(x_1, T_1) \quad \text{and} \quad x_2 \rightarrow \dot{x}_2 = V(x_2, T_2) \quad (3)$$

so that for sufficiently small differences between T_1 and T_2 a first difference (perturbation) is sufficient. Then

$$\dot{x}_2 - \dot{x}_1 = [\partial V_i / \partial x_j](x_2 - x_1) + (\partial V_i / \partial T)(T_2 - T_1)$$

or

$$\dot{y} = [\partial V_i / \partial x_j]y + (\partial V_i / \partial T)\bar{T} \quad (4a)$$

where y stands for the perturbation in x caused by the perturbation \bar{T} in T . We will also have the perturbed response

$$\begin{aligned} \bar{M} = M(x_{2e}) - M(x_{1e}) &= \sum_{k=1}^m \frac{\partial M}{\partial x_{ke}} y_k(z_e) \\ &= (\partial M / \partial x_{ie})' y(z_e) \end{aligned} \quad (4b)$$

Since both x_2 and x_1 are zero at z equal zero, $y(0)$ is zero. Note that the matrix, $[\partial V_i / \partial x_j]$ and vector, $(\partial V_i / \partial T)$ are functions of z only, so that the system of Eqs. (4a,b) is a set of linear differential equations in which the coefficients are functions only of the independent variable z . y is the response of the system to \bar{T} . What we desire is to solve Eqs. (4a,b) subject to the restriction that M be an extreme, so that it is necessary that

$$dM = (\partial M / \partial x_{ie})' dx = 0 \quad (5)$$

$(\partial M / \partial x_{ie})'$ is the transpose of the vector of partial derivatives of M with respect to x_{ie} , that is, x at the end of the reactor. A system like (4) is usually solved by Variation of Parameters (Boyce & DePrima [3] or Hochstadt [4]), finding first the homogeneous (complementary) solutions. The form of these solutions is more conveniently manipulated if we use the solution matrix rather than the solution vector (in contrast with usual forms for systems with constant coefficients). Therefore

$$\dot{y}_c = [B] y_c \quad \text{where} \quad B_{ij} = \partial V_i / \partial x_j \quad (6)$$

has the homogeneous solution matrix $[Y]$ such that

$$[\dot{Y}] = [B][Y] \quad (7)$$

and we take $[Y(z_e)]$ to be $[I]$ the identity matrix. Any other boundary condition on $[Y]$ may be obtained directly from this one. Using the Variation of Parameters we suppose $y = [Y]c$ and hope to find the vector c to fit the inhomogeneous part, which is the second term of Eq. (4)

$$\dot{y} = \{[Y]\dot{c}\} = \{\dot{Y}\}c + [Y]\dot{c} = [B][Y]c + (\partial V_i / \partial T)\bar{T} \quad (8)$$

Substituting from Eq. (6) we have

$$[Y]\dot{c} = (\partial V_i / \partial T)\bar{T} + \dot{c} = [Y]^{-1}(\partial V_i / \partial T)\bar{T} \quad (9)$$

and we see that the vector of the particular solutions c is directly related to the temperature profile, \bar{T} . Now, these functions depend only on z , and we intend to keep the same inlet temperature but to alter the shape of the profile. Therefore any one of the particular solutions c must have the property

$$c_k(z_e) = \int_0^{z_e} \dot{c}_k(z) dz \quad \text{with} \quad c_k(0) = 0$$

and since

$$y = [Y]c \quad \text{and} \quad [Y] = [I] \quad \text{at} \quad z = z_e$$

then

$$y(z_e) = c(z_e) \quad (10)$$

Then from Eq. 4b, using t as a dummy variable and recalling that $(\partial M / \partial x_{ie})$ does not depend on z

$$\begin{aligned} \bar{M} &= \int_0^{z_e} \dot{\bar{M}} dt = \sum_{k=1}^m (\partial M / \partial x_{ke}) c_k(z_e) \\ &= \int_0^{z_e} \sum_{k=1}^m (\partial M / \partial x_{ke}) c_k(t) dt \end{aligned}$$

then

$$\dot{\bar{M}} = \sum_{k=1}^m (\partial M / \partial x_{ke}) \dot{c}_k(z_e) = (\partial M / \partial x_{ie})' \dot{c} \quad (11)$$

(Note that $\dot{\bar{M}}$ is the derivative, with respect to the independent variable of the response \bar{M} to the perturbation \bar{T} .)

We now have to solve simultaneously $m + 1$ linear equations involving \dot{c} . There are m independent chemical reactions, and Eq. (11) for $\dot{\bar{M}}$. Since these equations must be linearly de-

Thus, the differential equations for the adjoint variables and their corresponding conditions at the end of the reactor show that the influence of the exit extents upon the value of the objective function can be obtained for any entering conditions to the reactor by integrating their adjoint variable differential equations from the end of the reactor to the entrance.

pendent, their determinant must be zero

$$\begin{vmatrix} \dot{M} & (\partial M / \partial x_{ie})' \\ (\partial v_i / \partial T) \bar{T} & [Y] \end{vmatrix} = 0 \quad \text{or} \quad \begin{vmatrix} \dot{M} & u' \\ w & [Y] \end{vmatrix} = 0$$

using vectors u and w for notational convenience, then

$$\dot{M} |Y| + \begin{vmatrix} 0 & u' \\ w & [Y] \end{vmatrix} = 0 \quad \text{and} \quad \dot{M} = - \frac{\begin{vmatrix} 0 & u' \\ w & [Y] \end{vmatrix}}{|Y|} \quad (12)$$

As we expand the numerator determinant of Eq. (12) first about w , the first column (deleting the i th row in Y) and then about u' in the first row (deleting the j th column in Y), we will obtain the cofactors of the elements Y_{ij} , in Y , which we label a_{ij} and Eq. (12) can be written

$$\dot{M} = - \frac{\begin{vmatrix} 0 & u' \\ w & Y \end{vmatrix}}{|Y|} = \frac{w' [a_{ij}] u}{|Y|} = \frac{w [\text{Adj}(Y')] u}{|Y|} = w' \lambda \quad (13)$$

because $[a_{ij}]$ is the adjoint matrix of the transpose of $[Y]$, (a sign change occurs as the $i + 1$ index in the determinant decreases to the i index for w). The adjoint variables, λ , are defined by Eq. (13) and

$$\lambda = [Y']^{-1} u + [Y'] \lambda = u$$

Since

$$\dot{u} = (\partial M / \partial x_{ie}) = 0$$

(for the extreme in M)

$$\{[Y'] \lambda\} = 0 = [\dot{Y}'] \lambda + [Y'] \dot{\lambda} + \dot{\lambda} = - [Y']^{-1} [\dot{Y}'] \lambda$$

But

$$[\dot{Y}] = [B][Y] + [\dot{Y}'] \lambda = \{[B][Y]\}' = [Y'] [B']$$

then

$$\dot{\lambda} = - [Y']^{-1} [Y'] [B'] \lambda \quad \text{and} \quad \dot{\lambda} = - [B'] \lambda$$

These are the differential equations for the adjoint variables. The boundary conditions of $[Y] = [I]$ at $z = z_e$ imply (for $m = 2$ for clarity) because I_{ij} is the unit ij cofactor from the identity

$$\lambda_1(z_e) = \frac{\begin{vmatrix} \partial M / \partial x_1 & \partial M / \partial x_2 \\ 0 & 1 \end{vmatrix}}{|I|}$$

$$\lambda_2(z_e) = - \frac{\begin{vmatrix} \partial M / \partial x_1 & \partial M / \partial x_2 \\ 1 & 0 \end{vmatrix}}{|I|}$$

Hence

$$\lambda(z_e) = \begin{vmatrix} u' \\ I_{ij} \end{vmatrix} = u = (\partial M / \partial x_{ie})$$

matrix.

Thus, the differential equations for the adjoint variables and their corresponding conditions at the end of the reactor show that the influence of the exit extents upon the value of the objective function can be obtained for any entering conditions to the reactor by integrating their adjoint variable differential equations from the end of the reactor to the entrance. These functions, therefore, explain how the optimal result is affected by changing the values of the extents of reaction at any point along the reactor such as the entrance. Since there is a direct correspondence between length in a plug flow reactor and time, it is equally clear how the adjoint variables apply to time optimization as well.

The adjoint variables are therefore nothing more than the additional homogeneous solution for the linear perturbation. Had the problem been cast in the form of time optimal control, they would have indicated the switching functions; introduced with an Hamiltonian or Lagrange multiplier problem, they would have been the corresponding multipliers [13].

The thing to see is that all of these structures rely essentially only on a Cramer's rule for solving a dependent set of linear equations and that the adjoint variables appear naturally as the added homogeneous solutions to the transpose of the system coefficient matrix, and they show how temperature changes along the reactor affect the objective function, which depends on the conversion at the exit from the reactor.

ACKNOWLEDGMENTS

One of the original reviewers of this article observed that the subject of this paper is contained in modern control theory texts. It is a pleasure to suggest to students that *Linear Systems* by Thomas Kailath (Prentice-Hall 1980) is an excellent reference with good examples and exercises. The most directly relevant part is section 9.1 pp 598-606 and example 9.1-3 p. 605, but there are many other items of interest throughout the entire text.

The University of Missouri-Rolla awarded the Faculty Sabbatical during which this note was written. D. W. T. Rippin and his Systems Engineering Group of ETH Zurich provided the affectionate welcome and gentle scholarly support. Don MacElroy offered a most helpful suggestion toward the end of the work.

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NOMENCLATURE

		Determinant
[]	Matrix (square)
()	Vector (column)
()'	Transposed vector (row)
z		Length of plug flow reactor
x		Extent of reaction
V		Vector of reaction rates
y		Perturbation in x
T		Temperature
M		Objective function to be optimized
m		Number of independent chemical reactions
B		Coefficient matrix from partial derivatives of rates V
Y		Matrix of homogeneous solutions to Eq. 4a
I		Identity matrix
c		Vector of particular solutions for Eq. 4a
u'		Row vector ($\partial M / \partial x_{ie}$)'
w		Column vector ($\partial V_i / \partial T$) \bar{T}
λ		Vector of adjoint variables

Subscripts

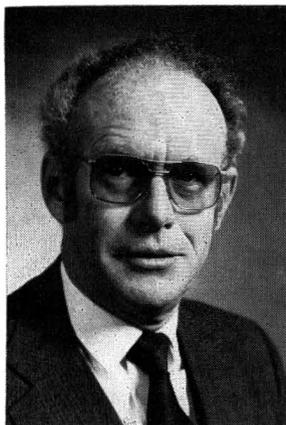
o	Entrance to reactor
e	Exit from reactor
i,j,k	Row column indexes

Superscripts

i	Index to independent chemical reactions (1 to m)
.	Differentiation with respect to length
-1	Inverse matrix
'	Transpose
—	Indicates perturbation value

Award Lecture

SEMICONDUCTOR CHEMICAL REACTOR ENGINEERING



The Chemical Engineering Division Award Lecturer for 1984 is T. W. Fraser Russell. The 3M Company provides financial support for this annual lectureship award. The lecture has been presented at the University of Florida, the University of Michigan, and Colorado School of Mines.

A native of Moose Jaw, Canada, Fraser Russell received his BSc and MSc in chemical engineering from the University of Alberta and his PhD from the University

of Delaware. He joined the department at Delaware in 1964 and is presently the Allan P. Colburn Professor of Chemical Engineering.

Prior to beginning his academic career, he spent two years with the Research Council of Alberta, where he did early development work with the Athabasca Tar Sands. He later joined Union Carbide Canada as a design engineer, where he completed the reactor and process design for all of Union Carbide's ethylene oxide derived chemicals. His innovative process design for these oxide derivative units became the first multi-purpose continuous processing unit built in Canada.

In research, Russell's efforts have been directed into two major areas: design of gas-liquid systems; and semiconductor chemical reaction engineering and photovoltaic unit operations. His research in gas-liquid system design has resulted in over 25 publications which have been widely used by industrial concerns and have led to improved design of gas-liquid contactors and reactors and biological waste treatment systems.

Russell is recognized as a respected and inspiring teacher and has received the University of Delaware's Excellence in Teaching Award. His efforts in education have resulted in the publication of two texts, *Introduction to Chemical Engineering Analysis with Morton M. Denn*, and *The Structure of the Chemical Process Industries with J. Wei and M. Swartzlander*.

In the research and development of thin-film photovoltaic cells, his efforts have centered on the need to apply chemical reaction engineering principles to improve the design and operation of reactors used in making the semiconductor material, and to ensure that solar cells developed at the laboratory scale can be manufactured in commercial quantities. He carries out this research as Director of the Institute of Energy Conversion, a laboratory with a staff of some fifty people devoted to the development of thin-film photovoltaic cells.

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THE QUANTITATIVE ANALYSIS of a reactor producing semiconductor film can be termed semiconductor chemical reactor engineering if the analysis creates procedures which improve the design, operation, and product quality of laboratory or larger scale reactors. The creation of a thin-film semiconductor, or indeed any thin film, requires an understanding of both molecular and transport phenomena. The process is analogous to that encountered in a typical catalytic reacting system (Fig. 1). Molecules must reach the surface of a substrate, adsorb on the substrate, diffuse and/or react on the substrate to produce a film possessing specified material and electronic properties. In a catalytic system, the product desorbs, leaving the substrate for the surrounding fluid phase.

A variety of reactors have been employed to move molecules or atoms to the substrate but much can be learned by considering two general types:

- Physical vapor deposition reactors
- Chemical vapor deposition reactors

In a physical vapor deposition reactor the required solid or liquid phase species are placed in a source. Energy is supplied to vaporize these species causing molecular beams to impinge on the substrate [1].

In a chemical vapor deposition reactor the molecular species are continuously supplied in a vapor phase which flows over the substrate. A

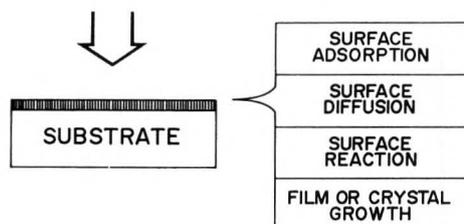


FIGURE 1. Surface molecular phenomena.

AND PHOTOVOLTAIC UNIT OPERATIONS

quantitative understanding of transfer from the bulk vapor to the surface is required and it may be necessary to contend with complex reactions in the vapor phase [2].

The performance of a reactor which produces a semiconductor film is judged by the quality of the film produced. Much effort is being devoted to ascertaining film quality by measuring optical and

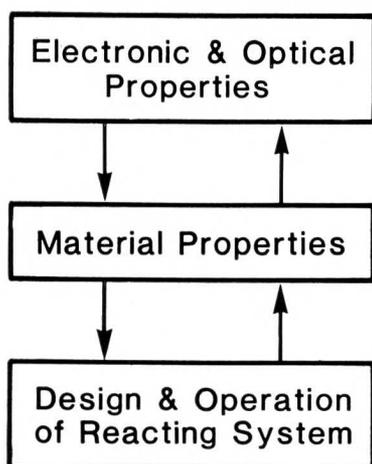


FIGURE 2. Simplified logic diagram.

electronic properties but film quality is ultimately determined by the performance of the semiconductor in some type of electronic device. A successful semiconductor chemical reaction and reactor analysis should provide experimentally verified models linking the electronic properties of the film to the design and operation of the reactor through a detailed understanding of the material properties of the film and the mechanism of film growth (Fig. 2).

The logical sequence summarized in Fig. 2 has been followed by the integrated silicon circuit community of researchers and industrial practitioners in dealing with the key step in integrated circuit manufacture of dopant diffusion into a film. It has not been a trivial task and well over two decades of effort have gone into the development of models relating device performance to doping concentration profile and doping concentration profile to the design and operation of the furnace [3]. Growing a polycrystalline or amorphous film, predictably,

with the desired electronic properties is an even more difficult task; one which remains an active integrated circuit research area today.

If one is interested in applications which could require millions of square meters per year of semiconductor film, the task of effectively predicting film growth becomes an order of magnitude more complex. Semiconductor films covering an area on the order of a square meter or more are needed for

- photovoltaic panels for power generation
- electro-photography
- electronic devices for thin-film displays

For these large-area applications it is necessary to carry out research on a scale between that used in a typical laboratory and that required for commercial operations. This unit operations scale research needs to have both a theoretical and experimental component which builds upon the laboratory scale research. The position of chemical reactor engineering and unit operations scale experimentation in the research logic is shown in Fig. 3.

I will illustrate the application of semiconductor chemical reactor engineering with research we have underway in physical vapor deposition of CdS at both the laboratory and unit operations

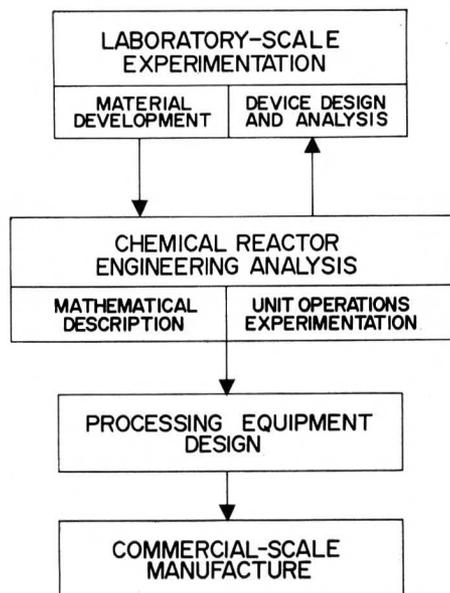


FIGURE 3. Role of chemical reactor analysis.

We originally became interested in the semi-conductor research because of a need to design larger scale reacting systems. However, the last five years of research has taught us that the chemical engineering analysis is very useful in the laboratory scale research effort, and indeed essential, if such research is to be done efficiently and with minimum expense (a key issue with today's research costs).

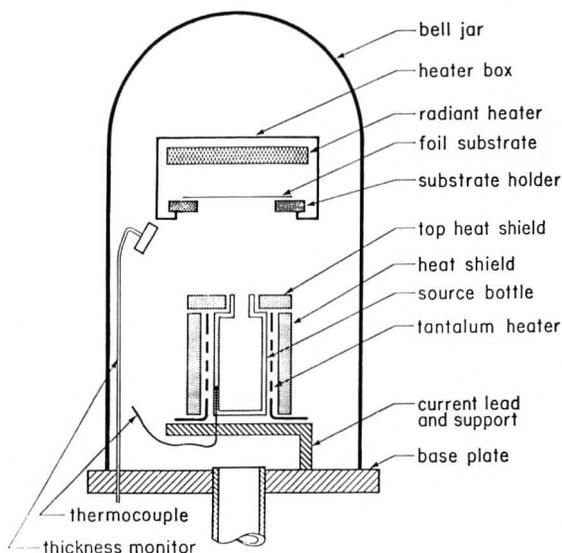


FIGURE 4. Physical vapor deposition reactor.

scale and chemical vapor deposition of amorphous silicon at the laboratory scale.

