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**UNIVERSITY
OF
ARIZONA**

G. K. Patterson
University of Arizona
Tucson, AZ 85721



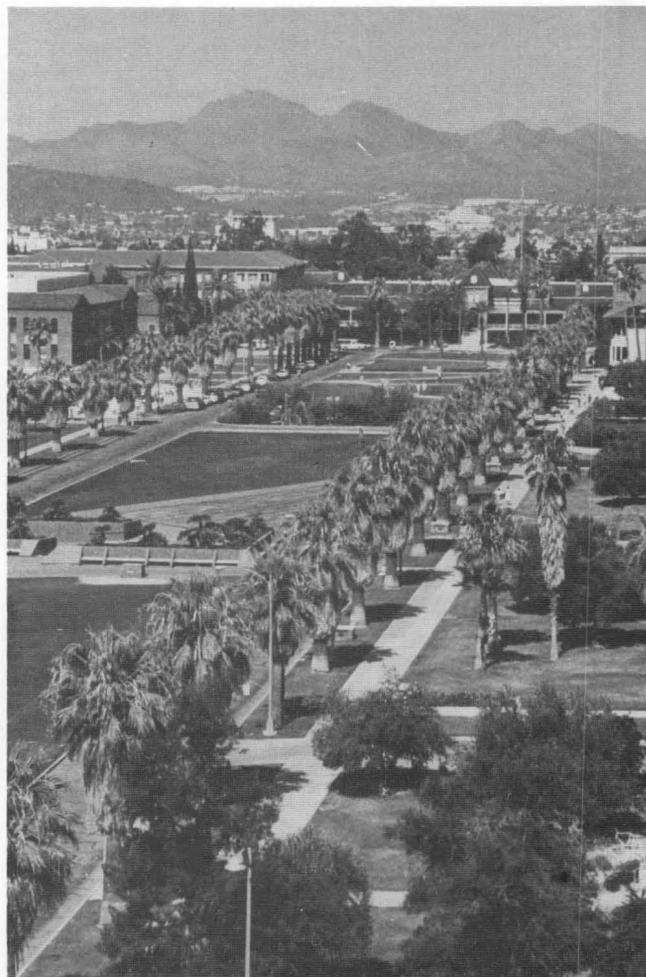
View of Tucson, home of the University of Arizona.

THE UNIVERSITY OF Arizona has come a long way in the 103 years since it was a one-room school house in the middle of the desert. The original 32 students have grown to more than 34,000 and the six charter members of the UA faculty now number about 2,200 (which does not include the more than 1,000 graduate assistants who aid in teaching and research). In order to administer such a large educational enterprise, The University of Arizona requires more than 7,500 staff personnel. Their work is carried out in 131 buildings spread across 540 acres in the heart of Tucson.

The University of Arizona is a very strong research-oriented university. In 1988, it was ranked 12th among U.S. public universities for research funding. Engineering at The University of Arizona ranked 17th in research funding, and the Chemical Engineering Department ranked 25th in research funding.

Chemical engineering was proposed for The University of Arizona in the mid-1950s. The dean of engineering at that time saw no place for chemical engineering in his college, so the College of Mines began development of the department. The first courses were taught by the Metallurgical Engineering Department.

The Chemical Engineering Department first took its place among the other engineering curricula and was duly proclaimed in print in the 1957-58 UA catalog. It is interesting to note that while it listed thirteen courses, it listed NO faculty—a problem quickly remedied, even though those who were interviewed had to pay their own travel expenses. A strong faculty was assembled by the first department head,



Aerial view of the campus.

Don H. White, and the department quickly gained recognition.

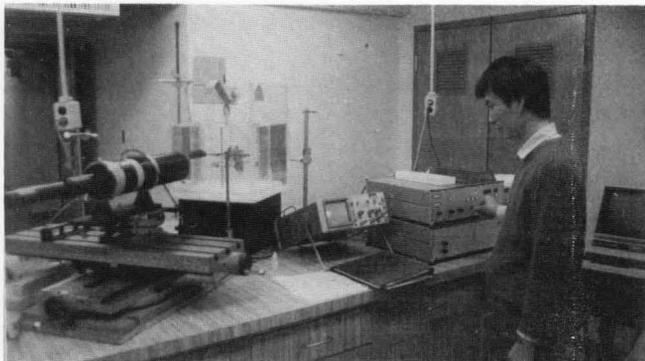
Due to strong leadership during those initial years, the department gained the reputation as a research and education leader with both industrial and academic sectors of the profession. The early emphasis on computer utilization, continued stress on design, and a strong foundation in chemistry have brought the department into the present where it enjoys international respect in the crystallization, combustion, pollution control, biomedical, biochemical, and turbulent flow areas.

Enrollment has averaged 150 undergraduates and 40 graduate students for the last ten years. An in-

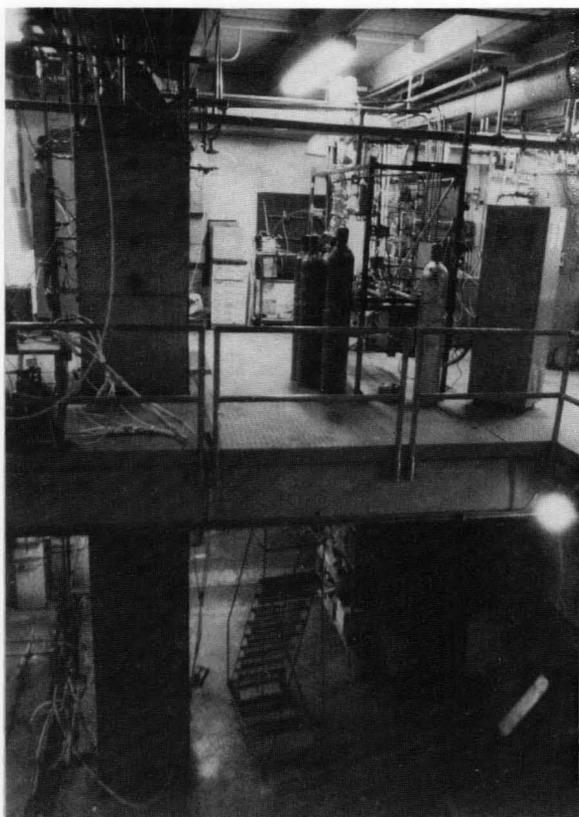
creasing emphasis on doctoral research has changed the composition of the graduate enrollment toward a majority pursuing the PhD. These students benefit from working at a highly technological campus with well-equipped laboratories.

The University provides several outstanding facilities of interest to students and faculty in chemical engineering. The Main and Science libraries contain over 2,500,000 volumes, and the combination ranks 21st nationally. The University Computer Center houses a CYBER 175, an IBM 4381, and three VAX 11-780's, one VAX-8650, one SCS-40 mini-supercomputer, and a large microcomputer laboratory. An IBM 3090 is used for financial and student records. Additionally, the University is one of eight member institutions in the Consortium for Scientific Computing at the John von Neumann Supercomputer Center in Princeton, New Jersey. Direct satellite link to this center provides interactive capabilities. In addition to those campus-wide facilities, the department has a multitude of student-accessible personal computers, both for undergraduate education and graduate research, including data acquisition, and numerous minicomputers serving similar purposes. The College of Engineering and Mines has several computers on a network which are accessible to chemical engineering faculty and students. Some of those are MV10000 and MV8000 Data General computers (the 10000 has an array processor), three VAX 11/750's, one VAX 11/780 and several DEC minicomputers of various sizes. All computer systems are accessible through interactive terminals and microcomputers located in the chemical engineering building. All computers on both the engineering and the university networks can send and accept files to and from the others.

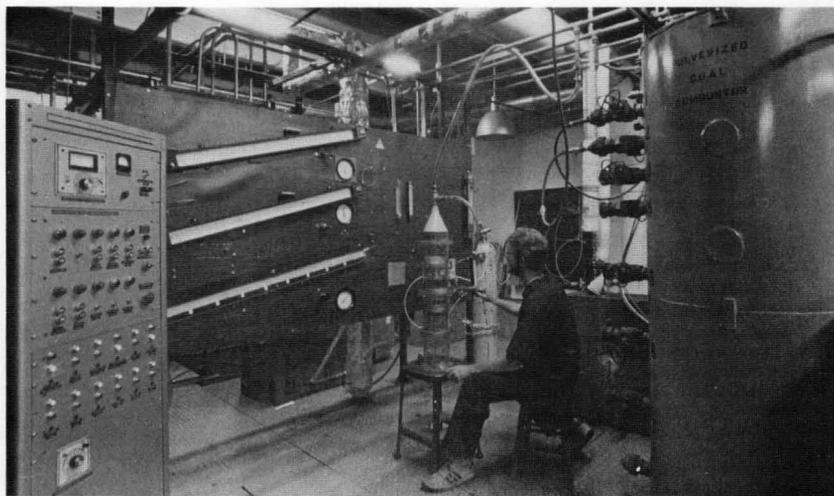
The departments of mathematics, physics, chemistry, biochemistry, microbiology, pharmacy, electrical



Laser doppler anemometry.



Two-story combustion facility.



Coal combustion research lab.

The graduate program is designed to provide advanced work with core courses in transport phenomena, thermodynamics, and reaction engineering, with additional selected work in mass transfer, heat transfer, fluid dynamics, control theory, and process simulation.

and computer engineering, and aerospace and mechanical engineering supply chemical engineering with the support necessary for good undergraduate and graduate research programs. Projects are done jointly by undergraduate and graduate students and faculty in chemical engineering, and in many cases other departments provide service to and/or cooperation with chemical engineering. A high degree of cooperative research and course-sharing exists between departments on the campus, assuring a rich and diverse atmosphere for research and study.

THE FACULTY

The original faculty member, Don H. White, was called upon by the Dean of the College of Mines to organize a chemical engineering department in 1958. He arrived in Tucson in September of 1958 to find eager junior and sophomore classes of chemical engineers expecting to be taught, but empty chemical engineering laboratory rooms and no other faculty. He quickly organized a small group of faculty to begin teaching the students who had been admitted in the fall of 1956. This first faculty consisted of Robert Damon, fresh out of Montana State, Richard Edwards from Mallinkrodt Corporation in St. Louis, and James Carley, engineering editor of *Modern Plastics* in New York City. Also here, for a short time, were James Hall and Ray Richardson.

Other early faculty included Edward Freeh in 1962, Neil Cox in 1962, Alan Randolph in 1968, Thomas Rehm in 1966, and Richard Williams and William Cosart in 1968. A second round of "early faculty" included Jost Wendt in 1972, Joseph Gross in 1972, and James White in 1971. At that time a new young university president (John Schaefer) led the university in its push to become a research university.

Not all early faculty stayed in the teaching profession. Robert Damon is now with Crown Zellerbach, James Carley is with Lawrence Livermore Labs, and James White is vice president of his own successful computer company (in partnership with a UA alumna, who is president). Richard Edwards retired in Tucson after becoming a vice president of the University of Arizona. Neil Cox went to the Idaho Nuclear Test Facility, and Richard Williams ended up at Exxon Research and Development. All the others are still active faculty in our chemical engineering group. William Cosart is Associate Dean of our College of Engineering and Mines.

TABLE 1
Faculty: University of Arizona

MILAN BIER	<i>Fordham University</i>
protein purification	
HERIBERTO CABEZAS	<i>University of Florida</i>
solution thermodynamics	
WILLIAM P COSART	<i>Oregon State University</i>
Associate Dean	
EDWARD J. FREEH	<i>Ohio State University</i>
control (adjunct)	
JOSEPH F. GROSS	<i>Purdue University</i>
biomedical transport processes; department head 1975-1981	
ROBERTO GUZMAN	<i>North Carolina State University</i>
bioseparations	
GARY K. PATTERSON	<i>University of Missouri-Rolla</i>
fluid mechanics; department head 1984-1990	
THOMAS W. PETERSON	<i>California Institute of Technology</i>
aerosols	
ALAN D. RANDOLPH	<i>Iowa State University</i>
crystallization	
THOMAS R. REHM	<i>University of Washington</i>
process design	
FARHANG SHADMAN	<i>University of California, Berkeley</i>
chemical reaction engineering	
JOST O.L. WENDT	<i>Johns Hopkins University</i>
combustion	
DON H. WHITE	<i>Ohio State University</i>
polymer processes	
DAVID WOLF	<i>Technion</i>
mixing; (visiting half years)	

As can be quickly discerned from this short history, the faculty in this department have been remarkably loyal. Undoubtedly, part of the reason is the persuasiveness of Don White, who was department head until 1974. Other factors contributing to such a stable faculty are the unduplicated climate and quality of life in Tucson and the excitement of being part of a rapidly growing university.

More recent faculty are Thomas Petersen, Farhang Shadman, Gary Patterson, Milan Bier, Heriberto Cabezas, and Roberto Guzman. The present faculty, their origins, and their main professional interests are shown in Table 1.

TUCSON: THE "OLD PUEBLO"

The University of Arizona is located in the heart of Tucson, a metropolitan area of over 700,000 people. Tucson is located sixty miles north of Mexico, at an

elevation 2,400 feet and in a valley surrounded by rugged mountains. Not much more than a century ago Tucson was a small, dusty Mexican outpost—a pueblo.

Life in Tucson places emphasis on the out-of-doors. The sun shines more than 300 days each year, making outdoor recreation a way of life for many Tucsonans (exemplified by the thirty-one golf courses in the area). Tennis, golf, and swimming are obvious favorites, but Tucson offers much more than that. Within an hour of the campus are the ski resort of Mount Lemmon, the internationally acclaimed Arizona-Sonora Desert Museum, and one of the world's largest accumulations of telescopes at Kitt Peak National Observatory. Backpacking and off-road vehicle trails are abundant and easily accessible. Camping equipment can even be rented from the campus Hiking, Outing, and Travel Center. For longer treks there are the ski resorts of the White Mountains and the incredible Grand Canyon. Tucson city parks and golf courses also provide varied recreation. For those who like to stay close to home, on campus there are several restaurants, a game room, three swimming pools, handball/racquetball courts, a weight room, a gymnasium, and a movie theater. A new comprehensive student recreation center is being constructed to add to these facilities.

UNDERGRADUATE PROGRAM

The undergraduate program in chemical engineering at the University of Arizona has developed as one of strength in fundamental chemical engineering utilizing basic science, requiring thirteen semester units of math, eight semester units of physics, twenty-three units of chemistry, and three units of any other advanced-level science. The math strength is consolidated by six units of applied math taught within the department. Altogether, thirty-seven units of courses are required within the department, along with fifteen units of other engineering outside the department. The addition of six units of freshman composition and sixteen units of humanities and social sciences leaves room for ten units of technical electives. The technical electives must be chosen from a list of specialties such that depth of study is achieved in some field.

Such a program of study is rigorous and attracts only the most motivated students. Even with a heavy study load, most students find time to participate in the student AIChE chapter, which has Friday afternoon picnics several times each year. The chapter also organizes the annual open house for high school students and sends members to talk to high school classes about chemical engineering. Each year the chapter sends a delegation to the regional student meeting.

The graduates of the undergraduate program have been very successful when entering industry or graduate programs at other universities. This is probably because they can rely on the strong fundamental science base that the curriculum provided—they are prepared to learn any specialized field of chemical engineering.

A relatively recent trend, which is of great benefit to the undergraduates, is their participation in the various graduate research programs. All the students seem to be highly motivated by their inclusion in the laboratory research of the graduate programs. An added benefit is that acquainting them with the joys of research and the graduate student culture undoubtedly results in more of them pursuing graduate work

Altogether, thirty-seven units of courses are required within the department, along with fifteen units of other engineering outside the department. . . . Such a program is rigorous and attracts only the most motivated students.

before taking a job. Additionally, contact with the other undergraduates and discussions of their research work convinces them of the value of the research projects. Such knowledge breeds understanding.