PHYSICAL VAPOR DEPOSITION

Laboratory Scale Research

A typical laboratory scale physical vapor deposition unit is shown in Fig. 4. The rate of evaporation of any material is determined by the surface temperature of the source material. For thermal evaporation this is a function of bottle geometry, the material surface area, and the design of the source heater. To make a semiconductor film, the material of interest is placed in the source bottle, heated to the point at which it evaporates or sublimates, flows out of the source bottle to the sub-

$$\frac{\partial \rho V}{\partial t} = \rho_g q$$

$$\rho V C_p \frac{\partial T_1}{\partial t} = -\rho_g q \Delta H_R + F_V E \sigma (T_2^4 - T_1^4) A_s$$

FIGURE 5. Model equations.

strate, and then condenses on the substrate, the temperature of which is carefully controlled.

The modeling and experimental verification of a model describing the rate of effusion for CdS which dissociates and sublimates has been thoroughly discussed by Rocheleau et al [4]. The mass and energy balance equations written for the material to be evaporated are shown in Fig. 5 (nomenclature in [4]). These equations can be solved numerically, given the initial dimensions of the material in the source bottle and the appropriate constitutive equations for the flow through the orifice in the source bottle. Fig. 6 gives the required equations in terms of the mass flux, r , related to

FLOW REGIME	ORIFICE	PIPE
Free Molecular ($\lambda_m/R > 1$)	$r = (\rho_1 q_c / 2\pi)^{1/2} (p_1 - p_2)$	$r = \frac{q_c R^2 p_1}{16\mu L} (p_1^2 - p_2^2) \left[4 \left(\frac{2}{f} - 1 \right) \frac{\lambda_m}{R} \right]$
Viscous ($\lambda_m/R < 0.01$)	$r = C_0 \sqrt{[2\rho q_c (p_1 - p_2)]^{1/2}}$	$r = \frac{q_c R^2 p_1}{16\mu L} (p_1^2 - p_2^2)$

FIGURE 6. Constitutive flow equations.

$\rho_g q$ through the area available for flow. The solution method is somewhat complex and complete details are given by Rocheleau et al [4] and Rocheleau [6]. Solving the equations yields the rate of effusion versus charge temperature, T_1 . A comparison of model prediction (solid lines) and experimental data (horizontal bars marked with the wall temperature, T_2) are shown for two different orifices in Fig. 7. The heat transfer from the source bottle walls to the subliming surface is the key issue in predicting rate of effusion from the source bottle.

Another type of experiment in which cadmium and sulfur are used in separate source bottles can be used to obtain information on the surface phenomena (Fig. 1). An extensive set of data has been obtained by Jackson [5] who also was able to predict the impingement rate of the molecular beam at any point on the substrate. The impingement rate of cadmium and sulfur on the substrate was calculated and the corresponding rate of CdS film

growth measured. About 1000 separate pieces of data were obtained to verify the predicted model behavior. The model equations for each species are shown in Fig. 8. The rate of reaction of cadmium to the CdS comprising the film is assumed to be

$$r(\text{rxt, Cd}) = k(\text{CdS}) [\text{Cd}^*][\text{S}^*]$$

This expression combined with the equations shown in Fig. 8 yields

$$r(\text{rxt, Cd}) = K(\text{CdS}) [\delta(\text{Cd}) r(\text{i, Cd}) - r(\text{rxt, Cd})] [\delta(\text{S}) r(\text{i, S}) - r(\text{rxt, S})]$$

The parameter, δ , is a condensation coefficient; $r(\text{i, Cd or S})$ is the rate of molecular impingement of Cd or S; $r(\text{rxt, Cd or S})$ is the rate of reaction of Cd or S; and K is a modified specific reaction rate constant whose detailed form is given by Jackson [5].

Comparison of the model behavior with some of the data is shown as Fig. 9 where the rate of deposition of CdS is plotted as a function of the

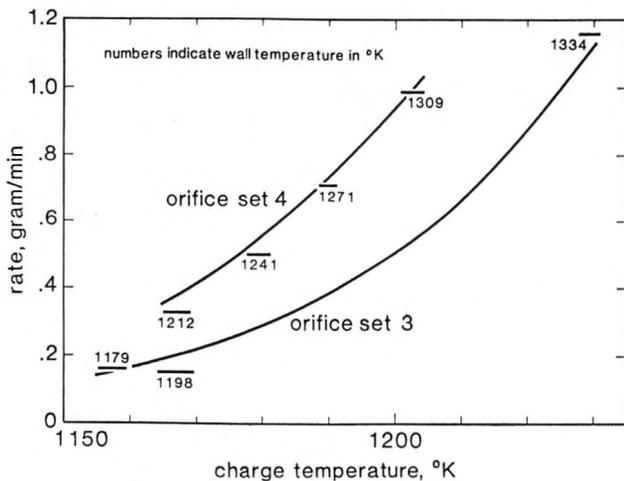


FIGURE 7. Comparison of model behavior with experimental data.

rate at which cadmium is delivered to the substrate. At low values of $r(\text{i, Cd})$ the rate of film growth is proportional to the rate at which cadmium is delivered; as the film growth becomes surface-reaction dependent, the lines curve. The horizontal line indicates a region in which there is not enough sulfur to react with all the cadmium being delivered to the substrate.

Experimental evidence indicates that photovoltaic-grade CdS can only be made when the rate of film growth is controlled by the rate at which

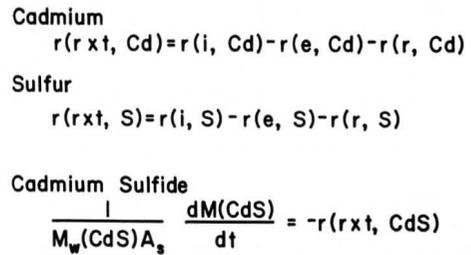


FIGURE 8. Component mass balances.

cadmium and sulfur react on the surface to form CdS. Furthermore, if sulfur is not present when a cadmium molecule arrives at the surface, the cadmium will reflect and not adhere. We are just beginning to try to relate these observations to film properties. This second laboratory scale study of Jackson's is an attempt to learn more about the semiconductor chemical reaction engineering necessary for the field to progress in an orderly fashion. A much more complicated set of chemical equations will be considered in the section on chemical vapor deposition.

Unit Operations Scale Research

For large area applications uniform defect-free film with the required properties must be deposited over areas on the order of meters in dimension. It may be necessary to deposit on a moving substrate to lower costs to the level required to make a large area application like photovoltaics economically feasible. In this section the cooperative research efforts in photovoltaic unit operations between the Department of Chemical Engineering and the Institute of Energy Con-

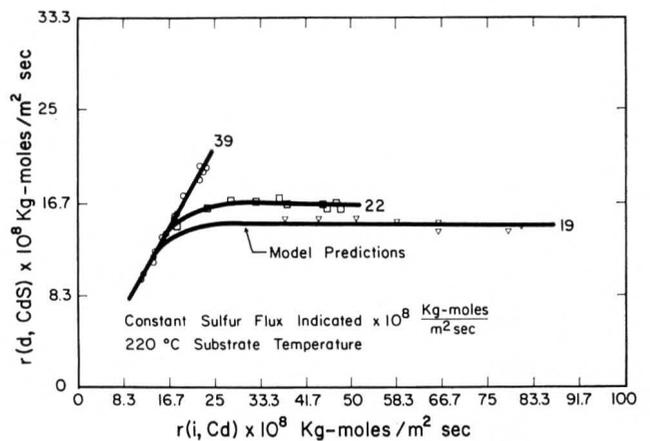


FIGURE 9. Deposition versus incident rate of cadmium in cadmium sulfide.

The theoretical and experimental work of Rocheleau, Rocheleau et al, and Jackson provide the verified models of the laboratory scale batch experiments that can be used to design apparatus and experiments at the unit operations scale.

version at the University of Delaware will be described.

CdS is the wide bandgap window semicon-

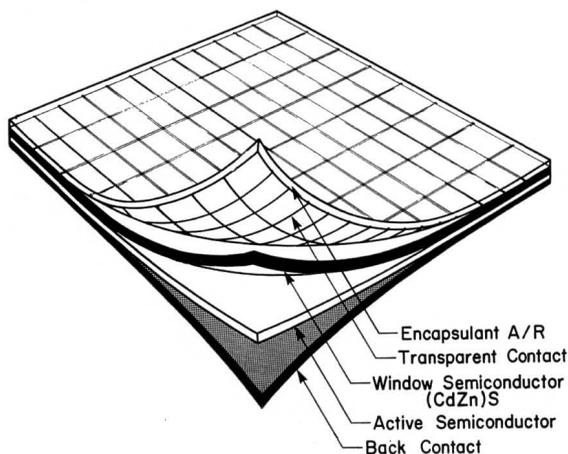


FIGURE 10. Thin-Film polycrystalline solar cell.

ductor for the following polycrystalline hetero-junction cells (Fig. 10)

- CdS/CuInSe₂
- CdS/CdTe
- CdS/Cu₂S

All of the above devices have achieved conversion efficiencies (percentage of sun energy converted to electricity) of just over 10%, although in the case of Cu₂S cells some ZnS had to be alloyed with the CdS. At this conversion efficiency, inexpensive electrical power generation begins to become feasible if modules containing the individual cells can be made cheaply. A first step in meeting this goal is to find a way to continually

TABLE 1
Approximate Throughput and Size Specifications

	Lab. Scale Exps.	Unit Ops. Scale Expts.	Commercial Scale Production
Throughput (m ² /year)	1-100	1,000-20,000	100,000-1,000,000
Deposition Chamber (m ³)	0.1-0.5	1-3	10-30

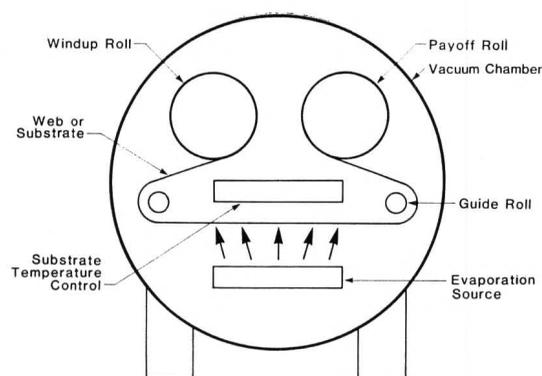


FIGURE 11. Unit operations scale deposition system.

deposit the CdS on a moving substrate.

The theoretical and experimental work of Rocheleau [6], Rocheleau et al [4] and Jackson [5] provide the verified models of the laboratory scale batch experiments that can be used to design apparatus and experiments at the unit operations scale. Throughputs and chamber sizes for typical units are shown in Table 1 for the three scales of operation of interest. The laboratory scale experiments are almost always batch experiments on a static substrate. The unit operations and commercial scale equipment for photovoltaics need to be designed for continuous deposition on a moving substrate.

A sketch of the unit operations scale equipment used at the Institute of Energy Conversion

TABLE 2
Deposition Unit Specifications

Chamber—1.28 m diameter × 1.34 m long
Vacuum—Pump-down to 5 × 10 ⁻⁶ torr in 2 hours
Web
Capacity—500 mm maximum width 250 mm roll diameter (200 m Cu foil)
Web
Speed—1.2 to 12 cm/min
Deposition
Zone—45 cm × 10 cm
Source—A proprietary design (U.S. Patent 4,325,986) providing:
• Constant rate—2 micron/min
• Uniformity over 20 cm wide zone
• 80% CdS utilization
Web
Temperature—200 to 225 °C
Throughput—0.6 to 6 m ² /shift

is shown in Fig. 11. This piece of equipment was designed using model equations similar to those presented as Fig. 5 and 6 and modified for a multi-orifice geometry and the different source-substrate geometry of the unit operations scale equipment. It was also necessary to expand the energy balance analysis to include radiative heat transfer between the source and substrate. The model equations, their behavior and their influence on the design and operation of the unit operations scale reactor are given by Rocheleau [6] and Griffin [7]. The specifications determining the equipment are shown in Table 2 and a photograph of the equipment is shown as Fig. 12.

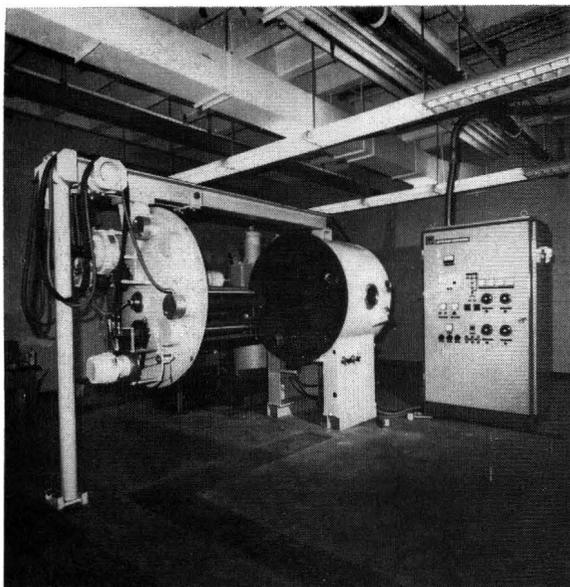


FIGURE 12. Photograph of unit operations scale deposition system.

The unit operations experimentation consisted of controlled deposition of CdS on rolls of zinc plated copper foil. Throughput of the foil ranged from 180 to 600 cm² per hour with film growth rates ranging from 0.5 to 2 μm/min. Substrate temperatures were varied between 200°C and 250°C. At throughputs of 400 cm²/hour, up to 3000 cm² of 25 μm thick CdS was prepared in a single run. Fig. 13 compares a cross-section of continuously deposited CdS with that of photovoltaic-grade batch deposited CdS. X-ray diffraction confirms predominantly c-axis orientation for the continuously deposited CdS. Resistivities of the continuously deposited CdS films ranged from about 1 to 100 ohm-cm. Resistivity of the best laboratory CdS ranges from 1 to 10 ohm-cm.

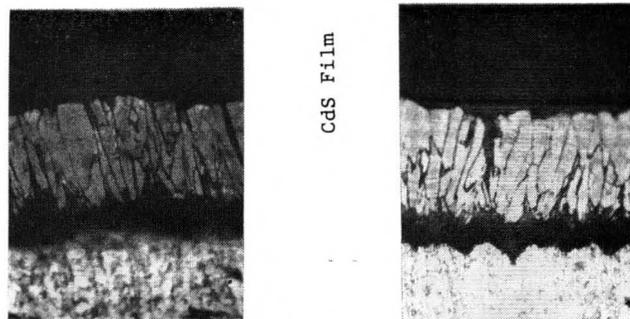


FIGURE 13. Cross-Section of CdS film. Cross-section of continuously-deposited CdS on left, cross-section of batch-deposited CdS on right.

The principal means of evaluating the CdS was to measure the photovoltaic response of cells fabricated using the material from the unit operations experiments. Results are summarized in Table 3 which shows the efficiencies of CdS/Cu₂S cells made using both laboratory scale and unit operations scale CdS. The Cu₂S layer can be made using a wet process by dipping CdS into a CuCl solution or it can be made using a dry process in which CuCl is evaporated onto the CdS and then allowed to react with Cu₂S. A quantitative description is given by Brestovansky et al [8]. Cells made by the dry process in the unit operations scale equipment had both layers, CdS and Cu₂S, continuously deposited on the moving substrate. Cells made by the wet process had to have the Cu₂S layer made in a batch operation. All cells had an evaporated gold front contact.

The efficiency figures show that the unit operations scale continuously deposited CdS is virtually of the same photovoltaic quality as the laboratory scale batch deposited CdS. It took some ten years of research to achieve the efficiencies shown for the batch deposited CdS. The continuously deposited CdS reached the efficiency shown in well under two years of unit operations experimentation. This could only have been achieved by drawing heavily

Continued on page 106.

**TABLE 3
Cell Efficiencies (CdS/Cu₂S)**

	Laboratory Scale (Batch)	Unit Operations Scale (Continuous)
Wet Process (CdS Only)	9%	8%
Dry Process (CdS/Cu ₂ S)	7%	7%

THE USE OF COMPUTER GRAPHICS TO TEACH THERMODYNAMIC PHASE DIAGRAMS

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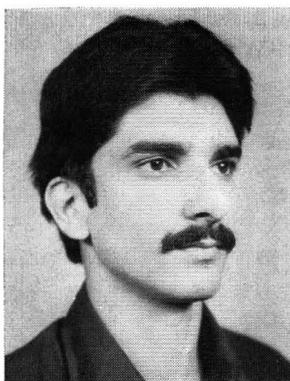
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THE TEACHING of thermodynamic phase diagrams poses problems which affect both the instructor and the students. The usual approach in which the three-dimensional pressure-temperature-composition diagrams for binary fluid mixtures are represented on a two-dimensional page is difficult for students to visualize. Traditionally, in order to simplify this complex situation, 'cuts' at constant pressure, temperature, or composition are made to show a truly two-dimensional diagram describing the relationship between two of the three independent variables. However, the inter-relationship of all the variables involved is lost with this approach, and the problem of comprehension intensifies as the complexity of the phase behavior increases. Construction of three-dimensional

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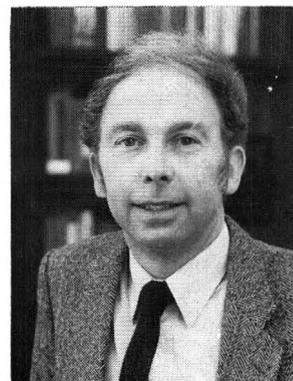
versity. He received his BS and PhD degrees at the University of London, and was on the staff at the University of Florida from 1962-76, when he moved to Cornell. He has held visiting appointments at Imperial College, London, at Oxford University, and at the University of California at Berkeley. He has co-authored two books, **Applied Statistical Mechanics** (Reed and Gubbins) and **Theory of Molecular Liquids** (Gray and Gubbins). (R)

models offers an alternative solution, but they are difficult and time-consuming to produce and offer no possibility for student interaction. At Cornell an alternative to traditional approaches was sought to improve the quality of teaching and the level of comprehension of the students. Computer graphics offers an innovative solution to these difficulties: present-day graphics hardware can perform rotational transformations of three-dimensional images almost instantaneously and allows extensive manipulation of the viewed image by the user, making this an extremely powerful tool eminently suited to the task at hand. During the past two years a highly interactive "user friendly" graphics package has been developed depicting the three-dimensional phase behavior of binary fluid mixtures, and it has been used in both undergraduate and graduate courses with great success.

THE GRAPHICS WORKSTATION

The Computer Aided Design Instructional

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versity. He received his BS and PhD degrees at the University of London, and was on the staff at the University of Florida from 1962-76, when he moved to Cornell. He has held visiting appointments at Imperial College, London, at Oxford University, and at the University of California at Berkeley. He has co-authored two books, **Applied Statistical Mechanics** (Reed and Gubbins) and **Theory of Molecular Liquids** (Gray and Gubbins). (R)



FIGURE 1. An example of a typical workstation showing the Evans and Sutherland vector refresh graphics monitor with VT100 terminal, electronic tablet and stylus.