GRADUATE PROGRAM

The Department of Chemical Engineering has a strong and diverse graduate program. The Master of Science degree has been offered for many years (the first degree was awarded in 1961) and the first Doctor of Philosophy was awarded in 1964. Since that time 144 MS degrees and 23 PhD degrees have been granted. The department is heavily involved in a transition from a primarily MS graduate program to a primarily PhD graduate program. The ratio of PhD candidates to MS students has increased in the last four years from less than 0.3 to greater than 1.0.

Graduate studies in chemical engineering are administered by a graduate studies committee of the faculty under the general direction of the Graduate College. Work toward a master of science degree consists of a mix of course work and research leading to a thesis. The doctor of philosophy degree requires some additional course work (including a minor in a related area) and extensive research leading to a dissertation. Along the way a qualifying examination, a preliminary examination, and a final oral examination must be passed.

All graduate students must take, or have equivalent credit for, three basic courses: Advanced Trans-

port Phenomena, Advanced Thermodynamics, and Advanced Chemical Reaction Engineering.

The graduate program is designed to provide advanced work with core courses in transport phenomena, thermodynamics, and reaction engineering with additional selected work in mass transfer, heat transfer, fluid dynamics, control theory, and process simulation. The following interdisciplinary options with several courses in each are also available: biomedical engineering, bioprocess engineering, energy systems engineering, and materials engineering.

RESEARCH PROGRAMS

Each department of chemical engineering develops its own style and philosophy of research. At Arizona neither pure engineering science nor applied process development is emphasized at the expense of the other. Rather, the approach is to apply fundamental engineering science to the solution of process-relevant

problems of major engineering concern. This is indeed a formidable task and requires good relationships and communication with the industrial world where such process-relevant problems are identified. About half of the chemical engineering faculty members at Arizona have had several years experience in industry and are encouraged to maintain close industrial ties through consulting arrangements.

Our department plays a significant role in the energy and biotechnology fields. In energy-related work, numerous projects emphasize both the economic and environmental aspects of current energy concerns. These projects combine practical experimental and theoretical studies with the latest in analytical tools.

Biochemical engineering studies are being conducted in a number of new and exciting areas. In fermentation and bioreactor studies, microorganisms and enzymes are used to generate useful products. In the bioseparation area, mixed products are separated and purified. Our bioseparation group is one of the premier groups in the world, particularly in the area of electrophoretic methods of separation. Other separation methods, notably two-phase aqueous extraction and chromatography, are under development.

An interdisciplinary program emphasizing materials processing is available in cooperation with the Materials Science and Engineering Department. Similarly, courses of study are also designed to include electronic materials processing through the Electrical and Computer Engineering Department. Current research topics in the department are described in Table 2.

Research funding from outside agencies and companies has grown dramatically in the last five years, particularly since inclusion of the Center for Separation Science. Total funding is now about \$1.5 million for a permanent faculty of eleven. Growth in the biotechnology area was recently spurred by a university program which provided new capital and support funds.

QUALITY AND QUANTITY

The department has a rigorous undergraduate program which has produced graduates who have contributed to the chemical engineering profession since its first graduating class in 1960. Many entered graduate studies at other universities and did well in their programs, as indicated earlier.

From the beginning, the department has worked hard at building its graduate program, with the aim of having a PhD program of national impact. That capability grew sporadically at first, but it was marked

Continued on page 60.

TABLE 2
Departmental Research Topics

Aerosol Dynamics: *Physical and chemical mechanisms governing particle formation, transport, and transformation • application to atmospheric problems, combustion and clean rooms.*

Biochemical and Biomedical Engineering: *Transport phenomena in the microcirculation • development of physiological pharmacokinetic models • thermodynamic properties of protein solutions • protein separation and purification techniques • dynamic modeling of kidney-stone formation • bioreactor design and scale-up • transport in fermenters*

Catalysis and Kinetics: *Sulfur oxide emissions control via catalyzed lime reactions • catalytic gasification of coal*

Combustion: *Control of NO_x/SO_x during coal combustion; reburning as a method of NO_x control • mechanisms of fly ash formation in pulverized coal combustion • model characterization of flame chemistry*

Computer-Aided Design: *Development of unit operation modules for undergraduate education*

Crystallization: *Use of chemical inhibitors as nucleation/growth rate modifiers • laboratory modeling of kidney stone formation • real-time control of crystal population dynamics • use of supercritical fluids as crystallization media • crystallization in microgravity (space)*

Fuels: *Fuel combustion efficiency and relationship to pollutant formation • coal gasification and liquefaction • high-pressure liquefaction of biomass*

Polymers: *Viscoelastic properties of polymers • shear degradation of polymer molecular weights • polymer extrusion methods*

Separations: *Large scale free-flow electrophoresis as a means of protein separation and purification*

Solar Energy: *Solar desalination of sea water and brackish solutions • solar desiccation methods for air conditioning*

Surface Analysis: *Scanning auger spectroscopy of fly ash particles and catalysts*

Thermodynamics: *Modeling of multicomponent and polyelectrolyte properties in solution*

Turbulence: *Effect of mixing on reactor yields • laser-doppler measurement of turbulence properties in mixing • computer simulation of turbulent mixing and reaction*

MEET YOUR STUDENTS

2. Susan and Glenda

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

Susan and Glenda are seniors in chemical engineering at a private northeastern university. They are both bright and personable. They like to study with friends and enjoy the lengthy bull sessions that the study sessions sometimes turn into. They both have a hard time saying no to requests for help with classwork, even if they don't have the time for it. Neither one cares for laboratory courses. They have almost identical grade point averages—about 3.2/4.0.

The resemblance ends there, however. Susan was an outstanding student in junior high and high school, and in college she has gotten B's in almost all of her courses, with an occasional A. Her instructors have an easy time grading her homework and test papers: the solutions are neatly laid out, with each step clearly following the preceding one, and she gets a great deal of credit even when her answers are incorrect.

Glenda is another story. Her transcript is a mixture of A's and C's. She usually starts out in a class by doing poorly on the homework and failing the first quiz, and she may spend the rest of the semester trying to catch up. Her problem solutions are jumbles of apparently unrelated numbers and equations with the answer magically appearing at the end; she rarely gets much partial credit, and if anyone asks her to explain what she did, she has an extremely difficult time doing so.

Sometimes, however, Glenda seems to undergo a transformation. She begins to solve homework and test problems with ease, occasionally using methods that were not taught in class. She may then go on to get an easy A in the course, or, if the class moves on to completely new material, she may revert to her previous performance level and struggle until either another breakthrough is achieved or the semester ends. Even after she makes a breakthrough, her problem solutions are frequently incomprehensible to anyone else; the difference is that the answer that suddenly appears at the end is correct. She has been hurt on several occasions by instructors who implied that she had cheated, although no one ever had any proof. (In fact, she never cheated.)

Susan is a *sequential learner*, Glenda is a *global learner* [1]. Sequential learners tend to gain understanding in a linear fashion, with each new piece of in-

formation building logically from previous pieces. They tend to solve problems the way they learn—in a linear, stepwise fashion—and their solutions make sense to others. They generally have little trouble in school because of their sequential way of learning and solving problems: their courses, books, and teachers are all geared to their style.

Global learners function in a much more all-or-nothing fashion. They absorb information almost randomly, in no apparent logical sequence. In consequence, when they are first learning a subject nothing may make sense to them, and they may be incapable of solving trivially simple problems. But then at some point a key piece of data is taken in, a critical connection is made, the light bulb goes on, and they "get it." They may be fuzzy about details after that, but they see the big picture in a way that most sequential learners never achieve. Thereafter, when presented with new material that they can fit into this picture, they may appear to assimilate it instantly, and when solving problems they may leap directly to the solution without seeming to go through the required intermediate steps. They may also see surprising connections between newly-learned material and material from other subjects and disciplines.

Strongly global learners often have difficulty in school. Before they make their mental breakthrough in a given subject, their struggle to solve problems that their sequential counterparts handle with ease makes them feel stupid. Even after they make breakthroughs, their inability to explain their problem-solving processes can get them into trouble, as when Glenda was suspected of cheating. These difficulties—which most of them experience from the first grade on—are truly unfortunate, since global learners collectively constitute one of society's most valuable and underutilized resources. If they are allowed to progress in their seemingly disjointed manner, some of them will go on to become our most creative researchers, our systems analysts—our global thinkers.

Felder and Silverman [1] suggest ways that engineering instructors can accommodate the learning styles of global learners. Most of these suggestions involve providing a broad perspective on the course material, relating it to material in other courses and disciplines and to the students' prior experience. Perhaps the best thing we can do for these individuals, however,

Continued on page 11.

Edwin N. Lightfoot

... of Wisconsin

BY HIS COLLEAGUES

University of Wisconsin
Madison, WI 53706

ED LIGHTFOOT is an extraordinary individual driven by enormous energy and curiosity. He is an engineer in Olaf Hougen's sense of the word:

Successful solutions to industrial problems depend upon engineering judgement and experiment with the unknown and undocumented science as well as with the principles that have already been well established. This is the principal distinction between the scientist and the engineer.

The broad interdisciplinary nature of Ed's professional interests has led to significant contributions in a number of fields. He is sought and respected as a collaborator by physicians, biologists, physiologists, mathematicians, engineers, and businesspeople. He has produced forty PhD students, published two books, and written nearly two hundred research pub-

TABLE 1
Honors: E. N. Lightfoot

- 1962 Fulbright Scholar *Norway*
- 1972 Erskine Fellow *New Zealand*
- 1975 Wm. Walker Award *AICHE*
- 1979 Elected to National Academy of Engineering
- 1979 Food, Pharmaceutical and Bioengineering Award *AICHE*
- 1980 Hilldale Professor *University of Wisconsin*
- 1984 Lacey Lectureship *Caltech*
- 1985 Elected to Norwegian Society of Sciences and Letters
- 1985 Honorary Doctorate *Norway*
- 1986 Stanley Katz Lecturer *City College of New York*
- 1986 Goff Smith Lecturer *University of Michigan*
- 1987 Kloor Memorial Lecturer *Indian Institute of Sciences*
- 1988 Reilly Lecturer *University of Notre Dame*
- 1988 Benjamin Smith Reynolds Award for Teaching Excellence



lications appearing in *AICHE Journal*, *Journal of the American Chemical Society*, *Industrial and Engineering Chemistry*, *Chemical Engineering Science*, *Journal of Chemical Engineering*, *Journal of Physical Chemistry*, *Journal of the Electrochemical Society*, *Applied Microbiology*, *Transactions of the Faraday Society*, *International Journal of Heat and Mass Transfer*, *Chimie et Industrie-Genie Chimique*, *Journal of Biomedical Materials Research*, *Biophysics Journal*, *Physics of Fluids*, *Journal of Undersea Biomedical Research*, *Annals of Biomedical Research*, *Science*, *Separation Science*, *Journal of Food Science*, *Progress in Water Technology*, *Journal of Applied Physiology*, *Respiration Physiology*, *Journal of Theoretical Biology*, *Laboratory Animal Science*, *Water Resources Research*, *Biotechnology and Bioengineering*, *Environmental Research*, *Protein Purification*, *Environmental Toxins and Chemicals*, *Israel Journal of Chemistry*, *Chemical Engineering*

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His incredible record of productivity carries over to the classroom, and his students are the beneficiaries of his efforts to bring new ideas and challenges to his courses. He is an extremely enthusiastic lecturer whose courses are at the frontier of knowledge.

TABLE 2
Lightfoot Students Who are Currently Teaching

1960	A. D. Di Benedetto	University of Connecticut
1962	G. B. Wills	Virginia Polytechnic Institute
1964	D. W. Hubbard	Michigan Technical University
1964	E. L. Cussler	University of Minnesota
1966	D. O. Cooney	University of Wyoming
1973	R. E. Safford	Mayo Clinic
1974	K. A. Solen	Brigham Young University
1975	H. O. Ozelge	Middle East Technical University
1981	T. A. Hatton	Massachusetts Institute of Technology
1984	B. O. Palsson	University of Michigan
1984	A. M. Lenhoff	University of Delaware

Education, Critical Reviews in Food Engineering, Recent Developments in Separation Science, Annual Reviews of Fluid Mechanics, and Journal of Pharmaceutical Science.

His incredible record of productivity carries over to the classroom, and his students are the bene-

ficiaries of his efforts to bring new ideas and challenges to his courses. He is an extremely enthusiastic lecturer whose courses are at the frontier of knowledge. They are progress reports on the continual evolution of his thoughts on science and pedagogy. Of particular value to his graduate students is his skill in the one-on-one interaction necessary in innovative research at the doctoral level.

Ed is the recipient of the 1989 Benjamin Smith Reynolds Award for excellence in teaching in the College of Engineering at the University of Wisconsin.

As everyone knows, Ed's gregarious and talks very fast (it's hilarious); with such animation and hyperventilation he nearly blacks out - It's precarious.

Bob Bird
on Ed's 60th birthday

Ed's love of being on the go is apparent by his travel schedule. The East Coast, West Coast, Rocky Mountains, India, Norway, New Zealand, Finland,



Warren Stewart, Bob Bird, and Ed Lightfoot, authors of Transport Phenomena.

Sweden, Taiwan, Australia, Canada, Switzerland, Denmark, Czechoslovakia, Mexico, and Spain are all on his itinerary. He was elected to the Norwegian Society of Sciences and Letters, received an Honorary Doctorate at the Norwegian Technical University at Trondheim, and was an Erskine Fellow at the University of Christchurch in New Zealand. At a different pace are his visits, with his wife Lila and five children (together with their dog, Rascal), to his cabin in the woods north of Madison, and his bicycle rides and cross-country ski tours through the lovely Wisconsin countryside.

Ed was born in Wisconsin 64 years ago and received his college education at Cornell University. A young John Prausnitz was taught mechanical drawing

at Cornell by an equally young Ed Lightfoot. After several years at Chas. Pfizer and Company, where he developed a patented process for vitamin B₁₂ production and purification, Ed joined the University of Wisconsin in 1953 to lead one of the first bioengineering programs in the United States.

At that time Olaf Hougen was promoting the development of educational material in transport phenomena. Ed joined Bob Bird and Warren Stewart in an enormously productive period of several years to produce the classic book *Transport Phenomena*. Much of the writing was done in a small cabin Bob Bird rented on the north shore of Lake Mendota to which Ed often commuted by canoe and sailboat. That book has gone through over forty printings and has been translated into Italian, Czech, Spanish, and Rus-

TABLE 3
Lightfoot: "My Most Satisfying Research Projects."