Facility (CADIF) at Cornell houses "state-of-the-art" computer graphics equipment used solely for teaching (and developmental work towards education). The central computers for the facility are Digital Equipment Corporation (DEC) VAX machines, an 11/780 and an 11/750, running the VMS operating system, with DEC PDP 11/44 machines as post-processors. Attached to these machines are two different types of graphical display equipment for student use: vector refresh stations with dynamic three-dimensional capabilities and color raster stations for applications requiring color. In this application, the vector refresh workstations were used exclusively, these being the highly sophisticated Evans and Sutherland Multipicture Systems. Each workstation has a digitizing tablet and electronic stylus as the primary input peripheral for cursor control, with a DEC VT100 terminal for alphanumeric input. A typical workstation is shown in Fig. 1. An electrostatic plotter is also available for hardcopy output, a useful and necessary addition allowing students to submit a record of their progress to the instructor.

The software, which is the heart (or perhaps more appropriately, the brains) of this application, was written in FORTRAN making use of system graphics software routines developed at CADIF. The consideration of ergonomic factors to produce a well designed application in terms of its "user-friendliness" was considered essential to promote ease and clarity of use of the graphics package as

well as increased flexibility. Some of the ways this was achieved include the following points: extensive 'help' messages and prompts for required input were made available, clear consistent "menus" for optional choices of interactive response by the program were produced, and the ability to recover from mistakes or unintentional "miskeying" was provided. It was an original tenet of this study that students should not have to read a computer manual before using the programs. The emphasis is thus on learning engineering principles without requiring prior expertise in computing.

REPRESENTATION OF THE PHASE DIAGRAMS

The phase equilibrium data for binary mixtures needed for the representation of the phase diagram (i.e. pressures, temperatures and compositions) were generated using a theoretical model. The original Redlich-Kwong equation of state was employed for this purpose, chiefly because of the simplicity of its representation (since only two adjustable parameters are involved) and the reasonably realistic description of binary phase behavior it provides. This approach was also used

It has proven to be extremely popular with the students, and has raised the level of comprehension of this potentially difficult subject above that achieved previously by using conventional means.

by Willers and Jolls [1] who produced three-dimensional phase diagrams on a Cal Comp plotter using the same equation of state.

The well-known Redlich-Kwong expressions describing the conditions for vapor-liquid or liquid-liquid equilibrium in terms of the pressures and chemical potentials of both phases were used to generate data points P , T , V_L , V_G , x_1 , and y_1 covering a region from the higher of the pure component triple points to a temperature above both critical temperatures. The nonlinear equations involved were solved using a multidimensional Newton-Raphson [2] technique. Close to the critical region, however, convergence problems were encountered which were due, we believe, to singularities in the Jacobian matrix. These difficulties were overcome by using the Marquardt [3] method which combines the advantages of Newton-Raphson and Steepest Descent algorithms. Here Argonne National Laboratory's 'MINPAK'

Computer graphics offers an innovative solution . . . present day graphics hardware can perform rotational transformations of three-dimensional images almost instantaneously and allows extensive manipulation of the viewed image by the user . . . an extremely powerful tool . . .

software package provided the subroutine for a Marquardt method of solution. Solving for vapor-liquid critical lines also provided a challenge. Neither of the previous techniques mentioned was able to reproduce these highly non-linear equations, and a specialized algorithm due to Deiters [4] was employed for their solution.

Scott and Van Koynenburg [5, 6] classified the experimentally observed types of fluid phase diagrams into six classes, based on the presence or absence of three-phase lines and their connection with the critical lines. So far we have been able to cover the two simplest classes, I and II, although extension of the programs to cover the other classes is well underway. These more complex systems will provide an even more striking visual illustration of the advantage of using computer graphics. In classes I and II both components have similar critical temperatures with the vapor-liquid critical line passing continuously between them. In class II, however, the mixture is more non-ideal and exhibits liquid-liquid immiscibility at low temperatures. For this class, in addition to the vapor-liquid region encountered for class I, two other regions exist in the phase diagram, those of liquid-liquid equilibrium and a three-phase liquid-

TABLE I

Examples of Classes I- and II- Type Behavior Available for Display By the User

CLASS I			
Binary Mixture	Azeo-trope†	Temp Range K‡	Pressure Range Bars‡
Pentane-Nonane	N	425-590(594)	2.38-24.30(33.7)
Cyclopentane-Nonane	N	425-590(596)	2.39-21.92(45.2)
Pentane-Ethylbenzene	N	425-615(617)	4.18-36.70(37.4)
Acetone-Trichloromethane	Y-	420-530(535)	11.86-51.18(55.6)
CLASS II			
Methane-Tetra-fluoromethane	N	80-224.5(228)	1.25x10 ⁻⁴ -38.76(46.0)
Perfluoropentane-Pentane	Y,Het + Hom	240-505(506)	4.18x10 ⁻² -39.28(39.7)

†N,Y = no, yes; + - = positive or negative deviation from Raoult's law; Het, Hom = heterogeneous, homogeneous azeotrope.

‡The figures in parentheses are the highest values of T_c and P_c occurring along the critical line.

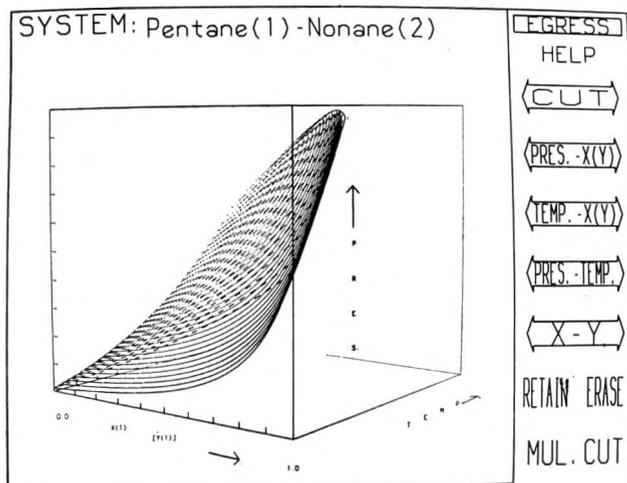


FIGURE 2. Three-dimensional phase diagram for a typical class I system, pentane-nonane. The solid and dashed lines show the vapor and liquid boundaries, respectively.

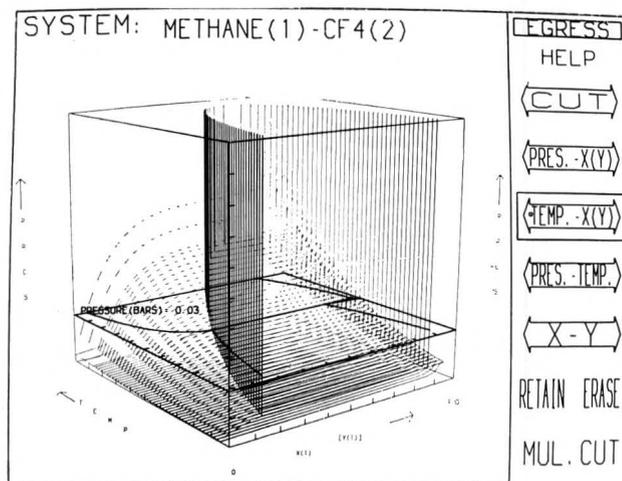


FIGURE 3. P-T-x diagram for the class II system, methane-tetrafluoromethane, showing the coexisting vapor-liquid equilibria (solid lines for the vapor, dashed for the liquid) and the region of liquid-liquid immiscibility (shown as solid vertical lines). Superimposed on the diagram (shown in bold) is a T-x cut at a pressure of 0.03 bars.

liquid-gas line. Examples of the binary systems chosen to illustrate the phase behavior of classes I and II are shown in Table 1. Some of the available systems exhibit azeotropic phenomena with either positive or negative deviations from Raoult's Law, and of either a heterogeneous or homogeneous nature. Photographs depicting some of the com-

puter-generated phase diagrams are reproduced in Figures 2-6 illustrating the kind of image displayed for the user to manipulate.

USER INTERACTION WITH THE GRAPHICS SOFTWARE PROGRAMS

The image of the phase diagram (e.g. as in Figs. 2-6) can be manipulated by the user by means of an electronic tablet and stylus (pen). As the pen is moved over (and slightly above) the surface of the tablet, a cursor in the form of cross-hairs moves over the display. When the pen is pressed down onto the tablet the graphics program is activated and performs an operation appropriate to the area of screen chosen, given that such an area is one of the several specially designated parts of the screen called "windows" on a so-called "menu" of options.

In this application of computer graphics the menu contained the following list of 'entrées' for the user to select

- READ:** Allows the user to choose different binary systems to examine by supplying one of a given set of data file names via the terminal.
- ORBIT:** This allows the phase diagram to be rotated about its pressure and composition axes in a continuous fashion as required.
- PAN:** Allows horizontal or vertical translation of the phase diagram.
- ZOOM:** Provides closer examination of a chosen area of the image by scaling the diagram up or down.

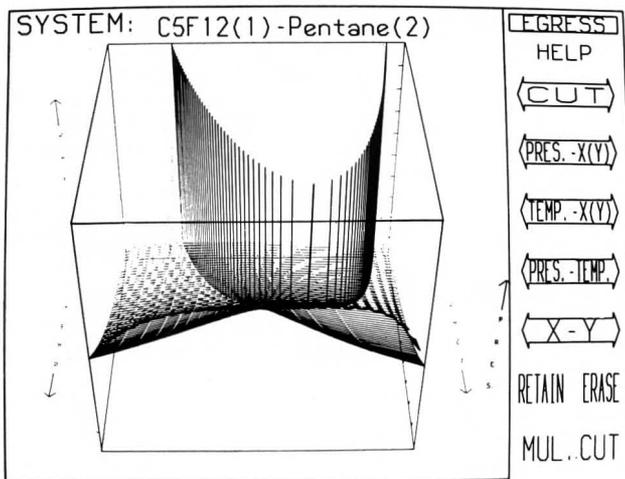


FIGURE 4. A 3-D view of another class II system, $C_5F_{12} - C_5H_{12}$. The original display has been rotated by 180 degrees and tilted downward so that the view is from the high-temperature end and somewhat above the phase diagram. The regions of vapor-liquid equilibria (showing an azeotrope) and liquid-liquid equilibria (solid vertical lines) are clearly visible.

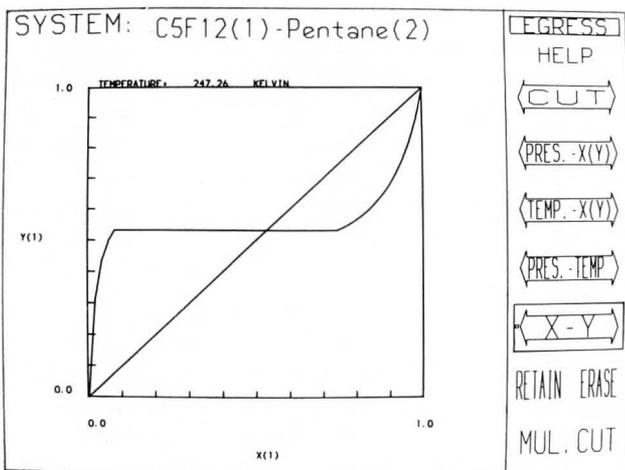


FIGURE 5. Two-Dimensional x-y diagram for the system $C_5F_{12} - C_5H_{12}$ derived from the three-dimensional phase diagram at 247.26K. This diagram shows the characteristic behavior of an azeotropic system with liquid-liquid immiscibility, as shown by the horizontal portion of the curve.

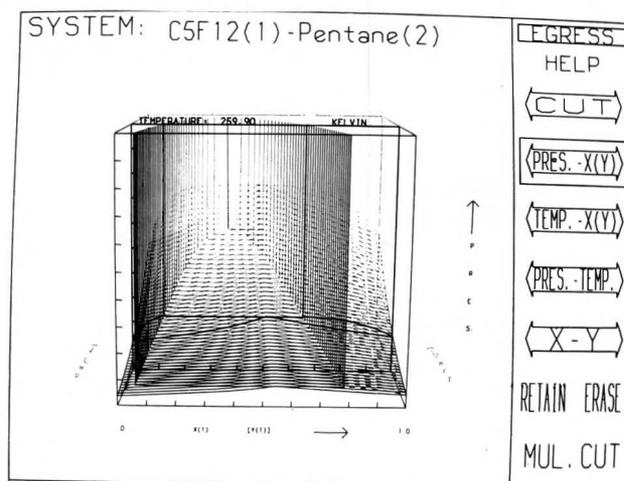


FIGURE 6. A view of the $C_5F_{12} - C_5H_{12}$ phase diagram as it appears in the initial orientation on the screen. Solid and dashed lines have the same meaning as in Figure 2. A P-x-y cut is shown superimposed in bold on the diagram at a temperature of 259.9 K.

- e) **STRETCH:** Scales either of both of the P, T axes relative to the composition axis for ease of viewing.
- f) **HELP:** Summons the HELP text.
- g) **RESET:** Voids all previous manipulations and resets the system to the beginning of the program.
- h) **SNAP:** Produces a hard-copy image of the screen on a nearby plotter.
- i) **EGRESS:** Allows the user to terminate his or her session.
- j) **T-X, P-X, P-T:** Each of these windows allows a particular highlighted "cut" of the phase diagram to be chosen by the user as shown in Figure 3 for a T-x cut at 0.03 bars for the system methane-carbon tetrafluoride, and in Figure 6 for a P-x cut at 259.9K for C₅F₁₂-pentane.
- k) **CUT:** Produces a P-x, P-T or T-x "cut" displayed alone (i.e. not superimposed on the whole phase diagram) depending on which of these three windows (P-X, P-T or T-X) was last active. Multiple cuts (of P-x at different temperatures for example) may be displayed simultaneously.
- l) Produces an x-y plot at constant temperature, as shown in Fig. 5 for the system C₅F₁₂-pentane at 247 K.

A 16mm movie lasting approximately thirteen minutes has been prepared to illustrate the capabilities of this graphics package; this was presented at the 1983 AIChE annual meeting in Washington, D.C.

SUMMARY

The interactive graphics package illustrating the phase behavior of binary mixtures which has been described in this paper has been used within the chemical engineering curriculum at Cornell since the fall semester of 1982. It has proven to be extremely popular with the students, and has raised the level of comprehension of this potentially difficult subject above that achieved previously using conventional means. The major advantage lies in the suitability of computer graphics as a means of visualizing three-dimensional objects (here the PTx phase space); the capability of the hardware to perform rapid and continuous rotations of the image; and, perhaps most importantly, the opportunity to interact, manipulate and control the image observed on the screen, brought about by flexible "user-friendly" software. All these features combine to contribute to the success of this technique in undergraduate instruction. □

ACKNOWLEDGMENTS

It is a pleasure to thank the Gas Research Institute for partial support of this work.

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ChE book reviews

FOUNDATIONS OF BOUNDARY LAYER THEORY FOR MOMENTUM, HEAT AND MASS TRANSFER

by Joseph A. Schetz

Prentice Hall, Inc., NY (1983)

Reviewed by

O. T. Hanna

University of California, Santa Barbara

This book on Boundary Layer Theory is indicated by the author to be applicable for students in mechanical, aerospace, chemical, civil, and ocean engineering. Some people would doubt that anyone could succeed in such a broad task. The author's stated goals for this book include (i) providing an understandable coverage of advances in turbulence modeling, (ii) presenting application of large digital computers to boundary layer problems, and (iii) treating mass transfer in an integrated manner with momentum and heat transfer. It would appear that the first goal has been met reasonably well; achievement of the second goal is questionable, and the third goal has definitely not been met to the satisfaction of chemical engineers.

The book is generally well written and well-organized. The coverage of laminar flows includes chapters on integral and differential equations of flow together with approximate integral solutions and exact similarity solutions. Unfortunately almost all of this material is available in a number of other sources and hardly any of it is more recent than 1960. The meager coverage of mass

transfer is likely to be of little interest to chemical engineers. Chapters 4 and 5 do contain some useful discussions of numerical solutions of boundary layer problems. However, there are no example problems or computer programs.

The major contribution of this book would appear to lie in Chapters 6 through 9, on turbulence modeling, which constitute more than half the length of the book. This material includes a useful historical perspective and spans the complete range of engineering approaches in this area up to the present time. The chronological discussion of work in turbulence modeling beginning with early mixing-length theory and progressing up to algebraic and various partial differential equation models should be of interest and value to chemical engineering. This discussion also integrates well the contributions to modeling from both experimental and theory.

In summary, the present book seems somewhat disappointing in its treatment of laminar boundary layers, but in contrast it contains material on turbulent momentum transfer which should be of interest to chemical engineers. In this context the book can be recommended as a useful reference. □

INDUSTRIAL HYGIENE ASPECTS OF PLANT OPERATIONS

*by L. J. Cralley, L. V. Cralley, and J. E. Mutchler
Macmillan Publishing Company, New York,
1984: \$60.00*

Reviewed by

Klaus D. Timmerhaus
University of Colorado

This is the second volume of a new three-volume series that is being prepared to provide recognition, measurement, and control of potential hazards normally present in various industrial plant operations. The first volume covered process flows while the third volume will treat equipment selection, layout and building design.

This volume, divided into two major sections of unit operations and product fabrication, encompasses a broad range of industries with authoritative information contributed by specialists from these industries. In the first section twenty-three contributors discuss unit operations as distinct entities along an industry-wide concept. Some of the unit operations considered include filtration, clarification, mixing, blending, grind-

ing, and spray, vacuum, freeze and fluidized bed drying. The second section includes thirteen contributions which cover the operations and procedures for assembling parts and materials into final products. The industries considered in this latter survey range from such basic industries as storage battery and tire manufacturing to the high technology industries of semiconductor and liquid scintillation counter manufacturing. One may argue with the manufacturing processes that were selected by the editors; however, the breadth of the selected processes and the hazards associated with these processes should provide a good introduction to the hazards associated with those manufacturing processes that were not included.

Even though most contributors to this second volume have adequately described each step in the unit operations and product fabrication flow of a specific manufacturing process and have included a discussion of the various health hazards that may be encountered with suggestions for their monitoring and control, many engineering readers will be disappointed by the qualitative approach taken by the contributors to this important subject. Only a few of the chapters in the volume have included quantitative information that would be necessary in the design and construction of process equipment that minimizes or eliminates identified industrial hygiene hazards. Where such quantitative information is included, it is generally quite sketchy and incomplete forcing the design engineer to consult other literature sources. Unfortunately, no guidance to such quantitative data is included by any of the contributors. Chemical engineers will also be somewhat disappointed in this volume because the "unit operations" portion of the title implies that some of the contributions will examine the conventional unit operations associated with heat, mass and momentum transfer. However, many of the key unit operations such as distillation, absorption, extraction, evaporation, heat transmission, etc. found in most typical petroleum and chemical processing plants have not been included.

Nevertheless, this volume does manage to bring together a wealth of experience in a broad range of industries and will aid engineers, managers, and industrial hygienists to more fully recognize potential hazards of industrial processes. This, in turn, will permit these professionals to evaluate such hazards and take the necessary steps to effectively control the problem. □

AN IMPROVED DESIGN OF A SIMPLE TUBULAR REACTOR EXPERIMENT

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DESIGNING A TUBULAR FLOW reactor experiment for an undergraduate laboratory is not a simple task. This is because the experiment will have to meet certain criteria, viz

- It is safe
- It is simple and cost effective
- It is instructive
- Its analytical needs must be simple and easy, to meet the time constraints of an undergraduate laboratory

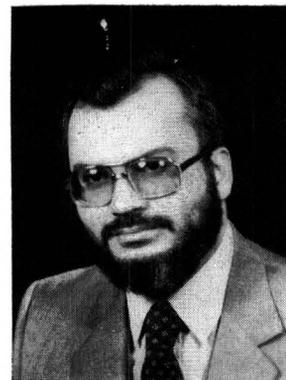
Anderson [1] developed a tubular flow reactor experiment for an undergraduate laboratory at Princeton that utilized the system acetic anhydride-water. This particular experiment requires relatively elaborate safety precautions. Moreover, since the reaction is exothermic, rather expensive temperature control equipment is required. Samples taken at the reactor inlet and outlet are analyzed by the aniline-water method which is relatively lengthy and subject to errors.

Hudgins and Cayrol [2] utilized the basic design of Anderson in developing a simple and interesting experiment. They utilized the classical reaction system of crystal violet dye neutralization with sodium hydroxide. This system was studied earlier by other investigators, mainly in a batch reactor (Carsaro [3]). The two novel aspects of the Hudgins-Cayrol experiment compared with that of Anderson are

- A colour change can be seen between the inlet and outlet of the reactor
- The temperature constraint is removed. This makes the experiment operable at room temperature

Also, from the safety standpoint, a relatively dilute sodium hydroxide solution (0.04 N according to Hudgins and Cayrol) is used.

However, the experimental set-up design given by Hudgins and Cayrol can be significantly



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improved. The design improvements suggested in this article should make the experiment easier to run and control, significantly improve the reproducibility of results, and expedite the process of data collection within the time constraints of an undergraduate laboratory.

The main objectives of this experiment are

- To study the effect of residence time on conversion in a tubular flow reactor
- To compare the experimental conversions with those obtained from plug-flow and laminar-flow reactor models

THEORY

As it was established by Corsaro [3], the reaction between crystal violet dye and sodium hydroxide is of the first order in the concentration of each of the reactants, i.e., the reaction is of the second order. However, the reaction can be made pseudo-first order if sodium hydroxide is used in great excess with respect to crystal violet dye. In other words

$$-r_{\text{dye}} = k' [\text{dye}] \quad (1)$$

The value of the rate constant, k' , is needed for this experiment. Students are requested to run a batch experiment to determine the value of k' at the same temperature of the flow experiment . . . (and) to prepare their own calibration curve of the dye concentration versus absorbance.

For the purpose of this experiment, 0.02 N sodium hydroxide solution is used with 6.86×10^{-4} M dye solution, i.e., the sodium hydroxide concentration would be about 282 times that of the dye, if equal volumes of reactants are used.

Experimental conversions are calculated, as will be described later, and compared with theoretical conversions predicted from the plug-flow model and the laminar-flow model.

For a first order reaction in a plug-flow reactor, the following equation applies assuming constant density of reaction mixture:

$$\tau = \frac{V}{v_0} = -\frac{1}{k'} \ln(1-x) \quad (2)$$

$$= -\frac{1}{k'} \ln \frac{C_A}{C_{A0}} \quad (3)$$

If C_A is taken as $[\text{dye}]_e$, i.e., the dye concentration at reactor exit and C_{A0} as $[\text{dye}]_i$, i.e., the dye concentration at reactor inlet, then one can rewrite Eq. (3) as follows:

$$\tau = \frac{V}{v_0} = \frac{1}{k'} \ln \frac{[\text{dye}]_i}{[\text{dye}]_e} \quad (4)$$

For a first order reaction in a laminar-flow reactor, the following equation applies assuming

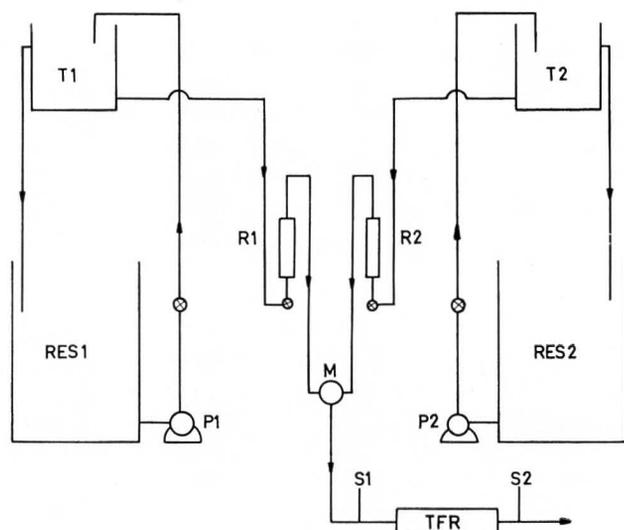


FIGURE 1. Schematic diagram for the experimental set-up. M: mixer, P: pump, R: rotameter, RES: reservoir, S: sampling point, T: constant head tank, TFR: tubular flow reactor.

no change in volume by reaction as well as no mixing in both radial and axial directions (4)

$$x = 1 - \left(\frac{N_R}{2}\right)^2 E\left(\frac{N_R}{2}\right) + \left(\frac{N_R}{2} - 1\right) \exp(-N_R/2) \quad (5)$$

where

$$N_R = k'\tau$$

$$\tau = \frac{V}{v_0} = \frac{L\pi r^2}{v_0}$$

The function $E(y)$ is defined by:

$$E(y) = \int_y^{\infty} \frac{\exp(-\phi)}{\phi} d\phi$$

The function $E(y)$ is tabulated in standard tables as $-E_i(-X)$.

EXPERIMENTAL

A schematic diagram of the proposed experimental set-up is given in Fig. 1. The experimental apparatus is comprised of the following components.

- | | |
|---------------------|---|
| Reservoirs | : (RES 1) 200-L polyethylene tank for the sodium hydroxide solution |
| | (RES 2) 20-L polyethylene tank for the dye solution |
| Constant Head Tanks | : (T1) 20-L polyethylene tank for the sodium hydroxide solution |
| | (T2) 4-L polyethylene tank for the dye solution |
| Pumps | : (P1) Magnet drive gear pump; Model P/N 81152 manufactured by Micropump Corp., Conford, California. Purchased from Cole Parmer Co. |
| | (P2) Centrifugal pump. Cole Parmer catalogue No. K-7004-30 |
| Mixer | : (M) Little Giant Pump. Model 2E-38NT. Purchased from Can Lab |
| Rotameters | : (R1) Size R-6-15-A rotameter. Max flow 450 ml/min with SS-float. Purchased from Brooks Instrument Co. |
| | (R2) Size R-6-15-B rotameter. Max flow 1300 ml/min with SS-float. |

Purchased from Brooks Instrument Co.

- Reactor** : 40 meters of 3/8 in. I.D. Tygon tubing, wound on spool (made of lexan), 28 cm in diameter and 55 cm in length*
- Valves** : needle valves to adjust flow
- Spectrometers** : Spectronic 20 (Bausch & Lomb) modified, as will be described later, to provide continuous measurements.

Two polyethylene tanks (RES 1 and RES 2) of capacity 20 liters and 200 liters serve as reservoirs for the crystal violet dye and sodium hydroxide solutions, respectively. Two pumps (P1 and P2) are employed to pump the reactants to two constant head tanks (T1 and T2). The overflows from the constant head tanks are returned to their respective reservoirs. The underflows from the constant head tanks go via rotameters (R1 and R2) to a small pump that acts as a mixer (M). The reactant streams are mixed in the mixer, M, and are pumped through the reactor. The tubular reactor is in the form of a helical coil wound on support. Connections are provided at the inlet and outlet of the reactor to the flow-through cuvettes of the spectrometers.

The main advantages of the proposed experimental set-up over that suggested by Hudgins and Cayrol are

- Reservoirs and constant head tanks are used. This arrangement provides more stable rotameter operation, especially at low flow rates.
- A flow-through accessory which is simpler in design and operation than that suggested by Hudgins and Cayrol has been used. The flow-through accessory shown in Fig. 2 allows one to use Spectronic 20 for continuous measurements.

PROCEDURE

Due to the limitation of the headroom in most undergraduate laboratories, the constant head tanks (T1 and T2) are placed about 3 meters above the rotameters' level. This limitation makes it only possible to attain maximum flow rate of 1300 ml/min of NaOH. The maximum flow rate of the dye is set at about 135 ml/min.

*One of the reviewers suggested the use of polyethylene instead of Tygon tubing, which discolors to a deep purple making it difficult to observe gradual colour-change along the reactor. It is believed that polyethylene is more resistant to the dye than Tygon tubing.

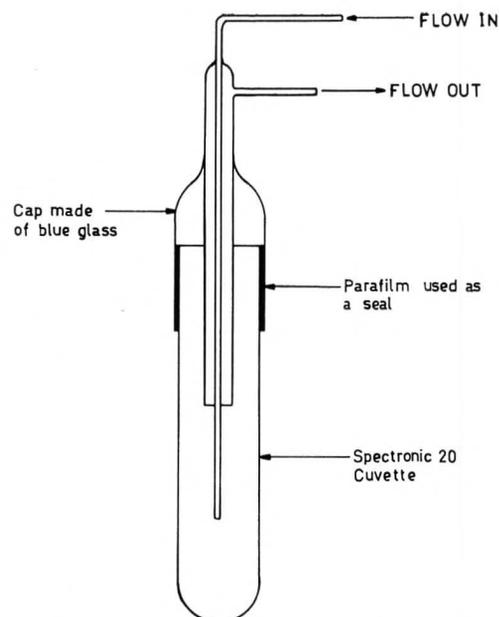


FIGURE 2. Flow-through cuvette for the Spectronic 20.

The flow rates of sodium hydroxide and the dye solution are set such that the ratio is 9:1. One should start at the highest possible flow rate to expel all air bubbles from the reactor.

One should wait for slightly longer than the residence time, for a particular flow rate, for steady-state to be reached. The reaction mixture is then allowed to flow through the Spectronic 20 flow-through cuvettes and the readings are recorded. Usually, one waits for two minutes and takes another reading as a duplicate. Experience has shown that the Spectronic 20 readings are highly reproducible. Other flow rates of NaOH and dye solution are chosen, keeping the flow rates ratio 9:1 as before, and the Spectronic 20 readings are recorded. The experiment usually lasts for one hour provided that the solutions are prepared prior to the laboratory period.

TABLE I
Holding Time and Conversion Data

Holding Time min	Reynolds Number	PFRM conv.	LFRM conv.	Exp. Conversion x
6.42	791	71.7	63.3	71.5
4.3	1181	57.1	50.3	53.3
3.23	1651	47.1	41.6	44.5
2.54	2000	39.4	34.96	36.9
2.13	2385	34.3	30.7	33.85

The value of the rate constant, k' , is needed for this experiment. Students are requested to run a batch experiment to determine the value of k' at the same temperature of the flow experiment. This has proven worthwhile, since temperature fluctuations in most undergraduate laboratories do not allow conducting a batch experiment at the beginning of the semester and giving the value of k to the students to perform the required calculations. Also, students are required to prepare their own calibration curve of the dye concentration versus absorbance. This leads to better results.

RESULTS AND DISCUSSION

Table 1 reports the residence time and the conversions from the plug-flow reactor model (PFRM), laminar-flow reactor model (LFRM) and the experimental conversions. Fig. 3, also, depicts the conversions against the residence time. The data reported in Table 1 and Fig. 3 were obtained from an experiment conducted on the set-up available in Windsor.

It is clear from Fig. 3 that, as expected, the experimental conversions fall between the con-

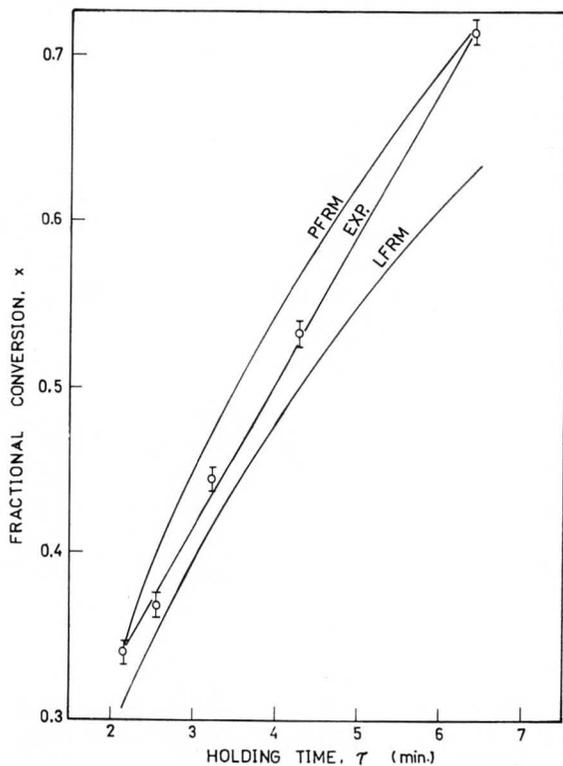


FIGURE 3. Comparison between conversion obtained from experiment and those obtained from LFRM and PFRM.

REQUEST FOR FALL ISSUE PAPERS

Each year CHEMICAL ENGINEERING EDUCATION publishes a special fall issue devoted to graduate education. This issue consists 1) of articles on graduate courses and research written by professors at various universities, and 2) of announcements placed by ChE departments describing their graduate programs. Anyone interested in contributing to the editorial content of the fall 1985 issue should write the editor, indicating the subject of the contribution and the tentative date it can be submitted. Deadline is June 15th.

versions obtained from the two theoretical models, viz., the PFRM and LFRM.

It is worthwhile to note here that the data reported by Hudgins and Cayrol indicate that the experimental conversion curve crosses the LFRM curve at short holding times, i.e., experimental conversions are lower than those predicted by LFRM, which is not possible. Such results may be attributed to the obvious design flaws in the set-up reported by those authors.

The change of colour of the reaction mixture between the inlet and outlet of the reactor is due to the conversion along the reactor. Such a visual effect helps the students to integrate the laboratory experiment with what they learned in the lecture part of the course about conversion in tubular flow reactors. \square

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NOTATION

- o = subscript symbol for initial
 i,e = subscript symbols for reactor inlet and exit, respectively
 C_A = concentration of component A, (mole/L)
 k' = pseudo-first order rate constant, (min^{-1})
 L = length of reactor tube, (m)
 N_R = k' = reaction number for a first order reaction
 r = inside radius of reactor tube, (m)
 $(-r)$ = reaction rate, ($\text{mol/L}\cdot\text{min}$)
 v_0 = volumetric flow rate, (L/min)
 V = reactor volume, (m^3)
 x = conversion
 τ = V/v_0 = space time (min)

*The B. C. (Before Computers) and A. D. of***EQUILIBRIUM-STAGE OPERATIONS***

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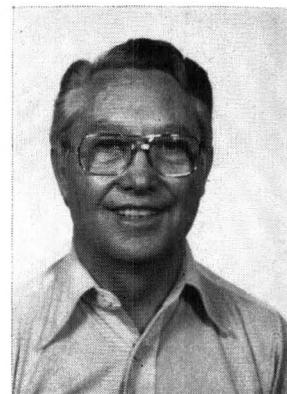
THE ART OF DISTILLATION and other multi-component, multistage separation operations has been practiced since antiquity. Although describing equations for distillation were formulated before 1900, flexible, efficient, and robust procedures for solving the equations did not appear in the literature until after the availability of digital computers beginning in 1951. This paper is keyed to that date with B.C. referring to "before computers."

In 58 B.C., Sorel developed the first theoretical equations for simple, continuous, steady-state distillation, but they did not find wide application until 30 B.C., when they were adapted to a rapid graphical construction technique for binary systems by Ponchon and then Savarit. This was quickly followed in 26 B.C. by a much simpler, but restricted, graphical technique by McCabe and Thiele. Computer methods have largely replaced the rigorous Ponchon-Savarit Method, but the graphical McCabe-Thiele Method is so simple and so illustrative, it continues to be popular.

A modern version of Sorel's equations (shown in Fig. 1) includes, in the case of a partial condenser, total and component material balances and an energy balance around the top section of the column. Phase equilibrium on each tray is ex-

The development of a separation process can be an exciting experience when computers and computer programs are available to perform the tedious calculations and allow time for more consideration of synthesis and optimization aspects.

*Tutorial Lecture presented at 92nd ASEE Annual Conference, Salt Lake City, Utah, June 22-28, 1984.



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pressed in terms of component K-values and one mole fraction sum per stage for either vapor or liquid is needed. Similar equations are written for the bottom section of the column and for the feed stage.

DEGREES OF FREEDOM ANALYSIS

A degrees of freedom analysis for the equations was first developed by Gilliland and Reed in 9 B.C. A more thorough treatment for all types of separations and other operations was reported by Kwauk in 5 A.D.

If the equations and variables are counted, for a column with N stages (including the condenser and reboiler) to fractionate a feed with C components, it is found that the number of equations is $N(2C + 3)$, while the number of variables is $N(2C + 4) + C + 7$. Variables include stage temperatures, pressures, vapor and liquid flow rates and component mole fractions; feed

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The nature of the equations of Sorel and the difficulty of their solution for multicomponent systems has long been recognized. The set of equations can be large in number. For example, with 10 components and 30 equilibrium stages, the equations number 690. Sixty percent of the equations are nonlinear, making it impossible to solve them directly.

flow rate, composition, temperature and pressure; reboiler and condenser duties; and number of theoretical stages above and below the feed. The thermodynamic properties, K and H , are not counted as variables because they can be written explicitly in terms of the other variables just mentioned. The degrees of freedom or number of variables that must be specified equals the difference between the number of variables and the number of equations or $N + C + 7$.

A simple set of specifications would include feed flow rate, composition, temperature, and

pressure; number of trays above the feed and below the feed; the pressure of each stage; and the reflux flow rate, L_1 . This totals $N + C + 6$, which is one short of the number of degrees of freedom. From my own practical experience in 5 A.D., failure to supply the one additional specification can result in a calculational procedure that will never converge. The additional specification might be the distillate flow rate V_1 .