- | | |
|--|--|
| <p>✓ E. N. Lightfoot and R. J. Taylor
"Recovery and Purification of Vitamin B₁₂"
U. S. Patent 2,787,578 (1954)
<i>This represents a major engineering effort at Chas. Pfizer and Co., which resulted in a full-scale production process for crystalline vitamin B₁₂. Ed found this type of process development work particularly attractive and has returned to this first love in his current research on the production of chemicals from agricultural wastes.</i></p> | <p><i>sion tables for divers and tunnel workers was unsound, a fact borne out by experimental studies reported at the same symposium.</i></p> |
| <p>✓ J. B. Angelo and E. N. Lightfoot
"Generalization of the Penetration Theory for Surface Stretch: Application to Forming and Oscillating Drops"
<i>AIChE Journal</i>, 12, 751-760 (1966)
<i>This work showed the applicability of asymptotic analysis in complex process equipment, as well as providing a mass-transfer model which has proven useful for applications as widely different as direct-contact heat transfer and oxygenation of sewage in U-tube aerators.</i></p> | <p>✓ J.F.G. Reis, P.T. Noble, A.S. Chaing, and E. N. Lightfoot
"Chromatography in Beds of Spheres"
<i>Separation Science and Technology</i>, 14 367-394 (1979)
<i>This research developed among the most practical descriptions of gradient elution chromatography, the mainstay of commercial protein fractionation.</i></p> |
| <p>✓ E. M. Scattergood and E. N. Lightfoot
"Diffusional Interaction in an Ion-Exchange Membrane"
<i>Transactions of The Faraday Society</i>, 64, 1135-1146 (1968)
<i>This was the first measurement of all of the multicomponent diffusivities in a membrane system and the first comprehensive treatment of boundary-layer polarization in test equipment.</i></p> | <p>✓ A.M. Lenhoff and E.N. Lightfoot
"The Effects of Axial Diffusion and Permeability Barriers on the Transient Response of Tissue Cylinders"
<i>J. of Theoretical Biology</i>, 106, 207-238 (1984)
<i>This work provides the basis for an understanding of transient mass transfer processes in the microcirculation, applied to such clinical situations as the identification of abnormal metabolism in the brain.</i></p> |
| <p>✓ V. Ludviksson and E. N. Lightfoot
"The Dynamics of Thin Films in the Presence of Surface-Tension Gradients"
<i>AIChE Journal</i>, 17, 1166-1173 (1971)
<i>This is one of a series of papers describing the effects of surface tension gradients on the dynamics of thin supported liquid films. These are important in a variety of systems, including electrochemical cells and secondary recovery in oil wells.</i></p> | <p>✓ B.O. Palsson, H. Palsson, and E.N. Lightfoot
"Mathematical Modelling of Dynamics and Control in Metabolic Networks"
<i>J. of Theoretical Biology</i>, 113, 279-298 (1985)
<i>This is the latest in a series of pioneering papers which helped to open the field of the dynamics and control of metabolic networks of chemical reactions to systematic study.</i></p> |
| <p>✓ E.N. Lightfoot, A. Baz, E.H. Lanphier, E.P. Kindwall, and A. Seirig
"Role of Bubble Growth Kinetics in Decompression"
VI Symposium on Underwater Physiology, San Diego, California (1975)
<i>This work predicted that the existing basis of decompres-</i></p> | <p>✓ E.N. Lightfoot and M.C.M. Cockrem
"What Are Dilute Solutions?"
<i>Separation Science and Technology</i>, 22, 165-189 (1987)
<i>This was a first major step in continuing efforts to speed the development of separations equipment and processes by relating economic goals to the underlying physico-chemical principles.</i></p> |
| | <p>✓ J.C. Liao and E.N. Lightfoot
"Applications of Characteristic Reaction Paths: Rate Limiting Capability of Phosphofructokinase in Yeast Fermentation"
<i>Biotechnology and Bioengineering</i>, 126, 253-273 (1988)
<i>This work shows how to locate bottlenecks in metabolic networks by using systems analysis techniques. It points out the importance of systems analysis in commercial biotechnology.</i></p> |

sian. It has been a regular "citation classic" for being referenced in the literature with a frequency comparable to such classics as Abramowitz and Stegun (Handbook of Mathematical Functions) and Carslaw and Jeager (Conduction of Heat in Solids). It is recognized as the most important textbook in the profession in the last quarter century.

In 1974 Ed published the pioneering text *Transport Phenomena and Living Systems* which showed how to use the art and science of chemical engineering to solve important bioengineering problems by including details of the physiological and pharmacological phenomena.

Recently he has devoted his efforts to the development of modern biotechnology, with special emphasis on the engineering of metabolic pathways and materials separations. He was the driving force in the organization of the Bioprocess and Metabolic Engineering Consortium at the University of Wisconsin. With the support of Abbott Labs, Agracetus, APV Crepaco Inc., Becton Dickson, Bio-Technical Resources, DuPont, Kraft, New Brunswick Scientific Co., Procter and Gamble, Promega Biotech, Universal Foods and Xylan, the consortium promotes the use of biological organisms and biochemical processes to produce specialty chemical products.

Just this year Ed led a University/Industry/State-of-Wisconsin team in the development and design of an industrial process to produce high purity lactic acid from waste cheese whey. This industry seeks to produce valuable chemicals and jobs from a particularly troublesome waste product of one of the state's largest industries. This service to industry and state follows Ed's successful approach to research in combining the science and practice of engineering. □

RANDOM THOUGHTS

Continued from page 7.

is to watch for them, and when we find them (which we will), explain and affirm their learning process to them. They probably already know all about the drawbacks of their style, but it usually comes as a revelation to them that they also have advantages—that their creativity and breadth of vision can be exceptionally valuable to future employers and to society. Any encouragement we provide could substantially increase the likelihood that they will succeed in school and go on to apply their unique abilities after they graduate.

Postscript: 10 years later

Susan graduated and went on to get a masters degree in chemical engineering, got a number of good job

offers, and went to work in the process design division of a large petrochemical company. She did extremely well and is now making rapid progress up the technical management ladder. Glenda went through a lengthy job search when she graduated—all those C's on her transcript worried prospective employers—and finally found a position with a small firm of design consultants. Her first project involved designing and installing process simulation software for a pharmaceuticals manufacturer. She did almost nothing on the project for months, despite increasing pressure from her supervisor. Then she came up with a package that not only did the required simulation but also used it to schedule production, manage inventory, and determine production bottlenecks and the best methods of eliminating them. The company estimated that the program led to savings of two million dollars in its first year of use. Glenda now gets the problems too difficult for anyone else in the firm to solve. Sometimes long periods go by without any apparent results, but no one pressures her any more. □

[1] R.M. Felder and L.K. Silverman, "Learning and Teaching Styles in Engineering Education," *Engineering Education*, 78(7), p.674 (1988). Susan is a representative sequential learner and Glenda is a representative global learner, but not all sequentials are just like Susan and not all globals are just like Glenda. These labels simply denote tendencies that may be strong or weak in any given individual, and everyone exhibits characteristics of both types to different degrees.

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FROM MOLECULAR THEORY TO THERMODYNAMIC MODELS

Part I. Pure Fluids

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Newark, DE 19716

THERMODYNAMICS AND physical properties are central to the practice of chemical engineering. This is evident from the fact that 70 to 90% of both investment and energy operating costs in a typical chemical plant involves the separations and purifications equipment which are designed largely on the basis of phase equilibrium. Further, the complete flow sheet of a chemical plant may depend on whether an azeotrope or two liquid phases are formed somewhere in the process. With the availability of modern process simulators it is usually the uncertainty in thermodynamic behavior, rather than the design algorithms or calculational complexity, which presents the biggest difficulty in accurate process design.

Because of their importance in process design, many thermodynamic and physical properties models have been developed. Indeed, there are more than 100 variations of the van der Waals equation of state in addition to numerous other equations of state and activity coefficient models. A problem that arises in teaching thermodynamics to chemical engineering students is providing a coherent scientific (rather than

merely empirical) basis for these models. A related problem is introducing students to the use of molecular theory for the development of thermodynamic models. This paper presents a framework which allows one to identify the molecular level assumptions underlying many thermodynamic models. We then continue on to test these assumptions using theory and computer simulation and to show how we can make better assumptions which lead to improved models. Here we consider only pure fluids and their equations of state; in Part 2 (to be published in the next issue of *CEE*) we will consider mixtures and activity coefficient models.

SIMPLIFIED STATISTICAL MECHANICS: The Generalized van der Waals Partition Function

The molecular theory from which one can derive thermodynamic models is statistical mechanics. For the case in which the temperature T , volume V , and number of particles N are the independent variables, the canonical partition function

$$Q(N, V, T) = \sum_i^{\text{states}} e^{-E_i(N, V)/kT} \quad (1)$$



Stanley I. Sandler earned a BChE degree from the City College of New York in 1962 and his PhD from the University of Minnesota in 1966. His research at Minnesota was on the kinetic theory of gases. He was a NSF postdoctoral fellow at the Institute for Molecular Physics at the University of Maryland for the 1966-67 academic year. He joined the faculty of the University of Delaware in 1967 and was its chair from 1982 to 1986.

His research has mainly been in the field of thermodynamics and fluid properties, with specializations in molecular theory, computer methods, and the experimental measure-

ment of phase equilibrium. He is the author of 135 papers, the editor of five conference proceedings books, and author of the textbook *Chemical and Engineering Thermodynamics*, which has been translated into Spanish and Chinese. The second edition has just appeared.

He was cochair of the Chemical Engineering Faculty Summer School of the ASEE in 1982, and was originator and chair of the 1988 Chemical Engineering Education in a Changing Environment Conference, held for the purpose of introducing new technology examples into standard undergraduate courses. He has served on the Editorial Advisory Board of the *AIChE Journal*, Industrial and Engineering Chemistry Fundamentals, and the University of Delaware Press. He is an ABET/AIChE chemical engineering accreditation visitor and is on the AIChE subcommittee for New Technology Educational Materials.

This paper presents a framework which allows one to identify the molecular level assumptions underlying many thermodynamic models. We then continue on to test these assumptions using theory and computer simulation and to show how we can make better assumptions which lead to improved models. Here we consider only pure fluids and their equations of state; part 2 . . . will consider mixtures and activity coefficient models.

is the starting point for our work [1]. Here the sum is over all the quantum states of N molecules in a volume V , k is Boltzmann's constant, T is temperature, and E_i is the energy of the system in the i^{th} quantum state. Once we know the partition function, all other thermodynamic properties can be computed as follows

$$A(N, V, T) = kT \ln Q(N, V, T) \quad (2)$$

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N} \quad E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} \quad (3)$$

$$S = kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} - k \ln Q \quad (4a)$$

$$C_V = 2kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} + kT^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_{V, N} \quad (4b)$$

etc.

Eq. 2, which relates the Helmholtz free energy to N , V , and T , is one of the fundamental equations of state in the sense of Gibbs; from it all other thermodynamic properties of a fluid can be obtained without any other information, as is evident from the equations above.

Identifying each quantum state of an assembly of molecules is at present an impossible task except for special cases such as the ideal gas. For the case of relatively simple molecules (for the moment excluding long chain hydrocarbons or polymers) the total energy of an assembly of molecules can be separated into translational (t), rotational (r), vibrational (v), electronic (e), and interaction (i) energies, each of which is independent of the others. Further, except for the interaction energy term, each of the contributions is a sum of the energies of the individual molecules. Therefore, for a pure fluid of N identical molecules we have

$$\begin{aligned} Q(N, V, T) &= \sum e^{-(E_t + E_r + E_v + E_e + E_i)/kT} \\ &= \left(\sum e^{-E_t/kT} \right) \left(\sum e^{-E_r/kT} \right) \left(\sum e^{-E_v/kT} \right) \left(\sum e^{-E_e/kT} \right) \left(\sum e^{-E_i/kT} \right) \\ &= \frac{1}{N!} (q_t(T))^N (q_r(T))^N (q_v(T))^N (q_e(T))^N \frac{Z(N, V, T)}{V^N} \end{aligned} \quad (5)$$

Here q_r , q_v , and q_e are the single particle rotational, vibrational, and electronic partition functions which are only a function of temperature. Also, $q_t = (2\pi mkT/h^2)^{3/2} V$ is the single particle translational partition function where m is the particle mass and h is

Planck's constant.

Of special interest is the last term, the configuration integral, which arises from the interactions between molecules. For spherical molecules in a volume element of macroscopic dimensions, classical mechanics can be used (thereby replacing summations with integrations)

$$Z = \int \dots \int e^{-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (6)$$

where $u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the interaction energy when a molecule is located between position vectors \mathbf{r}_1 and $\mathbf{r}_1 + d\mathbf{r}_1$, a second molecule between position vectors \mathbf{r}_2 and $\mathbf{r}_2 + d\mathbf{r}_2$, etc., and the integrals are over all values of the position vectors within the volume V . It is only the configurational integral Z which depends upon the interactions among the molecules and therefore, from Eqs. 3 and 4, it is the derivative of Z with respect to temperature that gives information about the average interaction energy among the molecules. We refer to this average total interaction energy as the configurational energy E^{CONF} .

To proceed further we need to make some statement about the interactions between the molecules. We will assume that the interaction energy for the assembly of molecules in any particular configuration can be computed as the sum of the interaction energies between all possible pairs of molecules (*i.e.*, the pairwise additivity assumption) so that

$$u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i > j} u(r_{ij}) \quad (7)$$

SQUARE-WELL POTENTIAL

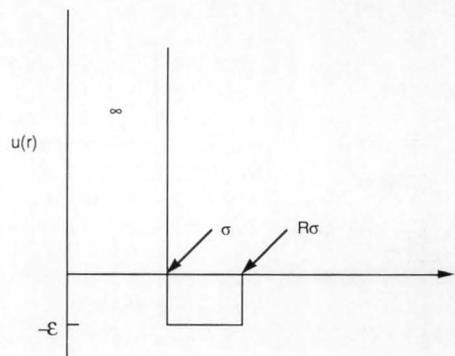


FIGURE 1. The square-well potential with an unpenetrable hard wall at $r = \sigma$.

and for the purpose of illustration here, we will consider two molecules to interact with the square-well potential of Figure 1

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq R\sigma \\ 0 & R\sigma < r \end{cases} \quad (8)$$

though other potential models may be used [2]. This very simplified model does have the essential features of a real interaction; it has a repulsive region ($r < \sigma$), an attractive region ($\sigma \leq r \leq R\sigma$), and vanishes at large separations.

The average total interaction or configurational energy, E^{CONF} , for a fluid of square-well molecules can be gotten from a simple analysis. If $N_c(\rho, T)$ represents the coordination number, that is the average number of molecules in the well of a central molecule at the density ρ and temperature T , then the interaction energy of that molecule with all others is $-N_c(\rho, T)\epsilon$. Since there are N choices for the central molecule, the total interaction energy is

$$E^{\text{CONF}} = \frac{-NN_c(\rho, T)\epsilon}{2} \quad (9)$$

where the factor of 2 accounts for the fact that each interaction is counted twice as each member of the interacting pair is considered to be the central molecule.

To proceed further it is useful to relate the configurational energy to the configuration integral using Eqs. 3 and 5 as follows

$$\ln Z(\rho, T) = \ln Z(\rho, T = \infty) + \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT$$

or

$$\frac{Z(\rho, T)}{V^N} = \frac{V_f^N(\rho)}{V^N} \exp\left(-\frac{N\phi}{2kT}\right) \quad (10)$$

Here, for convenience, we have defined $Z(\rho, T = \infty) = V_f^N(\rho)$, where $Z(\rho, T = \infty)$ is the configurational integral at infinite temperature when only hard core

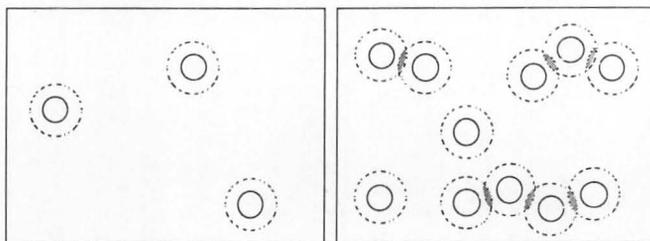


FIGURE 2. Free volume as total volume less the volume around each molecule from which the center of another molecule is excluded: (a) low density; (b) high density including overlap of excluded volume regions.

forces are important; V_f is referred to as the free volume. For the square-well fluid $Z(\rho, T = \infty)$ is the configuration integral for hard spheres since only the infinite repulsive energy, not the finite attractive energy, is important at $T = \infty$. The second term

$$\phi = \frac{-2kT}{N} \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT \quad (11)$$

which for the square-well fluid is

$$\phi = \epsilon T \int_{T=\infty}^T \frac{N_c}{T^2} dT = -\epsilon T \int_{1/T=\infty}^{1/T} N_c d\left(\frac{1}{T}\right) \quad (12)$$

is the free energy change accompanying a change from $T = \infty$ to the temperature of interest, T . We will refer to ϕ as the mean potential. Combining all of the above, we have

$$Q = (q_t q_r q_v q_e)^N Z(N, V, T) = \frac{1}{N!} (q_r q_v q_e)^N \left(q_t \frac{V_f}{V} \exp(-\phi / 2kT) \right)^N = \frac{1}{N!} (q_{\text{int}})^N (q_{\text{ext}})^N \quad (13)$$

where we have grouped the short wavelength rotational and vibrational motions and the electronic energy term into the internal partition function q_{int} , and the long wavelength translational motions into an external partition function q_{ext} . Eq. (13), in which the partition function has been separated into an internal part, a hard-core part (V_f or Z), and an interaction part (ϕ), will be referred to as the generalized van der Waals partition function [3].