NATURE OF SOREL'S EQUATIONS AND SPARSITY PATTERNS

The nature of the equations of Sorel and the difficulty of their solution for multicomponent systems has long been recognized. The set of equations can be large in number. For example with 10 components and 30 equilibrium stages, the equations number 690. Sixty percent of the equations are nonlinear, making it impossible to solve them directly. The magnitude of the values of the variables can cover an enormous range. For example, the mole fraction of a very volatile component at the bottom of the column might be very small, perhaps 10^{-50} . The value of a total flow rate might be 10^4 .

Commonly used procedures for solving such sets of equations, as discussed by Henley and Seader, are iterative in nature, requiring starting guesses for some or all of the variables. Early procedures were complete equation-tearing methods, suitable for manual calculations, wherein the equations were solved one-at-a-time in a sequential manner. With the advent of the digital computer, partial tearing methods appeared, wherein small groups of equations as well as single equations were solved at a time. Most recently, with the availability of larger and faster digital computers, very flexible simultaneous-correction methods appeared wherein all the equations were solved simultaneously by a modified Newton's method.

An additional characteristic of Sorel's set of equations is sparsity. That is, no one equation contains more than a small percentage of the variables. For example, for the case of 10 components and 30 stages, no equation contains even

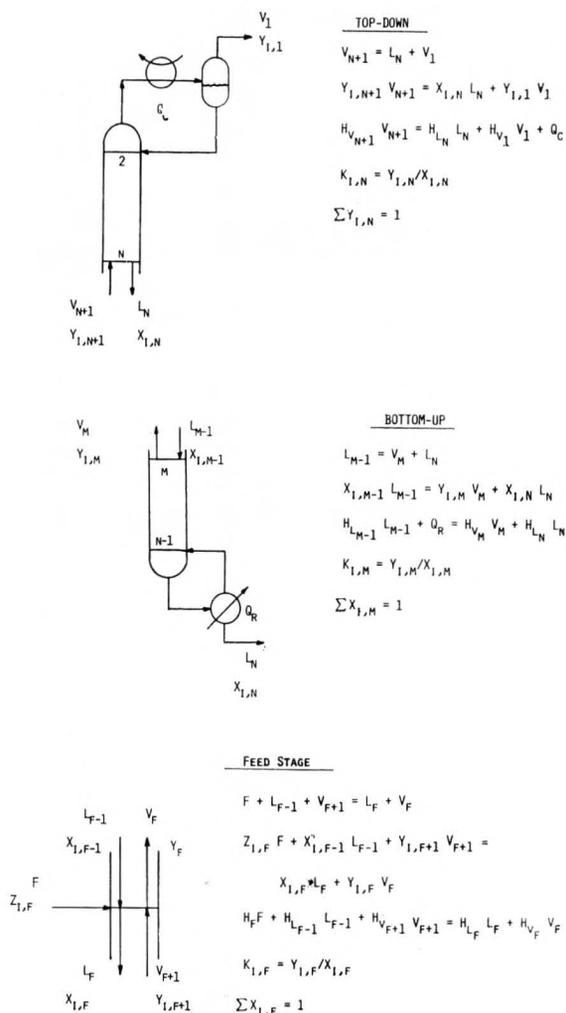


FIGURE 1. Modern version of Sorel's equations.

7 percent of the variables. This sparsity is due to the fact that each stage is only directly connected to, at most, two adjacent stages.

The nature of this sparsity has been exploited in the development of the above-cited methods by seeking certain sparsity patterns which are best observed by the use of incidence matrices. The rows of the incidence matrix represent the different functions or equations being solved. The columns of the matrix represent the different variables contained in the equations. Thus, for $N = 30$ and $C = 10$, the matrix is of size 690 by 690. If a certain equation contains a certain variable, some non-zero entry, such as an X, is placed in the matrix at the corresponding location. Other-

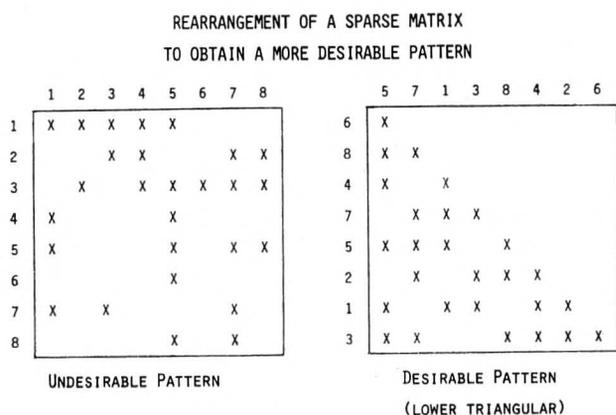


FIGURE 2. Incidence matrices.

wise a zero or no entry is made.

The sparsity pattern depends upon the order in which the columns and rows of the matrix are arranged. The arrangement shown at the left in Fig. 2 appears to be random without pattern. However, by interchanging certain columns and rows, the lower triangular pattern shown at the right is obtained. Such an organized pattern, if it can be achieved, is highly desirable because it indicates that the equations can be solved one-at-a-time starting with the equation for the first or top row, solving for the only unknown, and then proceeding down the rows, equation-by-equation, solving for one unknown at-a-time, but where necessary, using values of previously computed variables.

Since at least 10 B.C., a number of other desirable sparse matrix patterns have been recognized. Shown at the left in Fig. 3 is a block-diagonal pattern. The non-zero entries are all contained within the interior bold-lined region. Shown in the middle is a banded matrix, where

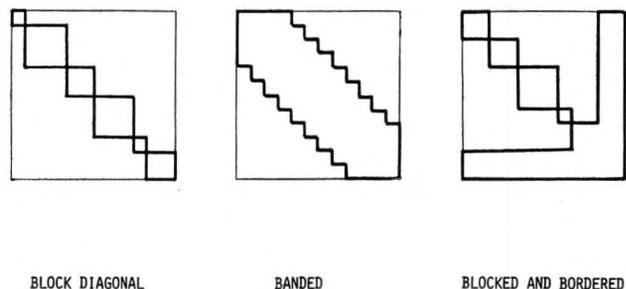


FIGURE 3. Desirable sparse matrix patterns.

all non-zero entries are contained on the main diagonal and a few adjacent diagonals. Shown at the right is a blocked-and-bordered matrix. Such organized sparse matrix patterns, when they exist, can be found readily by computer algorithms such as the MA-28 subroutine of the Harwell library.

EQUATION-TEARING STRATEGIES

For the four organized patterns just discussed, specialized sparse-pattern computer algorithms have been developed to solve, in an efficient manner, linearized forms of the nonlinear equations that describe the system. These sparse matrix methods strive to: (1) eliminate storage of zero coefficients and certain repetitious nonzero elements, (2) reduce arithmetic operations, in particular those involving zeros, and (3) maintain sparsity during computations.

Less-organized sparse-matrix structures can sometimes utilize organized sparse-matrix methods in an iterative manner by employing equation-tearing strategies. The structure shown in Fig. 4 is lower triangular, except for an additional non-

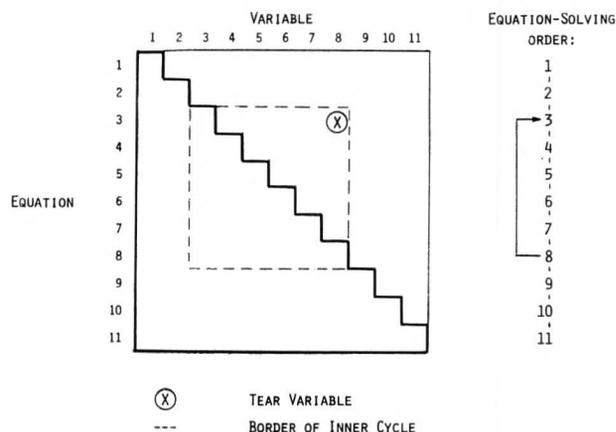


FIGURE 4. Application of tearing to a sparse matrix.

zero entry at column 8 in row 3. The linearized equations cannot be solved directly, one-at-a-time, starting with Equation 1, because when Equation 3 is reached, the value of variable 8 is not known; thus, Equation 3 cannot be solved for variable 3. A tearing strategy can be employed to overcome this difficulty, but an iterative calculational loop or cycle, shown by the dashed border, involving Equations 3 through 8, is necessary. Variable 8 shown as a circled X, is the single tear variable which, when given an estimated value, results in the tearing apart of that subset of equations so they can be solved individually in order. At Equation 8 in the cycle, variable 3 is calculated and the value obtained is compared to the value used in Equation 3. If the two values are sufficiently close, the cycle is converged and variable 9 in Equation 9 is computed, followed by solution of

**Chemical engineering educators
need to closely examine courses on separation
processes to make sure that students are
being instructed in modern and
efficient computational tools.**

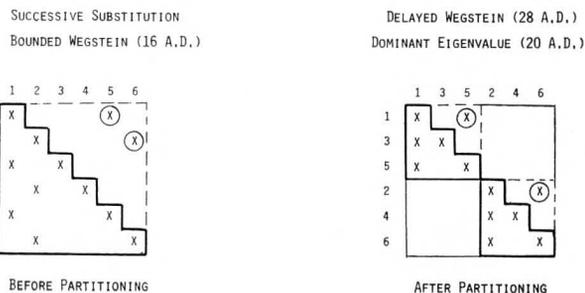


FIGURE 6. Partitioning when convergence acceleration methods ignore interactions among the variables.

convergence is impossible to achieve from any starting guess of the tear variable. For example, if the initial guess for x_2 is 8, the sequence obtained quickly diverges, as shown. After only one iteration, x_2 has increased in value to $5.9 \cdot 10^8$, which is far from the solution.

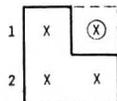
Alternatively, in tearing strategy #2, where the two columns of the matrix are interchanged to make x_1 the tear variable, convergence is readily achieved, as shown, from any initial guess, even $x_1 = 500$. The solution $x_1 = 4$, $x_2 = 9$ is obtained in just three iterations. These two drastically different results are obtained because Equation 1 is very sensitive to the value of x_2 and almost insensitive to the value of x_1 . Thus, in this example, x_2 should not be the tear variable when Equation 1 is solved before Equation 2.

In the example just considered, the guess for x_1 , at the beginning of each iteration is set equal to the value computed from Equation 2 in the previous iteration. This procedure, called successive substitution, can be slow to converge, and, therefore, a number of some simple and some complex procedures have been developed to accelerate convergence. These procedures are particularly useful when more than one tear variable must be used as in Fig. 6. The example at the left has two tear variables. Some methods, including successive substitution, bounded Wegstein, delayed Wegstein, and dominant eigenvalue, ignore interactions among the variables. When interactions do not exist, it should be possible to interchange columns and rows of the matrix to obtain

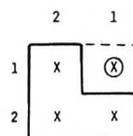
$$F_1 = 2x_1^3 + x_2^2 - 85 = 0$$

$$F_2 = 2x_1^2 + x_2^3 - 35 = 0$$

TEARING STRATEGY #1:		ITERATION	GUESSED x_2	x_1 FROM F_1	x_2 FROM F_2
1	2	1	8	110	5.9×10^8
2	1	2	5.9×10^8	3.0×10^{34}	--



TEARING STRATEGY #2:		ITERATION	GUESSED x_1	x_2 FROM F_1	x_1 FROM F_2
2	1	1	500	6.346546	4.029936
1	2	2	4.029936	8.999170	4.000010
2	1	3	4.000010	9.000000	4.000000



BETTER RESULTS WITH THIS STRATEGY BECAUSE F_1 IS RELATIVELY SENSITIVE TO x_2 BUT NOT TO x_1 , WHILE THE OPPOSITE IS TRUE FOR F_2

FIGURE 5. Sensitivity of the tearing method.

Equations 10 and 11 to complete the system. Otherwise, a new approximation for the tear variable must be determined and another iteration of the cycle completed.

For the tearing strategy to be successful and efficient, it is necessary that Equation 3 not be sensitive to the assumed value of Variable 8. If too sensitive, it is best, if possible, to reorder the equations and variables to obtain a less sensitive situation. As a simple example of this sensitivity, consider the two equations shown in Fig. 5. If x_2 is the tear variable and Equation 1 is solved first,

NEWTON
BROYDEN (18 A.D.)

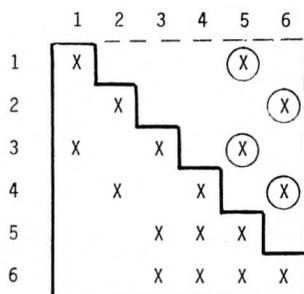


FIGURE 7. Convergence acceleration methods that account for interactions among the variables.

a block diagonal structure, shown at the right of Fig. 6, which allows separate computations of the two individual partitions, each containing just a single tear variable.

The more common case is when interactions among the tear variables exist, as shown in Fig. 7, where the two tear variables are 5 and 6. The iterative cycle includes all equations. Then, partitioning is not possible and, if the interactions are strong enough, convergence acceleration by Newton's method or a quasi-Newton method, such as that of Broyden, may be desirable.

SIMPLE AND COMPLEX SEPARATION OPERATIONS

The nature of the sparse-matrix pattern obtained from Sorel's equations and the corresponding calculational procedure depends on a number of factors, including: (1) selection of the working equations, (2) selection of the variables, (3) degree of flexibility in the specifications, (4) order of arrangement of the equations, (5) order of arrangement of the variables, (6) functionality of the physical properties, and (7) method by which any equations are linearized.

An additional factor that influences the nature of the sparse matrix pattern of Sorel's equations is the type of separation operation. In simple distillation, a single feed is separated into two products, a distillate and a bottoms; energy required to separate the species is added in the form of heat by a reboiler at the bottom of the column where the temperature is highest. Also, heat is removed by a condenser at the top of the column where the temperature is lowest. This frequently results in a large energy input requirement and

low overall thermodynamic efficiency, which was of little concern (except for cryogenic and high-temperature processes) before 22 A.D. when energy costs were low. With recent dramatic increases in energy costs, complex distillation operations (described by Seader in the 6th edition of Perry's *Chemical Engineers' Handbook*) and systems are being explored that offer higher thermodynamic efficiency and lower energy input requirements. Complex columns and systems may involve multiple feeds, sidestreams, intermediate heat transfer, multiple columns that may be interlinked, and in some cases, all or a portion of the energy input as shaft work.

COMPLETE TEARING METHOD

Simple and complex distillation operations have two things in common: (1) both rectifying and stripping sections are provided such that a separation can be achieved between two components that are adjacent in volatility, and (2) the separation is effected only by the addition and removal of energy and not by the addition of any mass separating agent (MSA) such as in liquid-

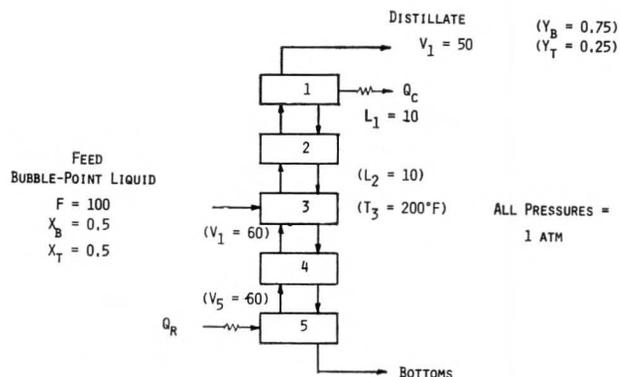


FIGURE 8. Example of specifications and tear variables for top down, bottom-up, stage-by-stage method.

liquid extraction. Sometimes, other related multiple-stage vapor-liquid separation operations, such as refluxed rectification, reboiled stripping, absorption, stripping, reboiled absorption, refluxed stripping, extractive distillation, and azeotropic distillation, as described by Seader, may be more suitable than distillation for the specified task. All these separation operations can be referred to as distillation-type separations because they have much in common with respect to calculations of thermodynamics properties, vapor-liquid equilibrium stages, and column sizing. For calcu-

lations involving such operations, prior to digital computers, the factors influencing the nature of the sparse matrix pattern from Sorel's equations were chosen so that a complete tearing method could be employed so the equations could be solved sequentially one-at-a-time. Many techniques were proposed, with the stage-by-stage methods of Lewis and Matheson in 19 B.C. and Thiele and Geddes in 18 B.C. being the most useful. In 6 A.D., features of these two methods were combined into a single method, applicable to computations with a digital computer. Specifications are the simple set discussed previously and illustrated in Fig. 8 by an example involving two components, benzene and toluene, and five theoretical stages. The tear variables ($2C + N - 1$) in number, and typical initial guesses for them are shown in parentheses. These tear variables include the component mole fractions in the distillate.

The initial guesses for the distillate composition are conveniently obtained by using a rearrangement of the Fenske equation with the minimum number of equilibrium stages set equal to one-half of the total number of specified equilibrium stages. The sum of the component flow rates in the distillate must equal the specified total distillate flowrate and, for each component, the sum of the flow rates in the distillate and bottoms must equal the feed rate.

The equations used are modifications of Sorel's equations, and include total material balances, component material balances, bubble-points, dew-points, energy balances, an adiabatic flash for the feed stage, and equations for re-estimating distillate mole fractions.

The incidence matrix, shown in Fig. 9, is lower triangular except for the six tear variables, which are represented as circled X's. They appear in vertical columns in the order L_2 , V_5 , V_4 , T_3 , $Y_{1,1}$, and $Y_{2,1}$. The latter are the assumed distillate mole fractions. The variables across the top and the equations corresponding to the rows are ordered by stage number, as shown, where the stages are numbered from the top down, with 1 as the partial condenser and 5 as the partial reboiler. The calculations begin in the upper left corner and proceed down the diagonal. At the upper left corner, the first two equations, which each contain only a single unknown, are solved directly for the bottoms rate L_5 , and the top-tray vapor rate V_2 . All remaining equations are enclosed within the dashed-line border, which contains all six tear variables. This large, squared region is the outer loop that con-

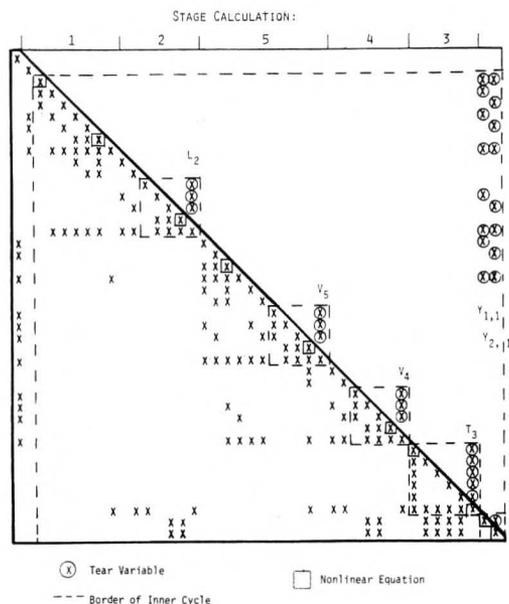


FIGURE 9. Incidence matrix for top-down, bottom-up, stage-by-stage method (6 A.D.).

tains 40 equations to converge.

The matrix is 42×42 , rather than 35×35 (calculated from $N[2C + 3]$) because the feed-stage temperature is computed with three different equations, and V_3 and the vapor and liquid mole fractions for the feed stage are computed with two different equations.

Calculations for the outer loop-inner cycle begin with stage 1, the partial condenser. All calculations involve just linear equations in the case of composition-independent properties, except for T_2 , which is computed iteratively from a nonlinear dew-point equation. Variables computed from nonlinear equations are boxed. Calculations for stage 2 are completed next. Seven equations are involved, with the last five contained in a dashed inner loop, containing a single tear variable, L_2 . At this step in the calculations, the stage above the feed stage has been completed and the calculation steps are now transferred to stage 5, the partial reboiler. Here, two nonlinear bubble-point equations are encountered for T_5 and T_4 , and another tear variable, V_5 , is contained in a 5×5 matrix. Similar calculations are made next for stage 4. Finally, the feed stage (3) is computed by making an adiabatic flash calculation. The last two equations at the lower-right corner are used to compute a new estimate of distillate composition by comparing the feed flash conditions with those computed from the top-down and bottom-up stage

The method works best for feeds of narrow-boiling-range components. Otherwise, estimates of distillate composition may be too uncertain and cause difficulty in convergence. If feeds are wide-boiling, the bubble and dew-point calculations become sensitive and convergence is jeopardized.

calculations, with an adjustment made to maintain the specified distillate rate.

In all, four inner loops are contained within one major outer loop. Thirteen equations are influenced directly by the guesses for the distillate composition and ten others are influenced indirectly by the corresponding bottoms mole fractions. Thus, although the complete tearing method is suitable for manual calculations, the method is relatively inefficient and limited to insensitive cases of simple distillation of nearly ideal solutions with low reflux ratios.

The method works best for feeds of narrow-boiling-range components. Otherwise, estimates of distillate composition may be too uncertain and cause difficulty in convergence. If feeds are wide-boiling, the bubble and dew-point calculations become sensitive and convergence is jeopardized. In any event, convergence may be slow, unless special acceleration techniques are used. However, the calculation by hand of just a few stages for a multicomponent mixture by this method is a very worthwhile learning experience; one not to be missed.

EQUILIBRIUM FLASH METHOD

Some of the limitations of the previous method were eliminated by McNeil and Motard (23 A.D.) in their development of a stage-by-stage algorithm that utilizes adiabatic or percent vaporization flash calculations. Their technique requires $[(N-1)(2C + 2) - 2]$ tear variables, but, as shown in Fig. 10, initial guesses for all but $(N-2)$ of these variables can be set to zero. The $(N-2)$ variables are interior stage temperatures, which are relatively easy to estimate.

If the feed is predominantly liquid, the procedure starts with an adiabatic flash at the feed stage followed by stage-by-stage adiabatic flashes in a downward direction until the partial reboiler is reached, where a percent vaporization flash is made. Subsequent adiabatic flashes are made moving up the column until the partial condenser is reached and another percent vaporization flash is made. Additional sequences of flash calculations are made moving down, and then up, the column until convergence is achieved.

The method is not particularly suitable for manual calculations because adiabatic-flash computations are tedious. However, flash computer subroutines are readily available, and it is relatively easy to construct an executive routine to apply the method. It is, therefore, another very worthwhile learning exercise, particularly because column startup is simulated. The method is applicable to complex distillation, and initial guesses for the tear variables are easily obtained from vapor pressure data. The flash calculations are usually not sensitive, but convergence, although

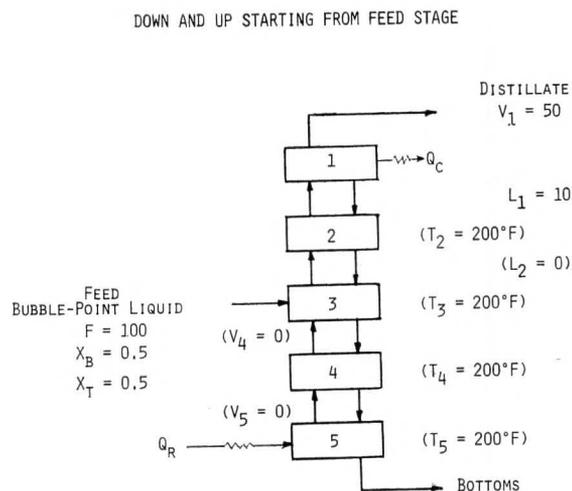


FIGURE 10. Example of specifications and tear variables for equilibrium-flash method of McNeil and Motard (23 A.D.).

almost certain, can be very slow, particularly for large ratios of internal traffic-to-feed flow rate.

MATRIX METHODS

Rather than use an equation-by-equation complete tearing technique for Sorel's equations, Amundson and Pontinen in 7 A.D., in a significant development, showed how the equations could be combined in a manner such that they could be solved in the order of type of variable, rather than by stage. However, only partial tearing was achieved and the method involved solving C sets of $N \times N$ simultaneous linear algebraic equations.

To do this, they used full matrix inversion, which often led to computational difficulties. These difficulties were overcome by taking advantage of the sparse tridiagonal form of the matrices and applying Gaussian elimination or LU decomposition in

and Wilkes, in no more than 20 lines of FORTRAN code.

BUBBLE-POINT METHOD

The bubble-point method of Wang and Henke in 15 A.D. utilized the tridiagonal matrix algorithm to obtain a computer method for solving distillation problems for relatively narrow-boiling feeds. The specifications for the same 5-stage, 2-component example used above are shown in Fig. 11. The tear variables are the stage temperatures and vapor flow rates. The distillate rate V_1 and the reflux rate L_1 are specified. Initial guesses for these tear variables are obtained with a minimum of effort by assuming constant molar overflow, in the manner of the McCabe-Thiele method. Estimates of the stage temperatures are obtained by linear interpolation of the distillate and bottoms temperatures, which may be computed by dew-point and bubble-point calculations assuming the most perfect split of the feed components, consistent with the specified distillate rate.

Wang and Henke utilized a form of Sorel's equations that permits the solution by variable type rather than by stage as in the first two methods described. The equations include a total material balance to compute liquid traffic, a component material balance combined with phase

EQUATIONS AND VARIABLES ORDERED BY TYPE

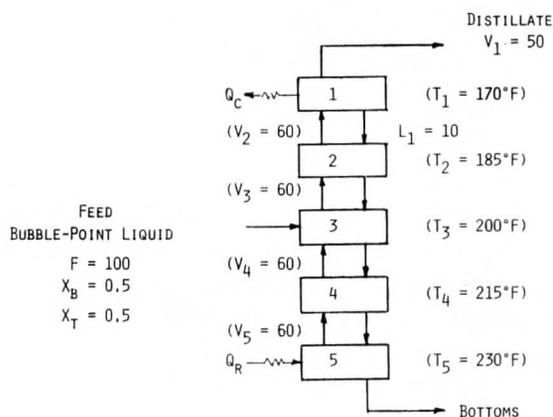


FIGURE 11. Example of specifications and tear variables for bubble-point method of Wang and Henke (15 A.D.).

the manner of Thomas. In 15 A.D. Wang and Henke applied the Thomas algorithm to narrow-boiling feeds, while Burningham and Otto reformulated some of the equations in 16 A.D., following the work of Sujata in 10 A.D., to apply them to wide-boiling feeds typical of absorbers and strippers. The need for two such partial-tearing methods was shown clearly in 13 A.D. by Friday and Smith, who referred to the two procedures as the bubble-point and sum-rates methods.

An $N \times N$ tridiagonal equation for each component is formed by combining the component material balance, phase equilibrium, and a total material balance to form an equation in liquid-phase mole fractions, stage temperatures, and vapor flow rates. By choosing the temperatures and vapor flow rates as tear variables, the equations become linear in the mole fractions, with no more than three mole fractions contained in any one equation, because one stage is connected to no more than two adjacent stages. For each component, the linear equations are ordered by stage. The result is a tridiagonal matrix equation, where the nonzero coefficients are contained only on the three principal diagonals. The solution of the matrix equation is easily achieved by Gaussian elimination, as shown e.g. by Carnahan, Luther,

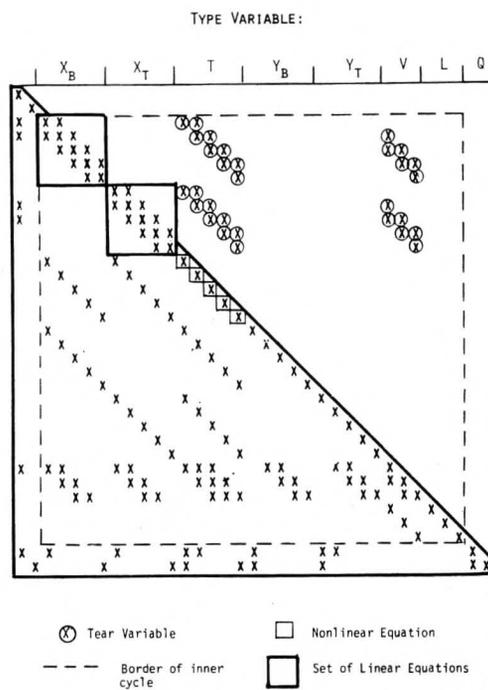


FIGURE 12. Incidence matrix for bubble-point method.

equilibrium and total material balance to compute liquid-phase mole fractions, bubble-point equations to obtain stage temperatures and vapor-phase mole fractions, and energy balances to compute vapor traffic.

Although the same variables are computed, starting from Sorel's equations, the incidence matrix, shown in Fig. 12, is quite different from the stage-by-stage method. The matrix is lower triangular except for the circled tear variables and $N \times N$ (5×5 in this case) block sub matrices for each component (two in this case). The overall size of the matrix for the example is only 35×35 because no variable is computed from more than one equation. At the upper left corner, the first two variables are the same as before and are computed directly as before. All but the last two of the remaining equations are contained in one large loop. Then the two tridiagonal submatrices are solved separately to obtain the liquid-phase mole fractions. All remaining variables are computed one-at-a-time. Stage temperatures are computed from the nonlinear bubble-point equation. This is followed by computation of vapor-phase mole fractions. Energy balances give the vapor traffic and total material balances give the liquid traffic. The cycle is repeated until the tear variables are converged. Then the duties of the reboiler and condenser are computed.

For narrow-boiling feeds, the initial estimate of stage temperatures and vapor traffic will be

quite close to the final result and convergence is rapid using successive substitution for the tear variables. For wider-boiling feeds, convergence is quite sensitive to the initial estimates of T and V and may not be rapid. In that event, use of a delayed Wegstein [Orbach and Crowe (20 A.D.)] or dominant eigenvalue technique [Rosen (29 A.D.)], rather than successive substitution, can reduce the number of iterations required.

The bubble-point method is not suitable for manual calculations because of the need to solve matrix equations. However, it is easily programmed if algorithms are available for solving single nonlinear equations and the tridiagonal matrix equation. The method is applicable to simple and complex distillation columns. Convergence may not be possible if the liquid phase is highly non-ideal. The method provides no flexibility in specifications. The user must specify the reflux rate or ratio and the total distillate rate; however, these specifications almost always permit a real, positive solution. An exception can occur where the reflux rate is too small, such that it diminishes to zero at some stage down from the top. The bubble-point method can be successfully applied to complex distillation e.g. two feeds, two side-streams, and one intercooler. Such problems are difficult for stage-by-stage tearing algorithms, but are relatively easy for partial tearing algorithms like the bubble-point method, where variables are computed by type.

EQUATIONS AND VARIABLES ORDERED BY STAGE

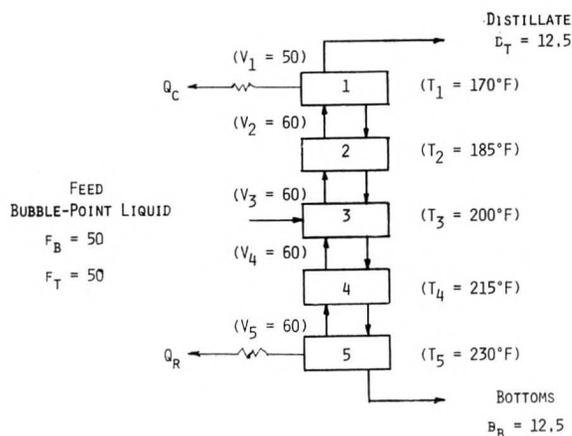


FIGURE 13. Example of specifications and starting guesses for simultaneous-correction method of Naphtali and Sandholm (20 A.D.).

NEWTON'S METHOD

More advanced computer methods that can handle a complete range of boiling-point of feed components and non-ideal liquid solutions, as well as offer more flexibility in problem specifications, involve handling the nonlinear equations simultaneously without the use of tear variables. Newton's method, and variants thereof, has long been the popular technique. The use of a simple two-equation manual exercise is sufficient to illustrate to students the basic concept of Newton's method, which may then be applied with computer programs to hundreds of equations when solving a multicomponent, multistage separation problem.

Computer methods that solve all of Sorel's distillation equations simultaneously may be referred to as simultaneous-correction methods. Many such methods have been proposed and the Newton-based Naphtali-Sandholm technique of 20 A.D. is repre-

sentative of one of the better ones. The equations and variables are ordered by stage. To reduce the size of the matrix to be handled, component flow rates replace mole fractions and total flow rates. Thus, for the five-stage, two-component example, shown in Fig. 13, the number of equations to be solved is 25, rather than the 35 previously. The specifications are different from previous ones in that distillate and bottoms purities replace reflux and distillate rates. Such specifications should be used with caution and the Fenske (19 A.D.) minimum-stage equation should be checked to make sure that the minimum number of required stages for the specified purities is less than the specified number of five. Theoretically, initial guesses must be provided for all 25 unknowns, but these guesses can be generated by the program based on guesses of just a few temperatures and vapor rates as shown. These guesses are called tear variables here, but are really not tear variables in the strict sense. The initial guesses are generated easily from the T and V guesses by solving the tridiagonal matrix equations of the Wang-Hanke method for the liquid-phase mole fractions, from which the initial guesses for the component flow rates are obtained readily from their definition and the component material balances.

The Naphtali-Sandholm method only involves three types of equations, namely stage component material balances, phase equilibrium in terms of K-values, and stage energy balances. The form of the equations is almost identical to the original equations of Sorel. Because bubble-point, dew-point and flash calculations are absent, sensitivity problems are largely avoided.

With equations and variables ordered by stage, the incidence matrix, shown in Fig. 14, is block tridiagonal in shape. The blocks are 5×5 in this example. The matrix is for the linearized form of the equations, which permits the application of Newton's method. Thus, the matrix is the Jacobian of partial derivatives and an X entry signifies a nonzero-derivative. The entire matrix is iterated to convergence.

The solution of the block tridiagonal matrix is obtained readily by modifying the previously mentioned Thomas algorithm for a tridiagonal matrix. The only significant changes are the replacement of matrix multiplication for scalar multiplication and matrix inversion and multiplication for division. If large numbers of components are present, the $(2C + 1) \times (2C + 1)$ submatrices

may be large and time-consuming to invert. The convergence criterion is based on the sum of the squares or so-called square of the Euclidean norm of the three different types of functions. Early iterations are often damped to avoid corrections that are too large.

Because of the block nature of the matrices in the Naphtali-Sandholm method, it is not at all suitable for manual calculations. Furthermore, the computer program is rather complex. Consequently, it is best to obtain the code from one of several

STAGE CALCULATION:

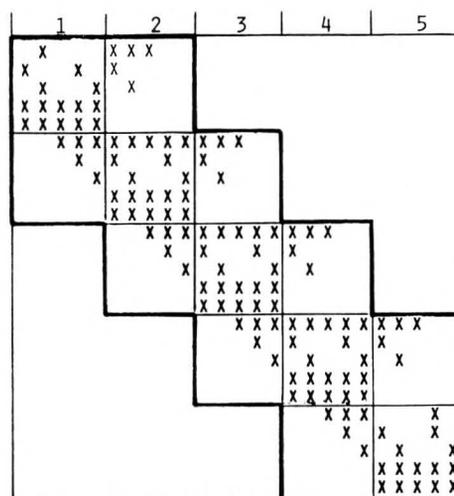


FIGURE 14. Incidence matrix for simultaneous-correction method.

sources, e.g. Fredenslund et al (26 A.D.). Versions ranging from PC to Mainframe codes are available. The method is applicable to all single-column, complex multistage operations, including those with highly non-ideal liquid solutions. Flexibility in specifications is provided at the top and bottom of the column by substituting specification equations for the condenser or reboiler energy balances. For example, specification options at the top include condenser duty, reflux rate, reflux ratio, distillate rate, component mole-fraction purity and component distillate rate. Convergence is rapid from good initial guesses, but may otherwise be slow and require damped corrections. The method can fail, particularly if initial guesses are very poor.

CONTINUATION METHOD AND MULTIPLE STEADY-STATE SOLUTIONS

Ideally, especially in practice, one would prefer

a multistage, multicomponent separation computer method that would offer complete flexibility in specifications and would always converge to a correct solution. Newton's method and most of its variants are known to be only locally convergent. That is, the initial guesses must be within a certain region of the variable space or convergence will not be achieved. This region can be expanded by adjusting the Jacobian in Newton's method or employing a hybrid method such as that of Powell (19 A.D.) or Marquardt (12 A.D.),

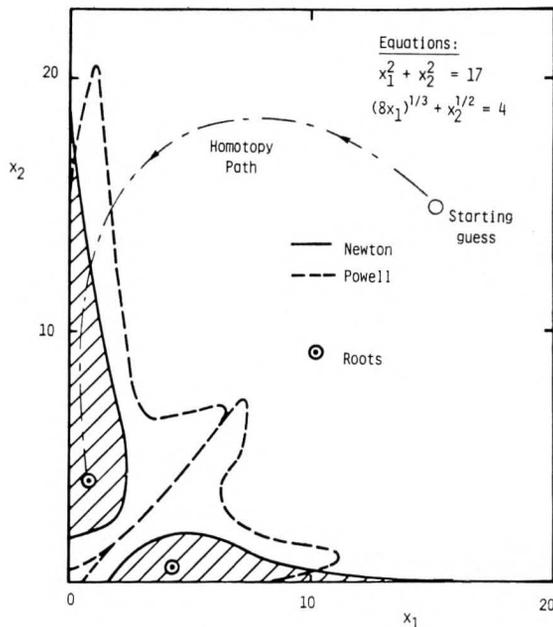


FIGURE 15. Example of regions of convergence for some methods of solving nonlinear equations.

which combine the best features of Newton's method with steepest descent. To achieve complete robustness, however, it is necessary to employ a globally convergent technique, such as differential homotopy continuation, for which four algorithms, in FORTRAN, have become available starting in 25 A.D. The one by Kubicek is particularly easy to understand and apply, but is not written for sparse matrices.