In Eq. (13) the internal partition function, q_{int} , is a function of temperature but not volume and as such does not affect the equation of state, though it is important when computing values of the ideal gas energy, entropy, and heat capacity. The hard core part, V_f or Z , will lead to a repulsive or configurational term in the equation of state, while the mean potential ϕ will lead to the interaction or residual term, as will be seen shortly.

Application of Generalized van der Waals Theory to Equations of State

With this background, we can examine the equations of state commonly used by engineers in terms of the assumptions that have been made about the free volume V_f and the mean potential ϕ . For example, though not explicitly stated this way, van der Waals used the literal interpretation of the free volume as the volume accessible to the center of mass of a new molecule of diameter σ when put into a volume V occupied by N similar molecules. As shown in Figure 2a, this results in $V_f = V - N\beta$ with $\beta = 2\pi\sigma^3/3$,

where the excluded volume $N\beta$ is equal to one-half the volume of N spheres of radius σ . (The factor of one-half arises from considering each molecule of the pair to contribute one-half of the excluded volume.) In essence, van der Waals also assumed that the coordination number is a linear function of density and independent of temperature, *i.e.*, $N_c = c\rho$, where c is a constant. We then have that $\phi = -N_c\epsilon = -c\rho\epsilon$, and

$$Z(N, V, T) = (V - N\beta)^N \exp\left(\frac{NN_c\epsilon}{2kT}\right) = \left[(V - N\beta) \exp\left(\frac{c\rho\epsilon}{2kT}\right)\right]^N \quad (14a)$$

from which we obtain

$$P = kT \left(\frac{\partial \ln Q}{\partial V}\right)_T = \frac{NkT}{V - N\beta} + \frac{c\epsilon N^2}{2V^2} = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} \quad (14b)$$

where $\underline{V} = V/(N/N_a)$ is the molar volume, $b = N_a\beta$, $a = -cN_a^2\epsilon/2$ and N_a is Avogadro's number. Consequently, we can now understand the molecular basis for the van der Waals equation of state in terms of the assumptions made about the coordination number and the free volume. Further, we can also relate the

parameters in this equation of state to the intermolecular potential function parameters.

Other equations of state can be analyzed in a similar manner. Table 1 contains the free volume and coordination number models imbedded in some other equations of state. Clearly different assumptions have been made for the free volume and coordination number in each of the equations in the table, and many others are possible. We can now ask which, if any, of the models in Table 1 is correct?

Use of Theory and Computer Simulation to Test Molecular Assumptions

We now need to answer the question raised at the end of the last section. From statistical mechanics we know quite a bit about the free volume; the simple van der Waals model is correct only in one dimension. In three dimensions it underpredicts the free volume at moderate and high densities because of the overlapping of the excluded volume regions shown in Figure 2b. However, the Carnahan-Starling expression [9]

TABLE 1
Free Volume and Coordination Number Approximations
in Several Equations of State

Equation of State		V_f	N_c
• van der Waals	$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$	$V - Nb$	$c\rho$
• Redlich-Kwong [4]	$P = \frac{RT}{\underline{V} - b} - \frac{a/\sqrt{T}}{\underline{V}(\underline{V} + b)}$	$V - Nb$	$\frac{C_1}{\sqrt{T}} \ln(1 + \beta\rho)$
• Redlich-Kwong-Soave [5]	$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)}$	$V - Nb$	$C_2(T) \ln(1 + \beta\rho)$
• Peng-Robinson [6]	$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$	$V - Nb$	$C_3(T) \ln \left[\frac{1 + (1 + \sqrt{2})\beta\rho}{1 + (1 - \sqrt{2})\beta\rho} \right]$
• Widom, <i>et al.</i> [7]	$P = \frac{RT}{\underline{V}} \left[\frac{1 + \eta^2 + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \frac{a(T)}{\underline{V}^2}$	$V \exp \left[\frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$C(T)\rho$
• Alder, <i>et al.</i> [8]	$P = \frac{RT}{\underline{V}} \left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \sum \sum A_{nm} \left(\frac{\epsilon}{kT} \right)^n (\rho\sigma^3)^m$	$V \exp \left[\frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$2 \sum \sum nA_{nm} \left(\frac{\epsilon}{kT} \right)^{n-1} \left(\frac{\rho\sigma^3}{\sqrt{2}} \right)^m$
• Lattice Gas Models	$\frac{PV}{RT} = \left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{[V + V_0 (e^{\epsilon/2kT} - 1)]}$	$V \exp \left[\frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$\frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 [e^{\epsilon/2kT} - 1]}$
	$= \left[\frac{N + 0.77b}{N - 0.42b} \right] - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{V [V + V_0 (e^{\epsilon/2kT} - 1)]}$	$\frac{(V - 0.42Nb)^{2.8333}}{V^{1.8333}}$	$\frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 [e^{\epsilon/2kT} - 1]}$

$$\frac{V_f}{V} = \exp \left[\frac{3(3\eta - 4)}{(1 - \eta)^2} \right] \quad (15)$$

with $\eta = \beta\rho/4$ is in almost exact agreement with computer simulation data for hard spheres, while, as can be seen from Figure 3, the simpler equation of Kim, Lin, and Chao [10]

$$\frac{V_f}{V} = \left(\frac{V - 0.42N\beta}{V} \right)^{2.8333} \quad (16)$$

is in very good agreement with Eq. (15) and has the advantage of still producing cubic equations of state when combined with some coordination number models.

Choosing among the coordination number models is more difficult. At low density the exact result for the square well fluid is

$$\lim_{\rho \rightarrow 0} N_c = \frac{4\pi}{3} \rho \sigma^3 e^{\epsilon/kT} (R^3 - 1) \quad (17)$$

so that at low density the coordination number is a linear function of density, as is predicted by all the models in Table 1, though none has the same temperature dependence. At higher densities, we do not have coordination number information from theory, al-

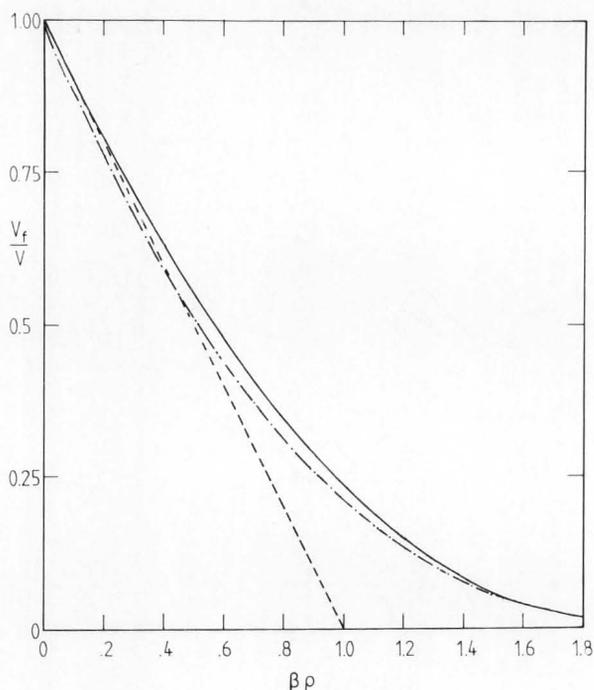


FIGURE 3. Free volume as a function of reduced density: — represents the Carnahan and Starling equation (Eq. 15) and the result of computer simulation; --- is the van der Waals model; and — · — is the Kim-Lin-Chao result (Eq. 16).

**TABLE 2
Absolute Average Deviation in the Compressibility Factor of the Square-Well Fluid Predicted by Various Equations of State**

Equation of State	aad Z
van der Waals	8.380
Peng-Robinson	2.159
Redlich-Kwong	1.332
Alder, <i>et al</i>	0.380
Aim-Nezbeda [13]	0.418
Aim-Nezbeda + 3 body	0.323
Ponce-Renon [14]	0.378
Equation (19)	0.240

though we can obtain such information from computer simulation methods such as Monte Carlo or molecular dynamics [11]. In brief, by considering many different configurations of molecules in a volume element which exist only in the memory of a computer, these simulation methods can be used to obtain average values for all mechanical variables such as energy, pressure, and the coordination number for any chosen intermolecular potential. Coordination number values so obtained for the square-well fluid [12] are plotted in Figure 4a as a function of dimensionless temperature ϵ/kT and density $\rho\sigma^3$. In Figure 4b we have drawn curves for some of the coordination number models of Table 1.

There are a number of things to be seen from these figures. First, unlike the van der Waals assumption, the coordination number is a function of both temperature and density, and the density dependence is nonlinear. Second, the density dependence is smooth, except at the lowest simulation temperature. When we examined the location of the molecules at these conditions we found that the fluid had separated into regions of high density and others of low density; that is, a phase separation had occurred. (Since we did not impose a gravitational field in our simulations, the separation was not of a low density vapor above a high density liquid, but rather of vapor and liquid regions interdispersed as would occur in a phase separation on the space shuttle.) The last and most important observation is that none of the coordination number models in common equations of state are in agreement with the simulation data.

Thus, we find that the equations of state commonly used in chemical engineering are reasonably satisfactory, not because they are fundamentally correct but rather as a result of a cancellation of errors between the free volume (repulsive) and mean potential

(largely attractive) terms. Further, since the expressions used for the mean potential or residual term in the common cubic equations have been empirically chosen to give reasonably accurate results when combined with the van der Waals free volume term, this also means that it would not be very productive to try to develop better equations of state by improving only the free volume term (*i.e.*, replacing the van der Waals term with the Carnahan-Starling or Kim-Lin-Chao expressions) while leaving the mean potential term unchanged, or vice versa. Both need to be improved.

The coordination number behavior found in our simulations (except within the two-phase region) can be described by a simple lattice gas model in which the likelihood of two neighboring sites being occupied is proportional to the Boltzmann factor of $\epsilon/2kT$ which leads to [12]

$$N_c = \frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (18)$$

where $V_0 = N\sigma^3/\sqrt{2}$ is the close-packed volume and N_m is the coordination number at close packing (18 when R in the square-well potential is equal to 1.5). The success of this simple, theoretically-based model in describing the square-well fluid is evident from Figure 4b.

Using Eq. (18) in the generalized van der Waals partition function together with the Carnahan-Star-

ling free volume expression (Eq. 15) leads to the relatively simple equation of state

$$\frac{PV}{RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^2} - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{[V + V_0 (e^{\epsilon/2kT} - 1)]} \quad (19)$$

In Table 2 the results of this and other equations of state for the square-well fluid are compared. We see from that table that the empirical equations (vdW, PR, and RK) are, in fact, not very good for describing this fluid. Better is the twenty-three term Alder *et al.* [6] equation which is a double power series expansion in temperature and density, with parameters that had been fit to their simulation data. The best equation, however, is Eq. (19) which has no adjustable parameters! That is, once the parameters in the potential model have been fixed, there is nothing left to adjust in Eq. (19) to fit the simulation data. The success of this relatively simple, theoretically-based equation over the empirical equations of state is the first example of the advantage of using the generalized van der

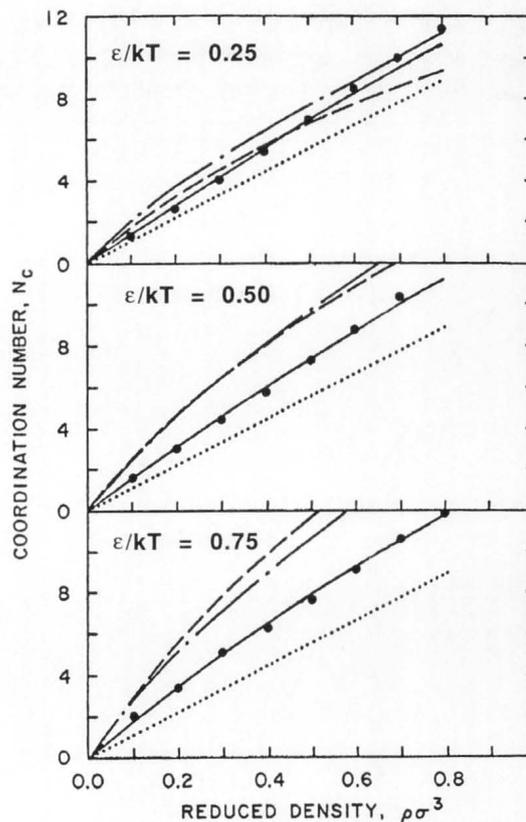
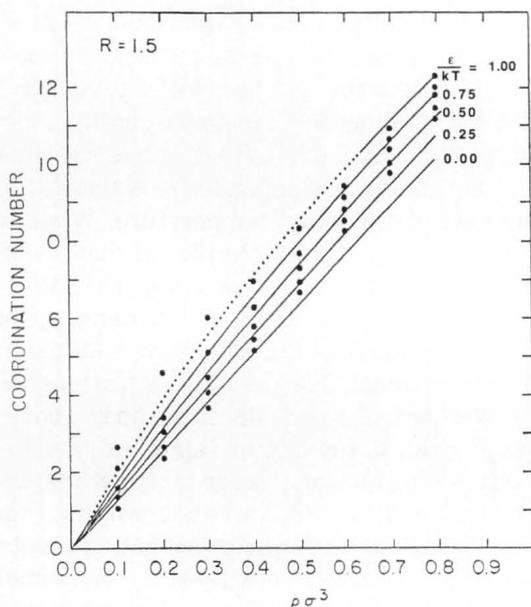


FIGURE 4. Coordination number of the square-well fluid as a function of reduced temperature and density. In all cases the points \cdot are the result of Monte Carlo simulation and the solid lines are the result of Eq. (18).

(a) All simulation results including the two-phase region at the lowest temperature ($\epsilon/kT = 1$); extent of two phase region is indicated by the dotted line;

(b) predictions of various equations including the van der Waals (...), Redlich-Kwong (---) and Peng-Robinson (-·-) models.

Waals theory as a basis for developing thermodynamic models.

Of course engineers are interested in the equation of state for real fluids, not merely models such as the square-well fluid. We show in Figures 5a and 5b how well Eq. (19) does in describing the phase behavior of argon and methane. Of even more concern to chemical engineers is the behavior of more complicated molecules which are not spherical, and chain molecules such as hydrocarbons and polymers.

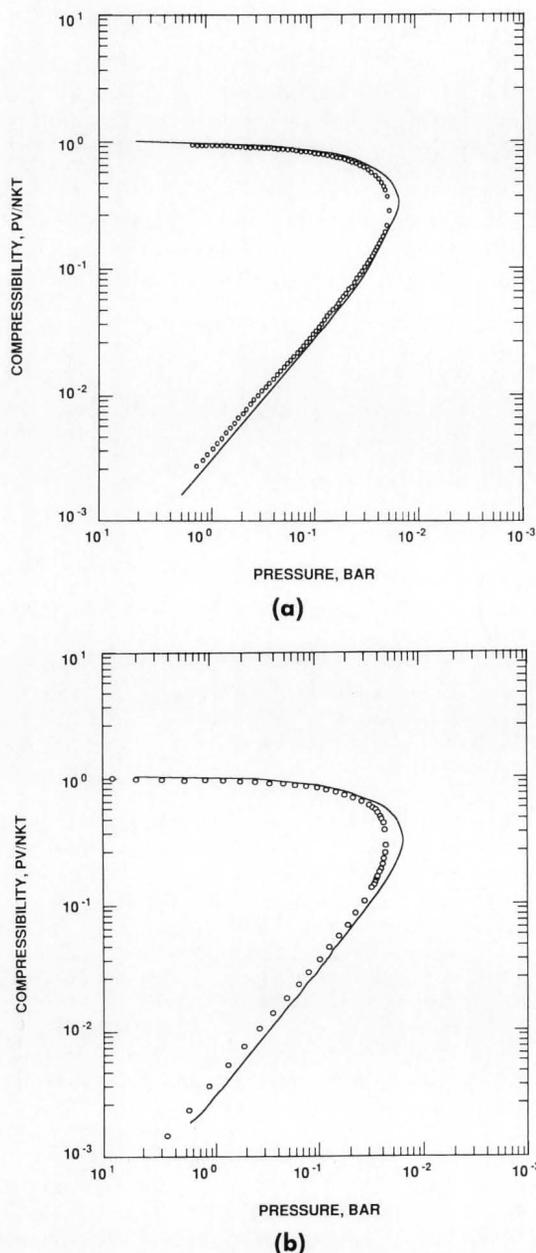


FIGURE 5. The compressibility of (a) argon and (b) methane. The points are experimental data for the two-phase or saturation envelope, and the line results from Eq. (19).

Extension to Chain Molecules

While, in principle, the generalization of the discussion above to nonspherical, and especially to chain molecules, is very difficult, a very clever approximate formulation was presented by Prausnitz and co-workers [15,16] more than a decade ago in the form of the perturbed hard chain theory (PHCT). In brief, this model considers a chain molecule to behave like a chain of m spherical beads, each of which interacts with the square-well potential. A difficulty in evaluating the partition function of a chain molecule is that some of its rotations and vibrations are unaffected by the presence of neighboring beads, and can therefore be treated as in Eq. (5), while others (the long wave length motions) are hindered. Following a suggestion of Prigogine [17], these latter degrees of freedom are assumed to have the same density dependence as the translational degrees of freedom. Letting C be the external degree of freedom parameter (which is unity for atomic fluids) we have

$$\frac{Z(\rho, T)}{V^N} = \left[\frac{V_f}{V} \exp\left(\frac{-\phi}{2kT}\right) \right]^{CN} \quad (20)$$

That is, a chain molecule is considered to have $(C-1)/3$ rotational or vibrational modes which are behaving as 3-dimensional translations, where C is taken to be an adjustable parameter.

The free volume for this fluid of chains is described

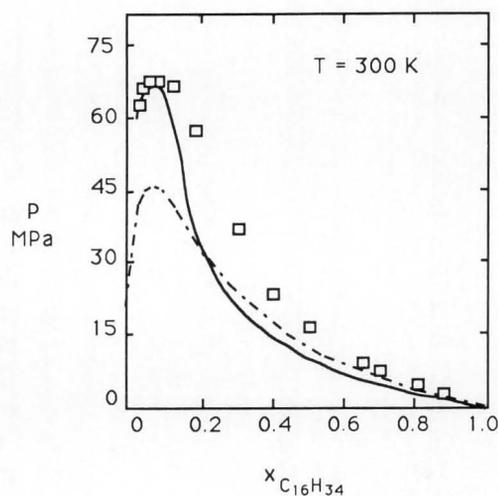


FIGURE 6. Bubble points of mixtures of methane and hexadecane at 300 K. The points are the experimental data of ref. 16, the solid line is the result of the simplified perturbed hard chain theory and the dashed line results from the Soave-Redlich-Kwong equation. The calculations, reported in ref. 16, are predictions in that no adjustable parameters were fit to the experimental data.

by the Canahan-Starling term with $\eta = m\beta\rho/4$; here we will replace the 23-term Alder expansion of Table 1 used in the original PHCT with our new single term expression of Eq. (18). The resulting equation for this simplified perturbed hard chain theory [18] is

$$\frac{PV}{RT} = \frac{1 + (4C - 3)\eta + (3 - 2C)\eta^2 - \eta^3}{(1 - \eta)^3} - \frac{CN_m V_0 (e^{\epsilon/2kT} - 1)}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (21)$$

This relatively simple, three-parameter (ϵ , C , and b or V_0) equation of state has been remarkably successful in describing the properties of pure fluids, especially for large molecules, as shown in reference 18, and even more successful in predicting the properties of nonpolar mixtures of molecules of very different size. This is shown in Figure 6, for the mixture of $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$ [16] where the predictions (no adjusted parameters) of the simplified perturbed hard chain theory are found to be more accurate than those of the Soave-Redlich-Kwong equation [5].

The success of the simplified perturbed hard chain equation is another example of the value of developing thermodynamic models from theory, rather than merely choosing algebraic functions or a power series expansion with parameters fit to experimental data or using power series expansions. Note that if we use the simpler Kim-Lin-Chao expression (Eqn. 16) for the free volume, we obtain an even more simplified perturbed hard chain equation

$$\frac{PV}{RT} = \frac{V + b(1.19C - 0.42)}{V - 0.42b} - \frac{CN_m V_0 (e^{\epsilon/2kT} - 1)}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (22)$$

The properties of this three-parameter cubic equation of state have not yet been thoroughly studied.

CONCLUSIONS

We leave the reader first with some new equations of state to explore. More importantly, however, we also leave him or her with a formulation which allows one to understand the molecular level assumptions in the equations of state now being used and a proper theoretical basis for developing new ones. We have also shown that many of the equations of state now in use do not have a good basis in theory. In fact, each consists of repulsive and interaction (or configurational and residual) terms which are incorrect, but which have been empirically chosen so that when they are combined, reasonable results are obtained. Thus there is much room for improvement and further research.

In the next paper we will consider the extension of the generalized van der Waals partition function to mixtures, which allows us to understand and test the

basis for activity coefficient models and equation of state mixing rules.

ACKNOWLEDGMENTS

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CHEMICAL ENGINEERING IN THE SPECTRUM OF KNOWLEDGE

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For at least two generations, chemical engineers have claimed the ability to “do anything.” Because their education has been so broad, they had both the basic tools and the self-confidence needed to tackle nearly any problem. This versatility has remained even as chemical engineers have shifted their attention from commodity chemicals to biotechnology or materials processing. Unfortunately, undergraduate education has not yet sufficiently changed to meet the new challenges. The prevailing repertoire of homework problems and classroom examples does not adequately reflect the advent of new fields and,



FIGURE 1. *Woman Before a Mirror*, Picasso (1930).

perhaps more serious, has failed to show the growing interconnections between chemical engineering and societal concerns.

The dichotomy between current chemical engineering practice and what is commonly presented to undergraduates may be illustrated by analogy to Picasso's painting, *Woman Before a Mirror* (1930), shown in Figure 1. A woman gazing at herself in a mirror sees a distorted profile rather than an accurate representation of her face and figure. The painting symbolizes her inability or unwillingness to see herself as a complete, integrated whole; she can only see a part of herself. Similarly, by confining illustrative examples in undergraduate chemical engineering to traditional topics, we fail to reflect properly how “real,” contemporary chemical engineering is practiced, and how intimately our branch of knowledge is related to issues of wider scope.

In practice, chemical engineering does not exist in a vacuum. As a field of knowledge, it is closely connected with many other disciplines. Therefore, modern chemical engineering education must transcend the compartmentalization of academic subjects. Students must be shown that what they learn in the classroom relates to the world outside. This relationship is best established through illustrative classroom examples and homework problems.

We present here three such problems, drawn from current societal concerns; these problems link chemical engineering with broad policy issues.

- The depletion of the ozone layer
- A nuclear-winter scenario
- Air pollution by chemical solvents

In these examples, we show the student how thermodynamics, fluid flow, and chemical kinetics can supply *partial* answers to significant social questions. At the same time, these problems serve to expose the student to issues which do not have a unique solution, where competing claims require consideration, and where chemical engineering skills must be integrated

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with insights from other perspectives to arrive at a comprehensive solution.

We do not claim to give unique answers. Rather, the solutions presented should be viewed as best estimates. It is the procedure, rather than the numerical outcome, which we hope to stress.

DEPLETION OF THE OZONE LAYER

The first problem (suggested by Professor H. S. Johnston) analyzes alternative strategies for counteracting the depletion of the stratospheric ozone layer by chloro-fluorinated hydrocarbons (CFCs). The production of CFCs has increased markedly over the last decade, to about one billion kilograms per year [1]. CFCs are used as refrigerants, propellants, and as foaming agents in the production of polystyrene and polyurethane packing materials. Distinguished by their lack of toxicity and chemical stability at sea level, CFCs become photoactive and deplete ozone in the stratosphere at altitudes above fifteen kilometers. Ozone decomposition is dangerous because ozone shields the earth from harmful ultraviolet radiation. Even a ten percent reduction in stratospheric ozone concentration would lead to a significant increase in skin cancer and cause a drastic increase in the number of cataracts. As a result of recent activity by the United Nations, a landmark international treaty has been negotiated which would cut CFC emissions by fifty percent by the year 1999 [2].

Rising CFCs enter the stratosphere at an altitude

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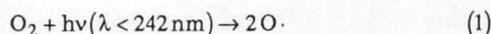


John Prausnitz is a professor of chemical engineering at the University of California, Berkeley. He is a member of both the National Academy of Science and the National Academy of Engineering, and was most recently elected to the American Academy of Arts and Sciences. His interests include the history and philosophy of science.



of approximately eleven kilometers. Below this layer, air temperature drops linearly with height, with a gradient close to the adiabatic limit (9.9°C per km) [3]. An inverted temperature gradient occurs in the stratosphere, however, caused by the absorption of incident solar radiation by oxygen and ozone, especially in the ultraviolet portion of the electromagnetic spectrum. It is this absorption which blocks harmful radiation from reaching the earth's surface.

In the stratosphere, oxygen radicals react with an oxygen molecule forming ozone [1]



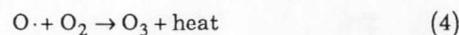
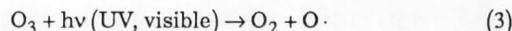
where

h = Planck's constant

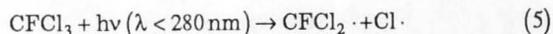
ν = frequency

λ = wavelength

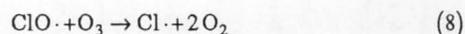
Ozone absorbs ultraviolet radiation and converts it into heat by



The heat released warms the stratospheric air mass so that the temperature rises with height. This rise creates hydrodynamic conditions where free convection is almost completely suppressed, and a stagnant layer of air results. Thus, CFCs travel through this quiescent layer by molecular diffusion alone. At this height, they become photo-active and form chlorine radicals. For example, if the CFC is fluorotrichloromethane



The chlorine radical reacts either directly with ozone or with an oxygen radical [1]. The chlorine radical acts as a reaction intermediate, continuously depleting the stratosphere of ozone:



The result of this reaction chain is a perturbation of the steady-state ozone concentration. While simulation of the complex set of reactions lies beyond the scope of an undergraduate course, it is educationally

useful and relevant to inquire what can be done to return the stratospheric ozone concentration to the level prior to the introduction of man-made chemicals.

Students are told that under present conditions a ten-percent reduction in the steady-state ozone concentration may occur by the year 2000. To counteract this reduction, one alternative might be to augment the ozone production rate artificially to achieve the desired O_3 concentration, that is, to produce ozone on the earth and to send it to the stratosphere.

Students are given data on natural O_3 rates of production from the literature [4]. While these rates vary with height, latitude and season, an average rate of

$$1 \times 10^6 \frac{\text{molecules}}{\text{cm}^3 \text{ sec}}$$

may be used to estimate the energy required to replace the "lost" ozone. As a homework problem, students are asked to calculate the minimum amount of energy required to replenish the ozone layer and to compare that to annual U.S. energy production.

To establish a solution, students must first determine the volume of the stratosphere and then calculate a global production rate. The free energy of formation of ozone gives the approximate minimum energy required.

The calculated global production rate is 1.2×10^7 moles of ozone per second. Since the free energy of formation of ozone is positive

$$\Delta G_f = 39.06 \frac{\text{kcal}}{\text{gmol}} \quad (9)$$

energy must be supplied for the reaction to proceed. The minimum energy needed to augment the O_3 production rate by ten percent would be

$$4.7 \times 10^{11} \frac{\text{cal}}{\text{sec}}$$

Converting this into more conventional units, and comparing it to the annual U.S. production of usable energy, we see that the energy required to increase the ozone production rate is prohibitive [5]. It would require a tripling of our annual energy production:

Energy to replace lost O_3 :

$$5.77 \times 10^{16} \frac{\text{BTU}}{\text{yr}} (57.7 \text{ Quads/yr})$$

1983 U.S. energy production:

$$2.71 \times 10^{16} \frac{\text{BTU}}{\text{yr}} (27.1 \text{ Quads/yr})$$

This simple analysis shows that, if continued unchecked, the problem of ozone depletion could be beyond our direct control well before the year 2000.

To forestall serious and lasting damage to the environment, it is therefore necessary to address the issue of CFC emissions and to consider alternate chemical materials to replace CFCs in current chemical technology.

NUCLEAR WINTER

We now turn to another form of energy release: the detonation of nuclear weapons. Until recently, scientists believed that, however devastating, the effects of nuclear war on global climate due to blast, heat, and radio-activity would be slight. Recent research has brought this conclusion into question [6], noting that detonation of a nuclear arsenal would cause large-scale forest fires which would blow huge quantities of dust into the stratosphere. This dust prevents sunlight from reaching the earth, triggering nuclear winter. As proposed by Professor M. C. Williams, students are asked to estimate the settling time for the stratospheric dust.

The students are told to model the dust as spherical particles ten microns in diameter, forming a dilute dispersion in the stagnant stratospheric layer. They are asked to calculate the settling time from a height of fifty kilometers, and are given a hint that Stokes' law may apply.

In this context, the condition of diluteness implies that the particles have a nearest approach of 100 diameters, or one millimeter. Even as a dilute dispersion, this layer of dust would be quite opaque, since it would be twenty kilometers thick. The incident solar radiation would be completely blocked from reaching the earth's surface. The earth would be engulfed in darkness and there would be no light for photosynthesis.

To apply Stokes' law, we assume a stagnant layer of air; this is an optimistic assumption, since any winds or natural convection would tend to keep particles airborne longer. It may also be argued that large particles scavenge some small dust particles. However, once the large particles settled, it is plausible to assume that there would still be a dilute dispersion of small-diameter dust.

First, the student calculates the terminal velocity, V_t , from a force balance:

$$6 \pi \mu R V_t = \frac{4}{3} \pi R^3 (\rho_s - \rho_{\text{air}}) g \quad (10)$$

where

- g = gravitational constant
- R = particle radius
- V_t = terminal velocity
- μ = viscosity of air
- ρ_s = particle density
- ρ_{air} = density of air

Assuming that $\rho_s \gg \rho_{\text{air}}$, and substituting known val-

ues, we obtain V_t for dust particles ten microns in diameter.

$$V_t \approx \frac{2}{9} \frac{(5 \times 10^{-4} \text{ cm})^2 \left(2.0 \frac{\text{g}}{\text{cm}^3} \right) \left(980 \frac{\text{cm}}{\text{sec}^2} \right)}{2.0 \times 10^{-4} \frac{\text{g}}{\text{cm sec}}} \quad (11)$$

$$V_t \approx 0.55 \frac{\text{cm}}{\text{sec}} \quad (12)$$

The settling time, τ , is the maximum height (50 kilometers) divided by the terminal velocity. For ten-micron spheres, $\tau = 9.09 \times 10^6$ sec., or about 105 days. This magnitude of τ is great enough to demonstrate the possibility of nuclear winter. If the initial dust content in the stratosphere were large enough to cool the earth to winter-like conditions, then at least one harvest, and perhaps two, would be destroyed. More serious, all summertime vegetation would perish, severely affecting wildlife dependent on such vegetation for food.

Settling time τ is inversely related to the square of particle diameter. Thus, τ becomes very large for very small particle diameters. For one-micron spheres, the settling time is 29 years!

This analysis does not consider the effects of nuclear explosions staggered in time. Staggering would delay the settling process considerably by re-injecting the stratosphere with dust. The consequences of nuclear war could cause climatic damage for a period of years.