The regions of convergence for a simple two-nonlinear-equation example are shown in Fig. 15. Newton's method will converge to $X_1 = 1$ and $X_2 = 4$ from an initial guess of $X_1 = 2$, $X_2 = 5$. As seen, another root exists at $X_1 = 4.07$ and $X_2 = 0.65$, which can be reached by Newton's method from a nearby initial guess. With Newton's method, the initial guesses must lie within the

rather narrow and confined cross-hatched regions. With Powell's hybrid method (which is available in the Harwell library, the IMSL library, and MINPACK) the region of convergence is expanded outward to the dashed lines. Both methods will fail badly from a starting guess of 15 and 15. The use of differential homotopy continuation gives convergence from any starting guess, with a typical homotopy path to one of the two roots, shown as a dash-dot line starting from (15, 15).

Many types of homotopy paths have been proposed, with the linear homotopy being common. The linear homotopy, h , is set equal to the function to be solved, $f(X)$, multiplied by a homotopy parameter, t , and added to a function $g(X)$, whose solution is known, multiplied by the function $(1 - t)$. The calculations start from the known solution at $t = 0$, where $h = g$ and $X = X^0$ and move along the path of h vs. t as t is gradually increased to a value of one, at which point $h = f$, whose solution X^* is to be determined.

Choices for the function $g(X)$, with a known solution, X^0 , are almost unlimited. For consistency with Newton's method, the Newton homotopy is useful, where $g(X)$ is set equal to $f(X) - f(X^0)$, where X^0 can be selected arbitrarily. With this homotopy, h equals $f(X)$ minus $(1 - t)$ times $f(X^0)$. Alternatively, $(1 - t)$ can be replaced by a new homotopy parameter, λ , to obtain a slightly more compact form for the homotopy expression. The path will then be from $\lambda = 1$ to $\lambda = 0$.

If the homotopy path is simple, without turns or rapid changes in X with t , classical continuation can be employed by selecting a sequence of values of t at $0, t_1, t_2, t_3$, etc., and 1, with X being solved from h at each step by Newton's method using an initial guess equal to the solution from the previous step. Thus, Newton's method is embedded into classical continuation. This technique of using continuation is not common though because it is not globally convergent and can not, in general, solve problems that fail with Newton's method alone, which amounts to moving in one step from $t = 0$ to $t = 1$. To be robust, one must closely follow the homotopy path and not just continually take steps in t with Newton corrections in X -space. For example, classical continuation as well as Newton's method will fail on the cubic equation, $x^3 - 30x^2 + 280x - 860 = 0$, because of two singular points at about $x = 7.418$ and 12.582 , where the derivative of the function becomes zero.

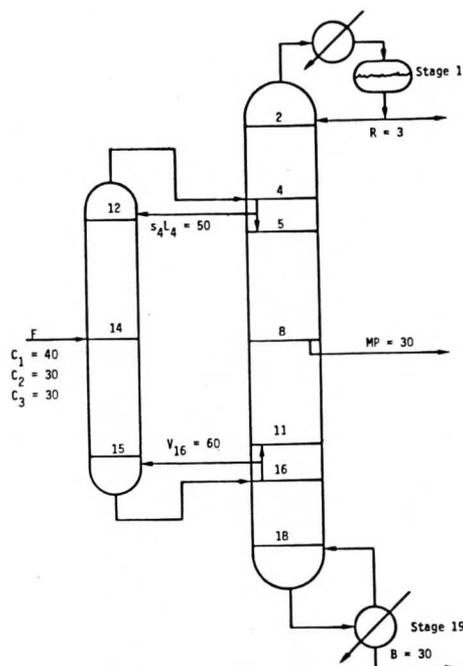


FIGURE 16. Example of specifications for an interlinked system of Petlyuk towers.

For initial guesses of x less than about 12.6, Newton's method fails to find the single real root at about 15.55. The homotopy path for this cubic function depends on x^0 the choice of $g(x)$. For $g(x) = x - x^0$ or $g(x) = f(x) - f(x^0)$, the two singularity points become turning points in the path, and it is important that the continuation method follow the path closely around these turning points to avoid cycling in the manner of Moses in the Sinai.

Consider the application of the homotopy-continuation method to the Petlyuk system of two interlinked towers shown in Fig. 16. The feed is a ternary mixture, which is to be separated into three products. A sloppy split is made in the pre-fractionator, with the final three products being produced in the second tower. Reflux and boilup for the first tower are provided by the second tower. The two towers in the system can be solved by alternating back and forth between separate iterations on the individual towers. But numerous studies have shown that it is more efficient to converge the two towers simultaneously. The stages for the two towers are ordered as shown starting at the top of the second tower, switching to the first tower after stage 11, and then switching back to the second tower after stage 15. Specifications

include interlink flows from stage 4 to stage 12 and from stage 16 to stage 15; the reflux ratio; the middle product flow rate; and the bottoms flow rate.

The types of equations solved are as in the Naphtali-Sandholm method except that balances include interlink flows and provision, if desired, for entrainment of liquid droplets, occlusion of vapor bubbles, and chemical reaction. Phase equilibrium equations can include a Murphree plate efficiency that can be specified by component and tray location.

A FORTRAN computer code for applying differential homotopy-continuation to such a problem was reported by Wayburn and Seader in 32 A.D. Considerable flexibility in specifications is provided, including at any stage, total flow rates or ratios, component flow rates or purities, and stage temperatures or heat transfer rates. The equations are linearized in the Newton manner and ordered by stage to a bordered, block-diagonal structure, which is processed by an efficient and stable block-row-reduction algorithm. An attempt is first made to solve the equations by Newton's method, using a line search on the Euclidean norm of the function residuals to determine the best damping factor. If Newton's method fails, then differential homotopy continuation with a linear

$$f(x) - \lambda f(x^0) = 0$$

$$\text{IVP: } \frac{df(x)}{dx} \frac{dx}{dp} - \frac{d\lambda}{dp} f(x^0) = 0$$

$$\left(\frac{dx}{dp}\right)^T \left(\frac{dx}{dp}\right) + \left(\frac{d\lambda}{dp}\right)^2 = 1$$

$$\text{IC: } p = 0, \lambda = 1, x = x^0$$

FIGURE 17. Equations for differential homotopy continuation.

Newton homotopy is employed.

The differential form of homotopy continuation was first proposed by Davidenko in 2 A.D. As shown in Fig. 17, the homotopy function, $f(X) - \lambda f(X^0)$, is differentiated with respect to arc length, p (i.e., distance along the path), to convert a system of M nonlinear equations to a system

of $M + 1$ ordinary differential equations that constitute an initial value problem. Because of the extra variable, p , an additional equation is needed. This is provided by the Pythagorean theorem applied in $(M + 1)$ -dimensional space. Fortunately, the set of differential equations is not stiff.

Rather than simply integrating the differential equations by, say, a Runge-Kutta method, it is pre-

the non-standard specifications. The four disperse submatrices of A and C , located above and below the three principal diagonals represent the interlinks.

By moving the number 4 and 16 rows and columns, which contain the disperse submatrices, to the borders, the block diagonal and bordered matrix form, shown in Fig. 18b, is obtained. Solution of the corresponding matrix is achieved block by block, starting at the upper left-hand corner, by a block-row reduction algorithm, which treats the right-hand border as part of the right-hand side vector.

The differential homotopy-continuation method has been applied to the interlinked system shown in Fig. 19 for a ternary aromatic system, over a range of reflux ratios from 4.55 to 5.75. Purity specifications of between 90 and 95 mole% are made for each product, and a bottoms rate of 380 is specified. The program must compute the required interlink flow rates, including L , the liquid interlink recycle from the second column back to the first column. In some cases, Newton's method converged, for this system, while in other cases, the differential-homotopy-continuation method had

NEARLY BLOCK TRIDIAGONAL AND BORDERED FORM

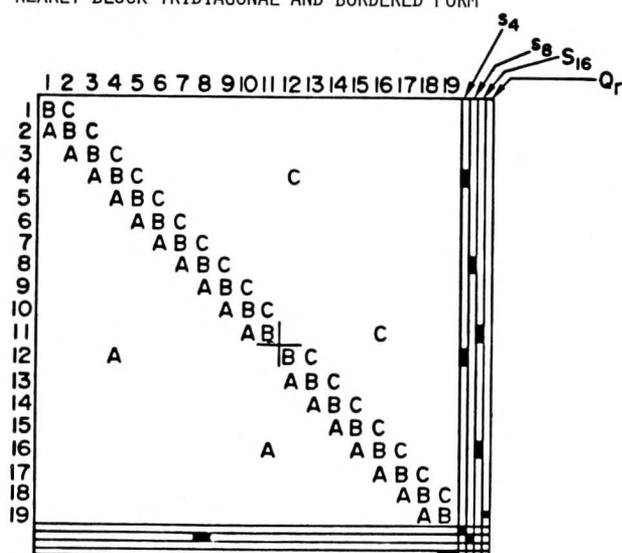


FIGURE 18a. Example of incidence matrix for homotopy-continuation method.

ferable and more efficient to follow the homotopy path by alternating between an Euler predictor for the differential equations and two Newton-step correctors for the nonlinear homotopy equations. The Euler step moves the variables somewhat off the path, but the Newton step corrects the variables back sufficiently close to the path. An important aspect of such a technique is the size of the Euler step, for which a number of stepsize algorithms have been proposed, as discussed by Seader and Wayburn.

The incidence matrix for the Petlyuk column example is in Fig. 18a, where the organization is by stage. Each letter, A, B, or C actually represents, in this example, a nonzero 7×7 submatrix, which applies to both the coefficients of the differential homotopy equations and the Jacobian partial differentials of the nonlinear homotopy equations. The matrix is almost block tridiagonal with bottom and right-side borders, which contain

BLOCKED AND BORDERED FORM

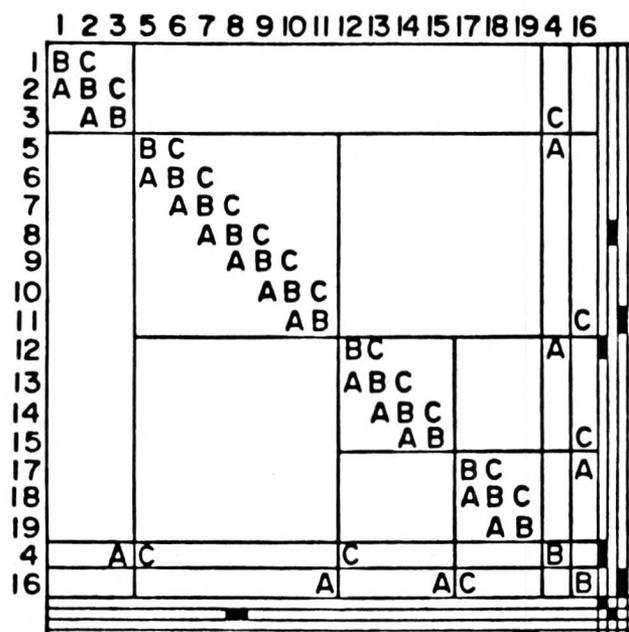


FIGURE 18b. Permuted incidence matrix for homotopy-continuation method.

to be applied to obtain a solution.

In Fig. 20, a plot of L , the liquid interlink rate versus the reflux ratio, shows unexpected multiple solutions, three in number. For example, at a reflux ratio of 5, the specifications were achieved with three different liquid interlink rates of about 110, 330, and 420 lbmoles/hr. Such multiple solutions have long been known to exist for certain cases of an adiabatic reaction in a CSTR reactor, but have not been observed previously for distillation. When such solutions are close together, as for solutions 1 and 2 at low reflux ratios, possible control problems could arise.

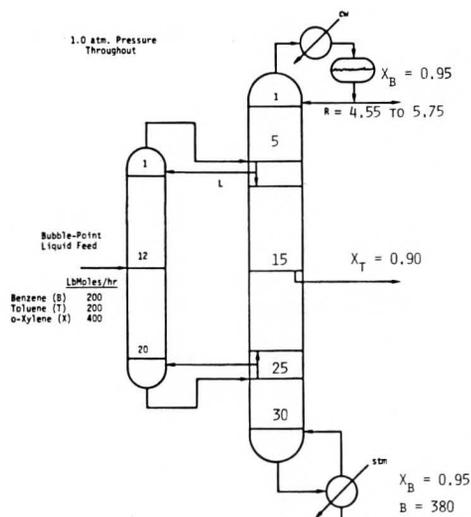


FIGURE 19. Example that gave multiple solutions.

The continuation method is not at all suitable for manual calculations. The computer code is lengthy, but is applicable to all kinds of complex multistage operations, including interlinked columns. Except for tray numbers, complete flexibility in specifications is permitted. When the homotopy is constructed properly, convergence is always achieved. The method is best suited for cases where the Naphtali-Sandholm fails or can't be applied. The method can find multiple solutions if they exist.

TRANSPORT MODEL

Sorel's equilibrium-stage-model of almost 100 years ago has served us well in the calculation of multicomponent, multistage separation operations. However, that model has always been suspect for applications to systems of known moder-

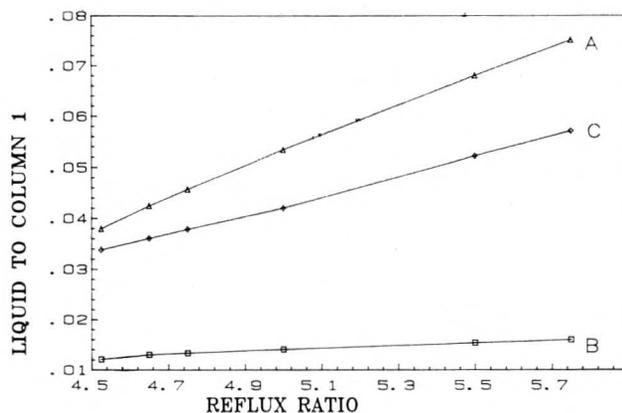


FIGURE 20. Multiple solutions to Petlyuk towers.

ate-to-low stage efficiency. For that reason, some programs, such as the S-C method of Naphtali and Sandholm and the differential-homotopy-continuation method of Wayburn and Seader incorporate a Murphree tray efficiency, which accounts to some degree for mass-transfer effects. However, the plate efficiencies must be specified, and heat transfer effects are ignored. A better approach is to apply a transport model to handle non-equilibrium directly. Such a model has just been developed by Krishnamurthy and Taylor, who account for multicomponent mass-transfer interactions and heat transfer. Their modeling equations are written separately for the vapor and liquid phases with coupling by liquid and gas mass transfer rates, and energy transfer rates. These transport rates are estimated from carefully formulated mass and energy transfer coefficients, applicable to multicomponent systems. For non-interlinked columns, the resulting equations lead to an incidence matrix that is similar to that of the Naphtali-Sandholm method, for which a solution technique is well established. Krishnamurthy and Taylor have applied their method, with good success, to several sets of experimental data from the operation of small laboratory columns. Data from commercial-size columns are now being sought to make further comparisons of predicted and measured compositions so as to evaluate the usefulness and applicability of this transport model.

CONCLUSIONS AND RECOMMENDATIONS

The digital computer has been responsible for sweeping changes in the manner in which multistage separation operations are synthesized and

TABLE 1
Recommended Additions to Content of Undergraduate Courses

1. Numerical methods for
 - A. Linear algebraic equations
 - B. Sparse matrices
 - C. Systems of nonlinear equations
2. Application of numerical methods to
 - A. Complete tearing, partial tearing, and simultaneous correction methods for multicomponent separation processes
3. Use of computer-aided simulation programs to
 - A. Analyze, correlate and predict multicomponent thermodynamic properties
 - B. Solve open-ended separation process problems involving energy integration
4. Second-law analysis

analyzed. Chemical engineering educators need to closely examine courses on separation processes to make sure that students are being instructed in modern and efficient computational tools. Some recommended additions to the content of undergraduate courses are listed in Table 1, where many of the items should prove useful in other chemical engineering subjects as well.

Numerical methods should be stressed for linear algebraic equations, including efficient handling of sparse matrices, and systems of nonlinear equations. These methods should then be applied using computers to utilize partial tearing and simultaneous correction methods for multicomponent separation processes. However, some manual calculations on simple examples should be performed using complete tearing methods to help develop a basic understanding.

More complex and open-ended separation problems should be assigned that stress energy integration. A second-law analysis [see Denbigh (5 A.D.), and de Nevers and Seader (28 A.D.)] of a process should be required, and attempts should be made to improve the process by finding economical means to reduce the lost work.

The development of a separation process can be an exciting experience when computers and computer programs are available to perform the tedious calculations and allow time for more consideration of synthesis and optimization aspects. □

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NOMENCLATURE

A, B, C, Coefficients in a tridiagonal matrix equa-

	tion; submatrices of partial derivatives in a block tridiagonal matrix
B	Bottoms product molar flow rate
f	An arbitrary function
F	Molar feed rate to a stage; mathematical function
H _F	Molar enthalpy of feed to a stage
h	The homotopy function whose arguments are x and t
H	The homotopy function whose arguments are x and λ
H _v	Molar enthalpy of vapor leaving a stage
H _L	Molar enthalpy of liquid leaving a stage
K	Vapor-liquid equilibrium ratio
L	Molar liquid flow rate leaving a stage
MP	Middle product molar flow rate
p	Path length
Q	Heat duty (R for reboiler; C for condenser)
R	Reflux ratio
s	Ratio of liquid drawoff to primary liquid (liquid not withdrawn or entrained)

S	Ratio of vapor drawoff to primary vapor (vapor not withdrawn)
t	Homotopy parameter.
T	Temperature; when used as a superscript denotes matrix transpose
V	Molar Vapor flow rate leaving stage
x	The vector of independent variables (unknowns) for the distillation equations; liquid-phase mole fraction
x ^o	The starting vector for the nonlinear equation solver
x*	The solution to the set of nonlinear equations
X	Mole fraction in liquid of a component; variable
y	Vapor-phase mole fraction
Y	Mole fraction in vapor of a component
Z	Mole fraction in feed of a component

Greek Letters

λ	Homotopy parameter
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DEPARTMENT: Cornell

Continued from page 61.

and measuring the properties of liquids and liquid mixtures using theory, computer simulation, and experiment. Cornell is one of very few institutions with strength in all three areas.

Keith guides the theory and the computer simulation (with help from Senior Research Associate **Steve Thompson**,) making use of recently developed accurate theories for dense fluids of complex molecules as well as improved computer simulation methods and computer hardware. Typically, highly nonideal substances (in the thermodynamic sense) are chosen for study; substances for which traditional methods of prediction fail. Examples include mixtures occurring in coal gasification and liquefaction, hydrogen-energy technology, synthetic fuel processing and supercritical fluid extraction. Other research underway or planned includes studies of adsorption at gas-liquid, liquid-liquid and solid-fluid interfaces, nucleation and droplet phenomena, polarization in polar fluids, and surfactant effects.