Similar calculations may also be used to consider the effect on the atmosphere of a large meteorite impact or prolonged volcanic activity. It has been proposed that either of these mechanisms may have caused the extinction of dinosaurs at the Cretaceous-Tertiary boundary [7].

AIR POLLUTION BY CHEMICAL SOLVENTS

For our final example, we examine a common air-pollution problem: smog caused by the evaporation of solvents in lacquers and paints. This example differs from the previous two because it concerns a response to existing legislation rather than evaluating a need for political or social action.

Solvents vaporize and are subject to photochemical reaction with ozone, forming smog. In some geographic areas, local legislation has been enacted for controlling the emission of volatile materials. Los Angeles was the first major metropolitan area to enact such legislation, in conjunction with the Environmental Protection Agency. Los Angeles' Rule 66 limits both the type and amount of solvents which may be used in paint formulations. To meet Rule 66 limitations, typical paint and lacquer solvents have to be reformulated.

This example concerns the cost of choosing a permissible solvent mixture for cellulose nitrate, which is widely used as a lacquer for textiles and furniture. Cellulose nitrate has been used for such applications for over a century, due to its low cost and the durability of nitrocellulose films. For use as a coating material, cellulose nitrate is dissolved in a mixture of solvents. The active (and relatively expensive) solvent is a polar liquid having functional groups containing oxygen: aliphatic esters of acetic acid, ketones, and glycol ethers are the most common solvents. Co-solvents and diluents may also be used to reduce cost. However, these diluents tend to be smog-forming aromatic hydrocarbons. Rule 66 limits both the aggregate volume fraction in the paint mixture of these diluents, as well as individual volume fractions of certain types of diluents. Olefins are limited to five percent by volume, eight-carbon aromatics are limited to eight percent, while toluene, trichlorethane, and branched ketones are also subject to the aggregate limit of twenty volume percent.

The students are introduced to a method of designing solvent blends based on a 2-dimensional map of Gardon's fractional polarity versus solubility parameter, shown in Figure 2. Fractional cohesion paramet-

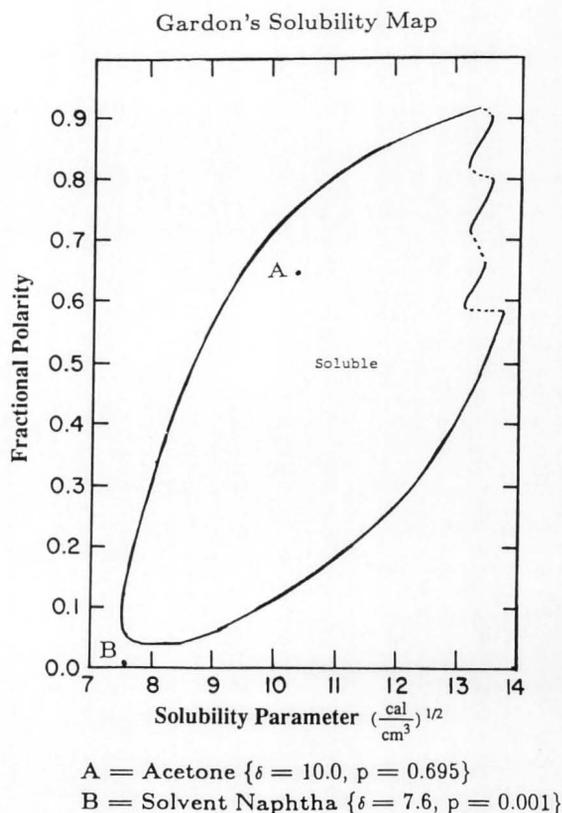


FIGURE 2. A solubility map for cellulose nitrate.

ers are used to represent the solubility behavior of polymer-solvent systems. Gardon has shown that a good solvent matches both the solubility parameter and the fractional polarity of the solute [8, 9].

Students are given solubility data and current prices for various categories of solvents, as listed in Table 1. They are asked to compare the cost of the cheapest acceptable solvent mixture to that of the least expensive mixture which also satisfies Rule 66. Several additional constraints must also be met to achieve an acceptable solvent for cellulose nitrate:

- The volume fraction of the active solvent should be three times that of the co-solvent (this insures solubility).
- High-boiling solvents should not exceed ten percent of the total solvent volume. (Required for proper drying characteristics.)
- The volume fraction of the diluent must not exceed three times that of the slow-evaporating, high-boiling component. (Required for even flow and uniform coating.)
- Proper flow and blush resistance requires that low-boiling active solvents do not exceed twenty percent of the total volume. (Nitrocellulose lacquers tend to precipitate resins if the temperature is lowered by rapidly evaporating solvents.)

Table 2 shows both the original inexpensive solvent mixture and the mixture which satisfies Rule 66.

TABLE 1
Suggested Solvents and Prices (Sept. 1986)

<u>ACTIVE SOLVENTS</u>	PRICE
Low boiling solvents:	
acetone	\$ 0.27/lb
methyl ethyl ketone	\$ 0.235/lb
Medium boiling solvents:	
methyl isobutyl ketone	\$ 0.38/lb
n-butyl acetate	\$ 0.52/lb
iso-butyl acetate	\$ 0.45/lb
High boiling solvents:	
methyl methoxy pentanone	\$ 0.50/lb
methyl amyl acetate	\$ 0.52/lb
 <u>LATENT SOLVENTS</u>	
iso-propyl alcohol	\$ 1.31/gal
n-butyl alcohol	\$ 0.34/lb
ethyl alcohol	\$ 1.81/gal
 <u>HYDROCARBONS</u>	
toluene	\$ 0.73/gal
xylene	\$ 0.80/gal
benzene	\$ 0.85/gal
solvent naphtha	\$ 1.30/gal

The cost of the original solvent mixture is \$1.48/gallon, while that of the environmentally benign, redesigned mixture is fifty percent higher, \$2.21/gallon.

This example shows students that chemical engineers have a role in establishing a cost-effective response which adheres to legislated concerns.

CONCLUSION

The examples presented here have been drawn from environmental issues. While forming a coherent set, they illustrate an important point: chemical engineering science offers useful contributions toward a better understanding of broad topics. Just as we combine kinetics, thermodynamics, and fluid mechanics into an engineering curriculum, so must we integrate chemical engineering with knowledge and concerns from other academic areas. Educational experience is enriched when its relevance is clearly demonstrated to the student.

We plead for integrating chemical engineering education with the world around us. The goal of such integration can be illustrated by looking at another Picasso portrait, *Dora Maar* (1937), in Figure 3. In contrast to the first painting, we now have an integrated portrait of the woman, that is, a representation which shows the subject in many dimensions. The artist combines both full-face and profile images to give

TABLE 2
Cost Comparison Between Solvent Mixtures

Standard Solvent (pre-Rule 66)

Active Solvents	
methyl ethyl ketone	\$ 0.235/lb
methyl isobutyl ketone	\$ 0.38/lb
methyl methoxy pentanone	\$ 0.50/lb
Latent Solvent	
isopropyl alcohol	\$ 1.31/gal
Hydrocarbons	
toluene	\$ 0.73/gal
Total Cost Per Gallon	\$ 1.48

Environmentally Benign Solvent

Active Solvents	
acetone	\$ 0.275/lb
n-butyl acetate	\$ 0.52/lb
methyl amyl acetate	\$ 0.52/lb
Latent Solvent	
ethyl alcohol	\$ 1.81/gal
Hydrocarbons	
includes solvent naphtha	\$ 1.30/gal
Total Cost Per Gallon	\$ 2.21



FIGURE 3. *Dora Maar*, Picasso (1937)

us a more complete description of his subject. By analogy, showing students how to link their technical skills with contemporary problems gives them a more complete image of what chemical engineering is and what it can do. Versatility means to establish connections, to practice a form of "networking" by building bridges between a variety of intellectual domains. By helping our students to become more versatile, they will see chemical engineering as a component in the spectrum of knowledge.

APPENDIX:

Viscosities at High Altitudes

The calculations presented in the preceding problems are meant to be estimates rather than exact values. They incorporate enough precision to allow the examination of possible environmental scenarios. It has been suggested, for example, that the estimates presented in the nuclear winter problem are sensitive to the value of viscosity used in the model. While vis-

cosities are only a function of temperature at low pressures, it may be instructive to analyze the variation of calculated viscosities as a function of height. According to the kinetic theory of gases, as modified by Chapman and Enskog (1906), the viscosity of air depends only on the square root of temperature. Thus, the viscosity varies as the particle falls through warmer regions of air. The range of values is relatively small, however. At the extreme of 200K, the viscosity is 1.30 cp, only 35% lower than the quantity used in the present work.

A second objection concerns the inapplicability of using bulk-viscosity values in regions of very low pressure. A simple calculation shows that the mean free path of a dust particle is less than one diameter up to heights of 20 - 25 kilometers. Even at 30 kilometers, the particle experiences over 2000 collisions per second. It would seem appropriate, given the statistically large number of collisions, to use ordinary viscosities to predict the particle's terminal velocity. The model is here applied to a particle falling from a height of 50 kilometers; if 30 kilometers were substituted for 50, there would be no change in the qualitative conclusion that injection of sufficient dust into the upper stratosphere may portend grave environmental damage.

ACKNOWLEDGEMENTS

We are grateful to Professors H. S. Johnston and M. C. Williams for guidance and helpful suggestions, and to Juan de Pablo for preparing the problem on chemical solvents. Davor Sutija thankfully acknowledges fellowship support from the Fannie and John Hertz Foundation.

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CHEMICAL PROCESSING OF ELECTRONS AND HOLES

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IN THE EARLY twentieth century the four engineering disciplines of chemical, civil, electrical, and mechanical were founded. In a very short period of time, each discipline evolved along relatively independent paths to produce, in part, quite different curricular contents. These differences are best exemplified by chemical and electrical engineering. Chemical engineering has developed into the most general of the founding engineering disciplines and is characterized by an isolated and rigid curriculum with an emphasis on the engineering sciences, particularly those which involve chemical change. Textbooks in our discipline tend to experience longevity, time as a variable is not emphasized, and mature technologies are often graduated (*e.g.*, nuclear engineering, environmental engineering, petroleum engineering, polymer engineering, metallurgical engineering, and biomedical engineering). In contrast, the electrical engineering curriculum is more option oriented, reflecting a historical retention of developed technologies (*e.g.*, power engineering, solid-state electronics, computer architecture, optical engineering). The increased technological content of the curriculum also translates to short textbook lifetimes.

Mother Nature, however, is totally unaware of our somewhat arbitrary partitioning of her behavioral patterns. As a result, the foundations of chemical engineering prepare the student to understand a variety

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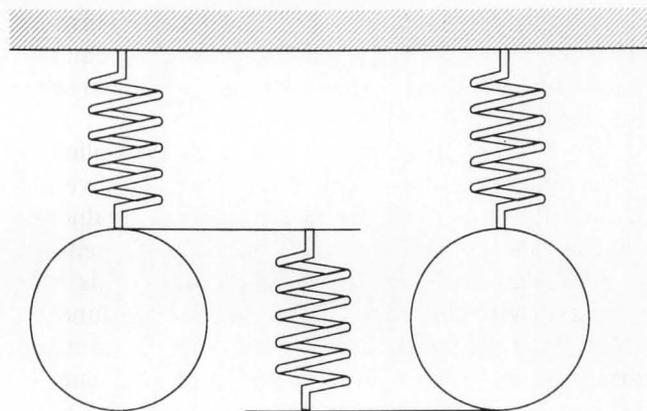


FIGURE 1. Mechanical analogy of electron energy state splitting.

of topics included in other curricula once the terminology and nomenclature are translated. One such example is the operation of solid state electronic devices in an integrated circuit. Presented below is a synopsis of four lectures given in an elective senior-level electronic materials processing course which introduces the student to solid state electronics. The terminology of chemical engineering is used primarily with the equivalent electrical engineering terminology contained in brackets.

ELECTRONS IN SOLIDS

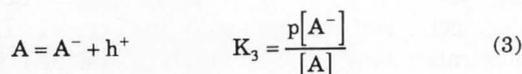
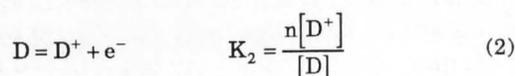
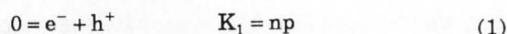
In order to understand the behavior of electrons in the solid state, the student must first appreciate the concept of electron energy states. This is introduced by comparing the free electron, for which all energy values are accessible; the hydrogen atom, for which only discrete states exist; and a large collection of H atoms in the solid state, for which the collection of electron states becomes so closely spaced in energy that we speak of bands of energy states (*e.g.*, 1s band, 2s band). The splitting of electron energy states when atoms are brought together is illustrated by recalling from quantum mechanics the bonding and anti-bonding states between two hydrogen atoms and also by the mechanical analogy shown in Figure 1. This figure illustrates two identical balls suspended from two

By their senior year, students have already received the foundations of chemical engineering. One of the objectives of these lectures is to convince seniors that the digital integrated circuit is nothing more than a chemical processing plant.

identical springs. Neglecting frictional losses, an initial displacement of each uncoupled ball will result in a single natural vibrational frequency. If the two balls are permitted to interact through the third spring shown in this figure, two natural vibrational states are possible for a given displacement of each ball: a low frequency state when each ball is initially displaced in the same direction and a higher frequency state when displaced by the same amount but in opposite directions.

The concept of energy bands is next applied to semiconductors by showing a plot of energy versus the density of electron states for both the conduction and the valence bands, pointing out the gap in energy for which no intrinsic states exist. This plot is then compared with the Fermi-Dirac distribution function which gives the probability of finding an electron at a certain energy value. Integration of the product of the density of states and the probability of a state being occupied for energies above the conduction band minimum gives the number of electrons in the conduction band. These electrons are essentially free because the vast majority of conduction band states are not occupied. A similar integration over unoccupied states in the valence band gives the concentration of holes (empty electron states). The Fermi-Dirac distribution contains a parameter called the Fermi energy that is a function of temperature, pressure, and concentration. The Fermi energy is equivalent to the electrochemical potential of electrons, a quantity that is understandable to chemical engineers.

The process of doping a semiconductor is next described by illustrating the incorporation of B and P in Si. The group III dopant B introduces an electron state with energy level located just above the highest valence band energy, while the group V dopant P introduces a state just below the conduction band minimum energy. A doped semiconductor material under equilibrium conditions is a good example of chemical equilibrium. Consider the following three reactions at equilibrium:



These three chemical reactions involve the chemical species free electron (e^-), free hole (h^+) neutral donor (D), ionized donor (D^+), neutral acceptor (A), and ionized acceptor (A^-) with corresponding equilibrium concentrations of n , p , $[D]$, $[D^+]$, $[A]$, and $[A^-]$. The chemical species O represents an electron combined with a hole in the valence band (normal state) with a large, nearly constant concentration.

Equations (1-3) are further constrained by the condition of charge neutrality

$$p + [D^+] = n + [A^-] \quad (4)$$

Since the electron and hole are highly mobile in the semiconductor, even at room temperature, the material reaches equilibrium very rapidly. These four equations contain six concentration variables. The total donor dose, $N_D = [D^+] + [D]$, and acceptor dose, $N_A = [A^-] + [A]$, however, are usually specified. Solution of Equations (1-4) in terms of N_D and N_A involves finding the roots of a 4th order polynomial in the variable n . If the donor and acceptor ionization energies are small compared to the bandgap energy, E_g , and comparable or smaller than RT , then reactions (2) and (3) are shifted to right and

$$N_D \approx [D^+] \quad N_A \approx [A^-]$$

This simplification leads to a quadratic equation with meaningful root

$$n = \frac{1}{2} \left\{ N_D - N_A + \left[(N_D - N_A)^2 + 4K_1 \right]^{1/2} \right\} \quad (5)$$

This example is easily understood by the senior chemical engineering student and is translated into electrical engineering terminology according to the relationships

$$K_1 = \exp(\Delta S^\circ / R) \exp(-\Delta H^\circ / RT) = N_c N_v \exp(-E_g / RT) = n_i^2 \quad (6)$$

In this equation N_c and N_v are conduction and valence band effective density of states

$$N_i = 2 \left(2\pi m_i^* kT / h^2 \right)^{3/2}$$

and m_i^* = effective mass of an electron or hole

and are related to the entropy of reaction (1). The quantity n_i is the intrinsic carrier concentration and represents the electron or hole concentration in the undoped semiconductor ($n = p$ in the intrinsic material since a hole is created for every electron promoted to the conduction band).

SEMICONDUCTORS UNDER NON-EQUILIBRIUM CONDITIONS

As in operational chemical plants, functioning semiconductor devices operate under non-equilibrium conditions by the action of external influences (*e.g.*, electric field, magnetic field, optical excitation, electron bombardment). The basic equations that describe transport of electrons and holes include species material balances, a statement of species flux in terms of available potential gradients, and Maxwell's equations since these two species are charged. The principles of basic device operation can be illustrated with a simplified set of these equations. Considering only low electric fields and one-dimensional transport in the absence of magnetic fields for an ideal (dilute) solution of electrons and holes, the species material balances [continuity equations] are:

$$\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + R_n \quad (\text{electrons}) \quad (7)$$

and

$$\frac{\partial p}{\partial t} = \frac{-1}{q} \frac{\partial J_p}{\partial x} + R_p \quad (\text{holes}) \quad (8)$$

where

q = magnitude of electric charge

t = time

J_i = flux of positive charge [current density](charge/cm².s)

R_i = net rate of production of species i (number/cm³.s) by homogeneous reaction [carrier recombination, optical excitation, impact ionization]

The charge fluxes [current densities] are given by

$$J_n = q\mu_n n\xi + qD_n \frac{\partial n}{\partial x} \quad (9)$$

and

$$J_p = q\mu_p p\xi - qD_p \frac{\partial p}{\partial x} \quad (10)$$

where

μ_i = mobility of species i (cm²/V.s)

ξ = electric field (V/cm)

D_i = concentration independent diffusion coefficient of species i (cm²/s)

Electrons and holes can migrate in response to both an electric field [drift] and concentration gradient [diffusion]. The most important Maxwell equation to de-

vice physics is the Poisson equation which relates the electric field gradient to the net charge distribution, ρ , according to

$$\frac{\partial \xi}{\partial x} = \frac{\rho}{\epsilon} \quad (11)$$

where

ϵ = semiconductor permittivity (F/cm)

The senior chemical engineering student who has completed courses in transport phenomena and introductory physics can easily understand the significance of these equations; the only new term in the transport equations is migration due to an electric field.

A simple and useful example of these equations is illustrated in Figure 2. A uniformly n-type doped semiconductor slab is illuminated on one side with light (Figure 2a). The photon energy is chosen so that

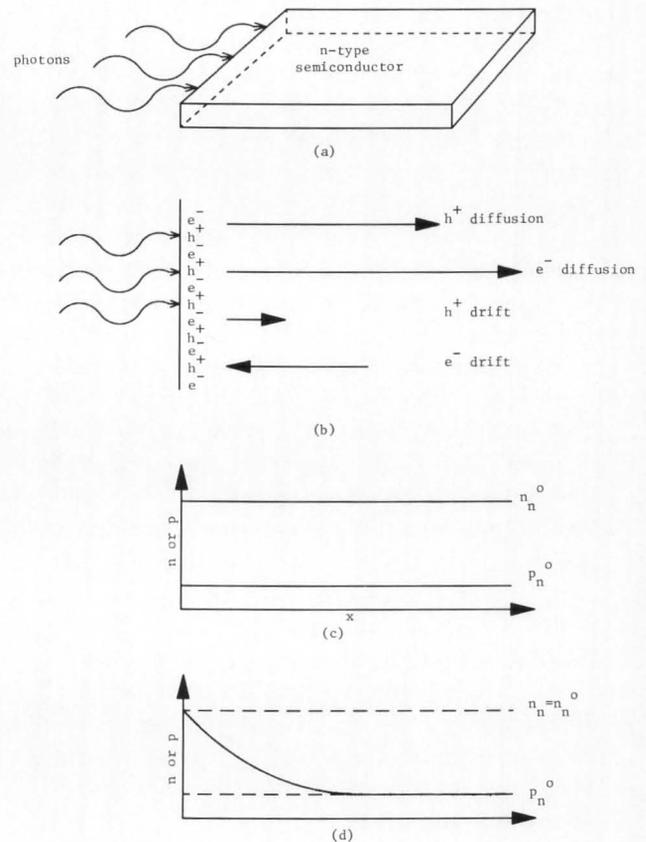


FIGURE 2. Surface absorption of photons in an n-type semiconductor; (a) schematic, (b) sketch of relative magnitude of hole and electron currents due to diffusion and drift, (c) carrier concentration at equilibrium (no illumination), (d) steady state carrier concentration with illumination.

absorption creates electron-hole pairs near the surface only (photon energy greater than the bandgap energy and large absorption coefficient). Before illumination the slab is at equilibrium (Figure 2c) and the concentration of electrons [majority carrier] greatly exceeds the concentration of holes [minority carrier]; for example, Si at room temperature and doped at

$$n = 10^{17} \text{ cm}^{-3} \quad \text{gives} \quad p_n^0 = 2.1 \times 10^3 \text{ cm}^{-3}$$

Upon illumination electron/hole pairs are generated at the surface and are transported into the slab by diffusion. The diffusion coefficient of an electron, however, is normally greater than that for a hole (by a factor of 3 for Si) and a small electric field is established. The direction of the field is such that the electron flux is reduced and the hole flux is enhanced (Figure 2b). Realizing there is no net current in the slab ($J_n = J_p$) and the carrier concentration gradients are nearly identical at a specified position [electroneutrality approximation], it can be shown that the minority carrier transports almost exclusively by diffusion provided the quantity

$$|(\mu_p / \mu_n - 1) p_n / n_n| \ll 1$$

This condition is satisfied if the photon flux is not too large ($p_n \ll n_n$). The same conclusion is not found for the electron [majority carrier], since there is a large population of electrons to respond to the electric field (Figure 2b).

As the carriers diffuse into the slab, they attempt to return to their equilibrium concentrations through homogeneous reaction [recombination]. The steady state minority carrier concentration profile can be determined by solution of Equation (10), with only the diffusion term, and Equation (8):

$$0 = D_p \frac{\partial^2 p_n}{\partial x^2} + R_p \quad (12)$$

The applicable boundary conditions are

$$p_n(x=0) \text{ equal to a constant (due to steady illumination)}$$

and

$$p_n(x = \infty) = p_n^0 \text{ (semi-infinite slab)}$$

An expression for the net rate of generation of holes, R_p , is required. The simplest homogeneous reaction mechanism is direct recombination of a conduction band electron with a valence band hole [band to band recombination]



The rate of production of h^+ by this reversible reaction is

$$R_p = k_1 - k_{-1} n_n p_n \quad (14)$$

The rate of the forward reaction is pseudo-zero order since the concentration of electrons in the valence band and holes in the conduction band are not significantly changed by the reaction at low doping levels. The rate constant k_1 can be eliminated in favor of the known equilibrium constant

$$K_1 = \frac{k_1}{k_{-1}} = n_n^0 p_n^0$$

to give

$$R_p = k_{-1} (n_n^0 p_n^0 - n_n p_n) \approx k_{-1} n_n^0 (p_n^0 - p_n) \quad (15)$$

The rate at which holes disappear by this particular mechanism is thus pseudo-first order since the equilibrium majority carrier concentration is barely disturbed at low illumination. In device physics texts the quantity

$$\frac{1}{k_{-1} n_n^0}$$

is termed the minority carrier lifetime, τ_p . The solution to Equation (12) with the recombination rate given above is:

$$\frac{p_n(x) - p_n^0}{p_n(x=0) - p_n^0} = e^{-x/(D_p \tau_p)^{1/2}} \quad (16)$$

The term $(D_p \tau_p)^{1/2}$ is called the diffusion length for obvious reasons.

In chemical engineering terms, the above problem is simply one of diffusion with first-order homogeneous reaction into a semi-infinite slab from a constant composition source. The simplicity of this example allows students to make the connection between semiconductor physics and their own background in chemical engineering. The problem is also useful since it is the basis for understanding minority carrier injection necessary to describe the operation of p-n junction devices (diode, bipolar transistor). Useful homework problems include analysis of: carrier concentration decay with steady and uniform photoexcitation (batch reactor), transient and steady-state transport of carriers generated by localized illumination with/without an electric field (transient and steady-state dispersion of a line source with plug flow/no flow), recombination rates for materials having mid-gap states (homogeneous catalysis), and surface recombination with uniform and steady illumination (homogeneous and heterogeneous reaction in a semi-infinite stagnant liquid).

p-n JUNCTIONS

The p-n junction is the basic building block of many solid state devices, including the junction diode and bipolar transistor. The lecture material begins with the equilibrium p-n junction and then examines the junction under non-equilibrium conditions with both a positive and a negative applied potential. Finally, the behavior of two p-n junctions (bipolar transistor) under non-equilibrium conditions is described.

When a piece of n-type semiconductor is metallurgically joined to a piece of p-type semiconductor, the hole and highly mobile electron species diffuse in directions of lower chemical potential. Electrons, in excess in the n-type material, will diffuse into the p-type material, where their concentration is extremely small, and holes will diffuse in the opposite direction. If immobile donor and acceptor ions were not present, this process would continue until the electron and hole chemical potentials were the same in both materials. As diffusion occurs, however, a positive space charge density in the n-type material and a negative charge density in the p-type material are "uncovered." The resulting charge distribution produces a diffusion potential [built-in voltage] that opposes further diffusion. When the spatial variation of the chemical potential is just balanced by the variation in electric potential, the joined semiconductors are in equilibrium and the electrochemical potentials [Fermi level] are constant. The discussion of the equilibrium p-n junction continues with a numerical illustration of a Si abrupt junction in which the charge distribution is approximated as a step function [depletion approximation]. The details of this example are given in most device textbooks [1-6] and it invokes our first use of Poisson's equation.

The steady state operation of a p-n junction with an applied external voltage is treated next. The equilibrium junction described above is dynamic, representing a balance between drift and diffusion currents. To understand the operation of the junction with a positive voltage applied to the n-type material [reverse bias], different sources of carriers are examined. If I place myself at the metallurgical junction and count the electrons and holes which cross the junction, I will see three sources of carriers. The first source is homogeneous reaction in the depletion region [generation]. The rate of electron production equals that of hole production as given by Eq. (15) $p_n \ll K_1$ since carriers are assumed to be depleted in this region. The electric field in the depletion zone will sweep an equal number of generated electrons and holes in opposite directions towards material of the same type. Therefore, at the metallurgical plane I can count the

holes coming from the n-type material side of the depletion region and the electrons originating from the p-type material side. The total charge crossing the plane is equal to the rate of hole production in the entire depletion region, or equivalent electron production, times the total width of the depletion region, W

$$J = q k_{-1} n_i^2 W \quad (17)$$

The second source of carriers crossing the junction plane are produced by diffusion of minority carriers to the boundary between the neutral and depletion regions, where they are swept across the depletion zone by the electric field. This problem is similar to the surface illumination problem treated earlier, except that the minority carrier concentration is reduced [depleted] at the boundary instead of elevated to a constant value by the photon absorption. The flux of minority carriers at the edges of the depletion region can be determined from Fick's first law of diffusion and Equation (16) with $p_n(x=0) = 0$. The currents arising from extraction of minority carriers are given by

$$J_p = q p_n^0 (D_p / \tau_p)^{1/2} \quad (18)$$

and

$$J_n = q n_p^0 (D_n / \tau_n)^{1/2} \quad (19)$$

The currents given by Equations (17-19) have the same sign and at equilibrium are just balanced by the third source of carriers; majority carriers from the neutral regions capable of overcoming the built-in potential. Application of a positive voltage, V_R , to the n-type material increases the potential which majority carriers must overcome, thus decreasing the majority carrier diffusion current (proportional to $\exp[qV_R/kT]$). The minority carrier extraction currents given by Equations (18) and (19), however, are independent of voltage while the current due to homogeneous reaction (Equation (17)) actually increases since the depletion region widens with increasing V_R , enlarging the reactor volume. Therefore, with increasing V_R , the majority current rapidly becomes small and the reverse bias current is given by the sum of currents in Equations (16-18). This current is small since the quantities

$$W, \quad p_n^0, \quad \text{and} \quad n_p^0$$

are small.

If the sign of the applied potential is reversed [forward bias], the potential barrier decreases and the number of majority carriers capable of overcoming the decreased potential barrier dramatically increases

(proportional to $\exp[qV_F/kT]$). Development of the current equations for the forward bias condition is similar to the reverse bias case, requiring only the use of Equations (15) and (16). Instead of extracting minority carriers from each side of the depletion region, they are injected, and instead of carrier generation in the depletion region, they recombine ($p_n > p^n$). The p-n junction device is thus shown to operate as a leaky check valve, permitting a large current to flow under forward bias and only a very small current to flow under reverse bias. An interesting homework problem is the analysis of a p-n junction under uniform illumination (solar cell, photodetector).

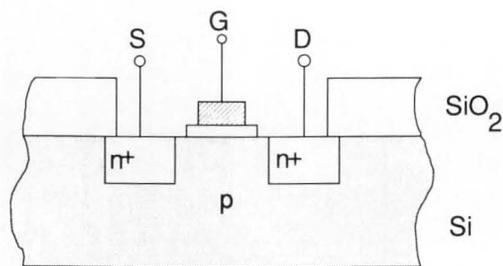
With a background in p-n junction behavior the operation of a p⁺-n-p bipolar (both electrons and holes participate) transistor (*transfer resistor*) is next discussed. This transistor consists of three slabs of semiconductors joined in the series p⁺-n-p and electrical contacts made to each slab. The transistor is biased such that the p⁺ (heavily doped) -n junction is forward biased and the second n-p junction is reverse biased.

The diffusion current at the forward biased p⁺-n junction is largely due to holes because of the heavy doping in the p⁺ slab [hole emitter junction]. These holes then diffuse as a minority species across the n-type slab [base]. If the width of this region is kept small compared to the diffusion length, $(D_p/\tau_p)^{1/2}$, most of the holes reach the depletion region of the reverse biased junction and are swept across this junction [hole collector junction] by the favorable electric field. These holes are now a majority carrier in the p-type slab and appear as the collector current. The electrons that enter the base contact and are extracted from the reverse biased junction either participate in a small diffusion current at the forward biased junction or react homogeneously with holes in the base region. With proper transistor design the collector current can be significantly greater than the base current [amplification], thanks to the "pumping" action of the emitter. The bipolar transistor can act as either a pump [amplification] or an on-off valve [switch].

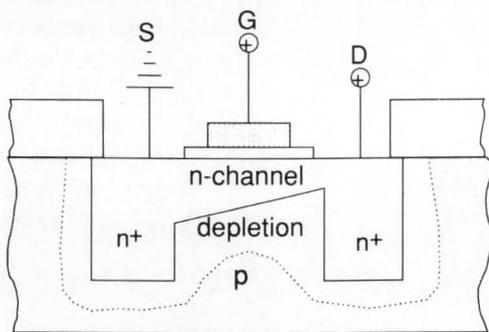
METAL-OXIDE-SEMICONDUCTOR (MOS) JUNCTIONS

Though the bipolar transistor can be made to act as a fast switch, the power requirements can be fairly high. In order to decrease the base current, an insulating oxide layer is sandwiched between the base and the metal contact as illustrated in Figure 3. The MOS transistor is a three-terminal device with a source (S), a gate (G), and a drain (D). In this particular configuration, the source and drain lead wires are connected to "pockets" of n-type material which are isolated by a p-type region. Application of a potential between the drain and source contacts will not produce any significant current since one of the junctions is reverse biased. The application of a positive voltage to the gate contact attracts electrons and repels holes in the semiconductor near the oxide interface, uncovering immobile ions. For a sufficiently large applied gate voltage [threshold voltage], the population of electrons near the interface will exceed that of the holes [inversion], and a continuous n-type channel forms between the source and the gate that permits a current to flow. Of course, the n-type channel and p-type material are separated by a depletion region. A further increase in the applied voltage will increase the n-type channel "pipe" diameter to produce a larger "flow rate." The device can be operated as either an "on-off valve" or "gate valve."