Bill Streett and Senior Research Associate **John Zollweg** carry out experimental studies of dense fluids. In progress are (i) experiments in vapor-liquid, liquid-liquid, and gas-gas equilibria at temperatures from 70 to 500 K and pressures to 10,000 atmospheres; (ii) equation-of-state (PVT) measurements of pure liquids and mixtures at temperatures from 70 to 500 K and pressures to 4,000 atmospheres; and (iii) measure-

ments of enthalpy of mixing in samples of liquefied gases at temperatures from 70 to 300 K and pressures to 20 atmospheres. Bill is currently developing new experiments to measure the surface and interfacial tensions and the velocity of sound in fluids under pressure.

The researches of **Paulette Clancy**, who became a member of the faculty in 1984, range from a statistical mechanical study (using perturbation theory) of multicomponent highly polar fluid mixtures to a development of phase diagrams (based on molecular thermodynamics) of semiconductor materials. In addition, she is involved in the application of computers to chemical engineering.

Herb Wiegandt's interest in desalting sea water, using a freezing process based on direct contact with butane, goes back to 1958. Recent efforts, with Bob Von Berg as a partner, have aimed at overcoming the problems associated with washing and separating the ice crystals which are typically very small.

Julian Smith, past Director of the School in a period of unprecedented growth, seasoned educator and co-author of *Unit Operations of Chemical Engineering* (now in its fourth edition, with Pete Harriott as co-author), has expertise in mixing, centrifugal separation, and handling of granular solids. He is teaching full-time and is active in the guidance of the school.

Ray Thorpe, who has advised graduate students in the areas of phase equilibria and separations processes, splits his time between

teaching and university administration: he is director of the Division of Unclassified Students.

Research Interactions

Many research projects involve active collaboration with other researchers at Cornell or elsewhere. Some are directly with other departments; some are through Cornell's numerous interdisciplinary programs, centers, and institutes—many industrially supported—that facilitate interaction among departments and with industry. Examples are the Biotechnology Institute; the Injection Molding Project; COMEPP (Cornell Manufacturing Engineering and Productivity Program); Applied Mathematics Center; Theory and Simulation Center (established by Ken Wilson, Cornell's 1982 Nobel laureate in physics); Materials Science Center; National Facility for Submicron Studies. Strong ties have been established with other departments and colleges of Cornell, and with workers at other universities around the world.

Paulette Clancy, Associate Director of COMEPP, is joined by Professor Scheele in a study of ways to improve the interface between the user and ASPEN software chemical process synthesis and design.

UNDERGRADUATE PROGRAM

Undergraduate chemical engineering enrollments at Cornell were almost constant during the twenty years before 1975, with about 40 bachelor's degrees awarded annually. Then, although freshman admissions to the engineering college were held constant, the number of students opting for chemical engineering roughly doubled, and for nine years the number of BS degrees awarded was between 65 and 75. After 1985, however, the number will return to 40 or so and is expected to stay at that level for the next several years.

The subject matter of the undergraduate program is much the same as at other institutions. For the first two years the students are not in chemical engineering but are enrolled in the "common curriculum" of the engineering college. Nevertheless, their curriculum has much that is different from that of other engineering students. In the freshman year chemical engineers take two semesters of chemistry, not one. Sophomores take two semesters of physical chemistry, with laboratory each term—a special course taught by Chemistry almost exclusively for chemical engineers—

and the required introductory course in mass and energy balances. Organic chemistry (two semesters, one with laboratory) is given in the third year, as are chemical engineering thermodynamics, rate processes and separation processes. The fourth year includes required courses in reaction kinetics, process evaluation, process control, and unit operations laboratory, and a spring term course in process design. Overall, 132 credit hours are required for the BS degree, including two courses in computer programming and applications, four engineering distribution courses, and six courses in humanities and social sciences. Ten of the required courses (32 credit hours) are in chemical engineering subjects.

The senior laboratory course is considered the most demanding by students and faculty alike. Each student reports on only five experiments during the term, but each report is thoroughly edited for both form and content by the faculty member in charge of that experiment and nearly always must be extensively revised by the student before it is accepted. The emphasis is on technical accuracy, completeness, and clarity of expression.

Oral presentations are stressed in the senior design course, in which each team of students makes weekly oral presentations before two faculty members or industrial visitors. In recent years experienced engineers from industry have been hired for full-time assistance in this course and in the senior laboratory. Their contributions have been supplemented, during short-term visits, by those of people from Exxon, Union Carbide, and other firms. Despite this, the laboratory and design courses demand large contributions of time by senior faculty members, and pose the most difficult problems for future staffing.

A Special Cooperative Program

For the past ten years the better students in the sophomore year have been encouraged to enroll in an unusual industrial cooperative program which gives them practical experience without lengthening their time at the university. Typically 15 to 20 students are accepted into the program after company interviews exactly like those for permanent employment. Co-op students take the fall-term third-year courses during the summer following their sophomore year; they work in industry during the fall and return to Cornell in the spring; work again for the same sponsor the following summer; and complete their senior year

in the regular sequence. Industrial assignments are carefully monitored to insure appropriateness, and each student is visited at the worksite by a Cornell person at least once during the course of the program.

THE PROFESSIONAL MASTER'S PROGRAM

This is a two-semester non-thesis master's program leading to the degree Master of Engineering (Chemical). It requires 30 credit hours of advanced technical work, including a substantial design project, with emphasis on practical applications. Most of the matriculants are not from Cornell or other U.S. schools; instead the program is attractive to foreign students, especially from developing countries such as the Dominican Republic, Guatemala, India, Kuwait, Taiwan and Venezuela. Over the years a chemical company in India has sent, one after another, three of its top technical employees to this program.

Required courses for the MEng (Chemical) degree include equipment design and selection, numerical methods, reactor design, the design project, and a chemical engineering elective. The remaining credit hours can be filled by elective courses in science or engineering or in the Graduate School of Management. The choice of subjects for MEng design projects is much wider than in the typical undergraduate design course, and more initiative and originality are expected of the students. Some of the projects are done in close collaboration with industrial firms.

RELATIONS WITH INDUSTRY

The school has always had close relations with industry and an unusually supportive group of alumni. Industry helps us in many ways: in the design courses; in a "Non-resident Lecture Series" (zero credit, but compulsory), given to seniors on the various kinds of professional careers; in unrestricted grants; in scholarships, fellowships, and sponsored research. Continuing fellowship support has been provided by Amoco, Chevron, Dow, DuPont, Exxon, Shell, Stauffer and Union Carbide, and recent large research projects came from IBM, Kodak and Mobil. In 1981 the Sun Company gave \$250,000 over three years to support research initiation on ideas too new and ill-defined to merit submission of a proposal to NSF or other granting agencies. This unusual grant led to a number of publications and several continuing sponsored research programs.

ADVISORY COUNCIL

An advisory council, largely from industry, was formed a few years ago. It meets in Ithaca twice a year to review progress and help the director steer a course for the school. About half the members are alumni. Recently expanded to 15 members, the council now includes four academic people: Andy Acrivos (Stanford), Gus Aris (Minnesota), Gary Leal (CalTech), and Bill Schowalter (Princeton). We don't always agree with the council's suggestions, of course, but as a group it has been marvelously effective in providing an "outside" viewpoint and keeping us from being too provincial or self-satisfied.

WHAT OF THE FUTURE?

Cornell is facing many of the same problems that face other chemical engineering departments around the country—faculty retirements and future faculty development, staffing of design and laboratory courses, the optimum use of computers for teaching, expansion of research and the graduate program, and renovation of aging facilities. The five professors hired right after World War II are nearing retirement, so for the next several years an average of one new faculty member per year will have to be hired to keep the number constant. Because of the loss of professors with industrial experience one or more people with an industrial background will probably be hired on a non-tenure-track basis to teach design and to supervise the laboratory courses.

A related problem is in the use of computer software. How much emphasis should be placed on teaching the use of ASPEN, for example? More generally, as personal computers become ubiquitous, what will happen to teaching methods? Will the course in mass and energy balances, for example, become a course in the use of available canned programs?

The total number of graduate students in the school, and the fraction going for a PhD rather than an MS, should rise somewhat over the next ten years, depending on the availability of financial support. This will increase the need for equipment and laboratory and office space. Relatively speaking, the Chemical Engineering School has a lot of space, but much of it is virtually unusable for modern research. A comprehensive building renovation plan, made by a firm of architects, proposes a complete reallocation and rearrangement of available space and the conversion

of the enormous unit operations laboratory into offices and small research labs. New electrical and other services will be provided, along with central air conditioning. The average faculty office will shrink from over 400 to a more modest 200 square feet and the offices will be grouped more closely, to stimulate greater interaction among the occupants. The total estimated cost is some fifteen times the original cost of the building. A fund drive for the first stage is being launched. □

AWARD LECTURE

Continued from page 77.

on the batch experience and using verified mathematical models to both design the equipment and direct the experimentation.

CHEMICAL VAPOR DEPOSITION

Laboratory Scale Research

A low pressure chemical vapor deposition (LPCVD) system for amorphous silicon is shown in Fig. 14 and the simplified process flow diagram as Fig. 15. Reactants, Si_2H_6 , and material for doping the film, PH_3 and B_2H_6 , in a stream of argon are controlled by valves at the inlet to the reactor. The tubular quartz reactor is temperature controlled inside an electric furnace. System pressure is controlled manually with a valve at the exit. Effluent gas can be analyzed by gas chromatography and unreacted material is decomposed in a furnace before venting. The detailed operation of this system is described by Bogaert [9].

This effort in amorphous silicon research, spon-

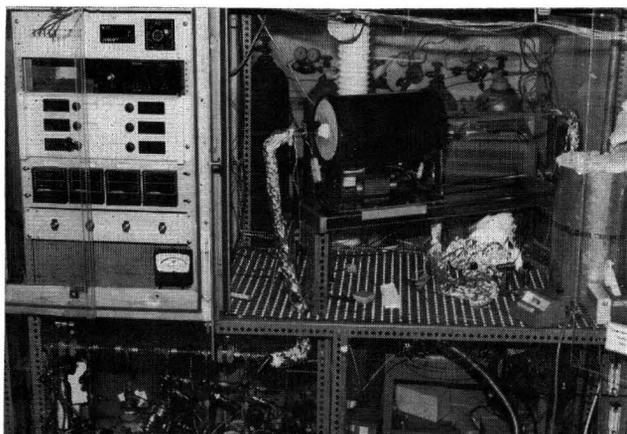


FIGURE 14. Photograph of Low Pressure Chemical Vapor Deposition unit (LPCVD).

sored by the Department of Energy through the Solar Energy Research Institute, is ongoing at the present time and is far from being complete. I am discussing it here to allow the reader to contrast and compare with the physical vapor deposition reacting systems just described.

The chemistry is much more complex for amorphous silicon than for CdS and not well

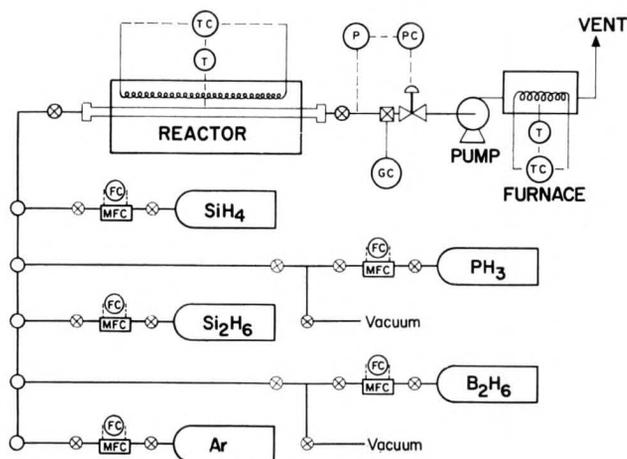
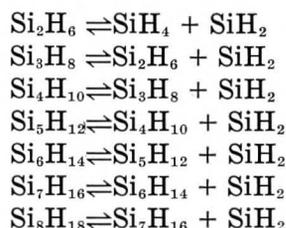


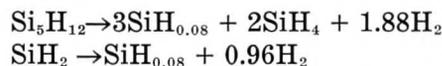
FIGURE 15. Simplified process flow diagram of LPCVD.

understood. The present state-of-the-art is shown below:

Gas Phase



Film Formation



This is a preliminary set of chemical equations. The gas phase equations are based on the results of Ring [10], John and Purnell [11], and Bowery and Purnell [12]. The film formation equations are based upon our own preliminary research.

The component mass balance equations for this tubular reactor system are given below:

Gas Phase

$$\left(\frac{4q}{\pi D^2} \right) \frac{dC_i}{dz} = \sum r(\text{rxt}, i) + k_g a (C_i - C_{is})$$

Surface

$$0 = k_g a (C_i - C_{is}) - k_s a (\gamma_i C_i)$$

Film

$$\frac{1}{MW_f} \frac{d\rho_f V_f}{dt} = k_s a (\gamma_i C_i)$$

Both the gas phase composition and the film growth rate are functions of axial position. Film growth rate (i.e., amount of amorphous silicon deposited) at any axial position can be determined but it has been possible to measure gas composition only at the reactor exit. The gas and solid phase mass balance equations are coupled through the chemistry of film formation and the transfer from the bulk gas to the surface.

Solution of the model equations produces the gas phase exit composition versus reactor holding time plots shown as Figs. 16 and 17. The solid lines were obtained using our present "best" estimates of the specific reaction constants. This "best" estimate is now obtained by using the experimentally determined growth rate in the solution of the set of mass balance equations. The agreement between data and the predicted values is only fair but we expect to improve the model

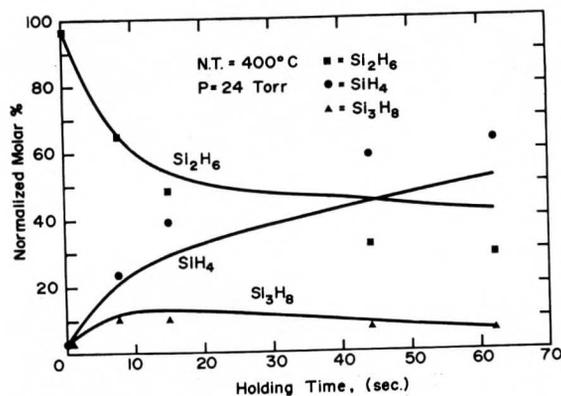


FIGURE 16. Normalized molar percentages versus holding time: Major silanes.

predictions as we learn more about the system.

This research on the chemical reactor and reaction engineering for amorphous silicon in the LPCVD reactor is closely coupled with studies of the material and electronic properties of the film and much effort has been devoted to finding the best conditions for good photovoltaic amorphous silicon. To date, we have been able to make a 4% solar cell using material from the LPCVD reactor. These efforts are described in the work of Hegedus et al [13].

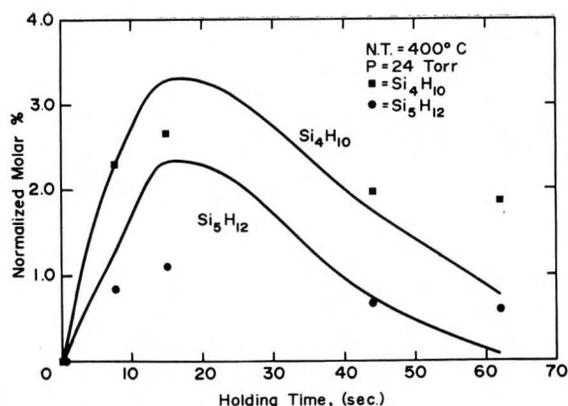


FIGURE 17. Normalized molar percentages versus holding time: Minor silanes.

CONCLUDING REMARKS

Incorporating chemical reactor and reaction engineering analysis into a semiconductor research effort requires the researchers to achieve a quantitative understanding of both the molecular phenomena and the transport phenomena associated with the creation of the semiconductor materials. A test of this understanding is the ability to write useful mathematical descriptions of the laboratory scale reacting system. Mathematical descriptions are an essential part of the analysis because they provide the language which allows the professionals doing the research to effectively and unambiguously communicate with each other. Communication is easier if the models are simple and, of course, the model predictions must be verifiable by experiment. In fact, the model behavior should be used to plan the experimental program because an enlightened use of a chemical reaction and reactor engineering analysis will identify critical molecular and transport phenomena problems and direct experimental attention to them with the proper priorities.

We originally became interested in the semiconductor research because of a need to design larger scale reacting systems. However, the last five years of research has taught us that the chemical engineering analysis is very useful in the laboratory scale research effort, and indeed essential, if such research is to be done efficiently and with minimum expense (a key issue with today's research costs).

It is not possible, in our view, to effectively design and operate larger scale systems without reaction and reactor engineering analysis. In photo-

voltaic applications it is also necessary to carry out analysis and experimentation at the unit operations scale. Those who have attempted to scale up without following these procedures have wasted time and money building equipment which is inadequate for the commercial scale processing of solar cells.

A useful start has been made in applying chemical engineering analysis to the deposition of thin-film semiconductors but much effort now must be devoted to the task of relating electronic and optical properties to the design and operation of a reacting system. When we have learned to do this properly, we can begin to "tailor-make" material with any desired property.

ACKNOWLEDGMENTS

Semiconductor chemical reaction and reactor research requires a team effort involving a number of professionals. I am particularly indebted to B. N. Baron, R. E. Rocheleau, S. C. Jackson and R. J. Bogaert, my chemical professional colleagues at the Institute of Energy Conversion. Their analysis, their effective experimentation and their discussions with me have been essential to the development of this field. None of the research could have been carried out without the excellent semiconductor material development and analysis and device design and analysis that my other colleagues at the Institute of Energy Conversion do so well. I am also in their debt for their willingness to educate a chemical engineer in the art and science of applied solid state physics.

Science and engineering research today requires some considerable management talent. The Department of Energy's photovoltaic office and the Solar Energy Research Institute have worked very hard to develop a rational plan for photovoltaic research that both produces results and handles the political pressures that arise in a budget conscious government. The management group within the Institute of Energy Conversion is unique in its capability to protect the director from administrative detail and to allow me to put most of my effort into technical work. I would like to thank S. Barwick and M. Stallings for this gift. □

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NOMENCLATURE

a	area
C_i	concentration of species i
D	diameter of reactor
K	effective reaction rate constant
k	reaction rate constant
k_g	mass transfer coefficient
MW	molecular weight
q	volumetric flow rate
r(e)	rate of evaporation
r(i)	impingement rate, species i
r(r)	rate of reflection
r(rxt,i)	net rate of reaction, species i
V	volume
Z	axial position in tubular reactor

Greek

δ	condensation coefficient
γ	stoichiometric coefficient
ρ	density

Subscripts

f	film property
g	gas phase
i	molecular species
s	denotes on the surface

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