The lecture presentation includes a graphical representation of the band diagrams in the equilibrium, accumulation (negative gate voltage), depletion, and inversion regimes. The operation of a functional



(a)



(b)

FIGURE 3. Metal oxide semiconductor (MOS) transistor; (a) cross section view of the device; (b) schematic of the gate voltage induced n-channel.

capacitor is also analyzed. The p-n junction has a small capacitance since the depletion width changes with applied voltage. Similarly, the MOS structure can be used as a capacitor. Actually, this structure has two capacitors connected in series; a parallel-plate-like capacitor with the oxide as the dielectric material and the accumulation/depletion regions of the semiconductor. The equations which describe the operation of an ideal MOS capacitor are relatively straightforward to develop [1-6] and are presented in the course.

CONCLUDING REMARKS

By their senior year, students have already received the foundations of chemical engineering. One of the objectives of these lectures is to convince seniors that the digital integrated circuit is nothing more than a chemical processing plant. Integrated circuits contain only a few types of devices (resistors, capacitors, transistors, and diodes). These four lec-

tures demonstrate their operation in terms that, for the most part, are understandable by chemical engineers.

A comparison between a large scale chemical processing plant and an integrated circuit is given in Table 1. A typical chemical plant processes hundreds of species, while the integrated circuit processes only two charged species, the electron and the hole. Powerful pumps move fluids through large diameter pipes at high flowrates in a chemical plant, while power requirements, dimensions, and flowrates are orders of magnitude lower in an integrated circuit. A high percentage of the land area at a plant site can be devoted to storage of raw materials and products. In contrast, charge storage in a p-n junction or MOS structure is very limited in an integrated circuit. As discussed above, control valves have analogs in an integrated circuit. Indeed, a diode is used to protect the circuit against excessive voltages, just as a check valve protects against excessive pressures. Relief in the integrated circuit is accomplished by simply dumping the current to ground. The E.P.A., however, does not permit this luxury at a chemical plant site. One of the major difficulties in the simulation of a chemical process is the large number of chemical reactions, often coupled and with unknown rate constants. In the electron-hole plant the reactions involve only recombination and generation, often of reduced order. Due to the size difference in the basic unit operations, the densities are dramatically different, though the costs per unit area are similar. As in chemical plants, the rates of most processes are limited by either reaction or diffusion. The diffusion coefficient and reaction rate constants for electrons and holes are very high. Combining these properties with the small dimensions found in an integrated circuit gives an extremely rapid response time to input parameter changes in the circuit.

TABLE 1
Comparison Between a Chemical Processing Plant and an Integrated Circuit

	Typical Chemical Plant	Typical Integrated Circuit
Raw material source	many but depleting	electrical ground
Number of species	10 ²	2 (electron, hole)
Transport	pipe (10 inch O.D.)	Metal interconnect (10 ⁻⁵ inch O.D.)
Flow rates	10 ³ moles/s	10 ⁻¹¹ moles/s
Pump	10 hp	10 ⁻⁹ hp (bipolar transistor)
Storage	tanks (10 ⁶ moles)	capacitor (10 ⁻¹⁰ moles)
Control	check valve on-off valve gate valve	diode transistor field effect transistor
Reactions	many	recombination/generation
Unit operation density	10 ⁴ /mi ²	10 ¹⁶ /mi ²
Cost	\$10 ⁸ (\$10 ⁹ /mi ²)	\$10 (\$10 ⁹ /mi ²)
Waste disposal	problem	electrical ground
Diffusion coefficient	10 ⁻² - 10 ⁻⁵ cm ² /s	10 - 10 ³ cm ² /s
Reaction rate constant (1st order)	10 ⁶ 1/moles s	10 ¹⁶ 1/moles s

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ARCHIVES OF HEAT TRANSFER: Volume 1*Edited by Naim Afgan**Hemisphere Publishing Corporation, 79 Madison Ave., New York, NY 10016; 466 pages, \$95, (1989)***Reviewed by****Cesar C. Santana and Judit Z. Halasz****State University of Campinas****Campinas, SP, BRAZIL**

The purpose of this book is to present selected contributions to the scientific meetings organized by the International Center for Heat and Mass Transfer between 1968 and 1987. It includes forty papers on fundamentals and applications ranging from boundary layers to high temperature heat exchangers.

According to the editorial preface, the aim of the book is to select contributions representative of the state-of-the-art in each category which had the most impact on each field during a time-span of twenty years. This aim has been achieved. Additionally, a very important and complete list of references is available for each topic.

In the reviewers' opinion, some of the papers had lost their up-to-date importance and new selections could probably have been considered.

Considering the book as a whole, it can serve as a good reference source for several subjects in heat and mass transfer research. □

PHOTOREACTIVE POLYMERS: The Science and Technology of Resists*by Arnost Reiser**John Wiley & Sons, NY; (1989) \$49.95***Reviewed by****David S. Soane****University of California, Berkeley**

Photoreactive Polymers covers a broad range of subjects, including a brief history of resists, negative photoresists, photophysics and photochemistry in solid polymers, photoinitiated polymerization, positive resists based on diazonaphthoquinones, the rudiments of imaging science, deep-UV lithography, electron beam lithography, X-ray and ion beam lithographies, and finally multilayer resists and plasma processing. The presentation of these subjects parallels approximately the chronological appearance of the resists and their associated technologies. Each topic is dealt with in the space of one chapter. Taken as a whole, this book provides a truly comprehensive overview of the science of photoreactive polymers.

Chapter One is unique in that no other monographs seem to have given such a thorough cover-

age of the dawning days of photoreactive polymers. This degree of care and research dedication has permeated throughout the book, and the author has achieved a rather unbiased treatment of all the subject areas of the book. I find that practically all the important issues and major developments have been described.

Chemistry, such as explicit details of chemical reactions, chemical and physical photoevents, proposed mechanisms, and the wide varieties of resists and their structures, is the strong suit of the book. For chemical engineering students who have not been exposed to much organic chemistry, especially photoreactive polymer chemistry, this book is an essential tool. It will undoubtedly save the readers much library time and provide the necessary background for advanced reading of current literature.

Comparatively, this book devotes less to processes that are much more familiar to chemical engineers, *i.e.*, processes that involve basic transport theories and polymer dynamics. Fortunately, these are the exact places where traditional chemical engineers may grasp the concepts most readily and further contribute to the advancement of the science and technology of resists. Even though an in-depth treatment of these areas has not been given, the basics of these processes and related research problems have been prominently identified. Adequate references have also been cited for beginners.

In short, this book is quite useful for chemical engineers who are interested in the field of photoreactive polymers. □

ChE books received

Corrosion: For Students of Science and Engineering, by K. R. Trethewey, J. Chamberlain; John Wiley & Sons, Inc., 1 Wiley Drive., Somerset, NJ 08875-1272 (1988) 382 pages, \$38.95

Fundamentals of Chemistry With Qualitative Analysis, Third Edition, by Brady and Holum; John Wiley & Sons, Inc., 1 Wiley Drive, Somerset, NJ 08875-1272 (1988) 1112+ pages, \$51.50

Concepts in Biochemistry, Third Edition, by William K. Stephenson; John Wiley & Sons, Inc., 1 Wiley Drive, Somerset, NJ 08875-1272 (1988) 229 pages \$19.40

Industrial Energy Management and Utilization, by L. C. Witte, P. S. Schmidt, and D. R. Brown; Hemisphere Publishing Co., 79 Madison Ave., New York, NY 10016; 666 pages (1988) \$40

Kinetic Aspects of Analytical Chemistry, by H. A. Mottola; Wiley-Interscience, 605 Third Ave., New York, NY 10158-0012; 285 pages

New Polymer Technology for Auto Body Exteriors, Schmeal and Purcell (eds); AIChE, 345 East 47 St., New York, NY 10017; 92 pages, \$15 members, \$30 non-members

Heat Transfer in Tube Banks in Crossflow, A. Zukauskas and R. Ulinskas; Hemisphere Publishing Co., 79 Madison Ave., New York, NY 10016-7892; (1988) 199 pages, \$69.50

THERMAL OXIDATION OF SILICON

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FOR NEARLY THIRTY years, silicon has been the semiconductor material of choice for the fabrication of microelectronic devices and integrated circuits (ICs). This situation has arisen and continues today despite the fact that silicon is not the best semiconductor material from the standpoint of device speed (*i.e.*, the electron mobility is not as high as in materials such as gallium arsenide and indium antimonide). However, in order to fabricate solid state devices and ICs in the surface of a semiconductor, it is necessary to greatly reduce the number of unsatisfied orbitals ("dangling bonds" or surface electronic states); otherwise, the electron (or hole) concentration at the semiconductor surface cannot be reproducibly established and controlled. A reduction in "dangling bond" density was demonstrated in the late 1950s by merely exposing the silicon surface to air so that a thin "native oxide" layer formed [1]. Subsequent studies showed that a further reduction could be achieved if intentional oxidation of the silicon surface was performed at high (> 600°C) temperature [2]. Currently, no other semiconductor/insulator solid state structure can achieve the low level of surface or interface states that is obtained in the Si/SiO₂ interface system. Furthermore, other formation methods (such as chemical vapor deposition) for SiO₂ do not yield the excellent interfacial properties that exist in the thermal growth of SiO₂ on Si. Finally, amorphous SiO₂ films thermally grown on Si are unparalleled in their dielectric properties, and can serve as diffusion barriers for common dopants (*e.g.*, boron, phosphorus, arsenic) in silicon IC process technology [3]. These facts have led to the extensive use of thermal SiO₂ in device components, device isolation, and as a passive insulator and a mechanical and chemical protection (passivation) layer. As a result, a large number of silicon oxidation studies have been performed since the early 1960s [4-7]. The investigations have yielded a reasonable description of the kinetics of silicon oxidation. However, a detailed atomistic model is still lacking. Therefore, fundamental research efforts in silicon oxidation continue [8-10].

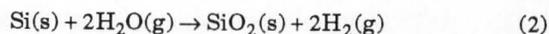
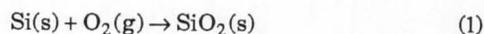
Dennis W. Hess is professor and vice chairman of the chemical engineering department at the University of California, Berkeley. He received his BS in chemistry from Albright College and his MS and PhD in physical chemistry from Lehigh University. Prior to joining the Berkeley faculty in 1977 he was a member of the research staff and manager of process development at Fairchild Semiconductor. His research efforts involve thin film science and technology and rf glow discharge (plasma) processes, as applied to the fabrication of electronic materials and microelectronic devices.



The fabrication of silicon ICs consists of a number of individual steps ("unit operations") that are carefully sequenced to yield an overall process. For instance, since ICs are built up of layers of thin films, various means of forming thin film materials (*e.g.*, chemical vapor deposition, sputtering, evaporation, oxidation) are needed. In addition, precise patterns must be established in these layers (lithography) and selective regions of the silicon doped (solid state diffusion) to control the resistivity level and type (n or p). Of these various process steps, silicon oxidation has probably been the most extensively studied. Furthermore, since the chemistry and chemical engineering principles behind silicon oxidation have been covered by the time a materials and energy balance course has been completed, this "unit operation" can serve as an elementary example of a process step in a non-traditional field.

OXIDATION PROCESS

Silicon is oxidized by exposure to oxygen or water vapor at elevated (> 700°C) temperatures. For these oxidants, the overall oxidation reactions to form amorphous SiO₂ can be written



Oxidant species diffuse through the growing SiO₂ film to the Si/SiO₂ interface where they react with Si. Therefore, Si is consumed and the Si/SiO₂ interface moves into the bulk Si as oxidation proceeds. It can be shown from the densities and molecular weights of Si and SiO₂, that if a thickness of SiO₂, X_o, is formed, 0.45 X_o silicon is consumed.

Thermal oxidation of Si is generally performed in a tubular quartz reactor contained in a resistance heated furnace. Silicon substrates are placed upright in slotted quartz carriers or boats, and pushed into the reactor. The oxide thickness is established by precise control of temperature, oxidant partial pressure, oxidation ambient, and oxidation time.

MODEL FOR SILICON OXIDATION

A general kinetic relationship describing the oxidation of silicon was proposed over twenty years ago [12]. Although the mechanistic details of the oxidation process have not been firmly established, the overall form of the rate expression that results from this model can assimilate data generated by numerous investigators over a wide range of temperature, silicon crystal orientation, oxide thickness, and oxidation ambient. As described in Figure 1, the approach to model formulation for silicon oxidation considers three fluxes that could control oxidation rate [12]. Oxidant (generally O_2 , H_2O , or both) is transported (F_1) to the surface of the growing SiO_2 film and is subsequently incorporated. Since nearly two orders of magnitude change in gas flow rate has no effect on silicon oxidation rate, these steps are considered rapid and thus are not rate limiting under normal conditions. Oxidant species then diffuse across the growing oxide (F_2) to the SiO_2/Si interface, where they react with Si (F_3) to form SiO_2 . The overall oxidation rate can be derived by writing analytical expressions for each flux, F , equating them, since steady state conditions apply, and determining oxide thickness as a function of time. The following formulation of this problem parallels the

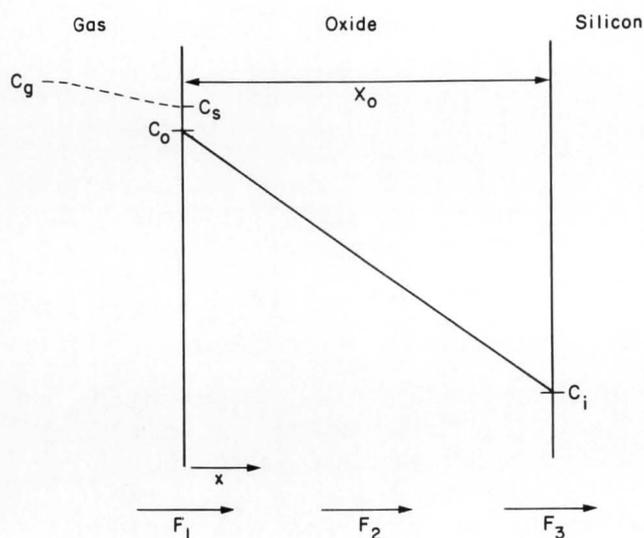


FIGURE 1

... since the ... chemical engineering principles behind silicon oxidation have been covered by the time a materials and energy balance course has been completed, this "unit operation" can serve as an elementary example of a process step in a non-traditional field.

original derivation of an expression for the oxidation rate of silicon [12, 13].

Referring to Figure 1, the gas phase flux F_1 is assumed to be proportional to the difference between the oxidant concentration in the bulk gas (C_g), and that near the oxide surface (C_s). The proportionality constant is defined as the gas phase mass transfer coefficient, h_g

$$F_1 = h_g(C_g - C_s) \quad (3)$$

In order to estimate the concentration of oxidant in the oxide (solid) surface, we assume that Henry's Law holds. Thus

$$C_o = k_{HL}P_s \quad (4)$$

where the concentration of oxidant in the outer surface of the oxide, C_o , is proportional to the partial pressure of the oxidant next to the oxide surface, P_s , and the proportionality constant is Henry's Law constant, k_{HL} . Finally, the oxidant concentration, C^* , that would be in equilibrium with the partial pressure in the bulk gas, P_g , can be written

$$C^* = k_{HL}P_g \quad (5)$$

If ideal gas behavior is assumed, the concentration of oxidant in the bulk gas and near the oxide surface can be written

$$C_g = \frac{P_g}{kT} \quad (6)$$

and

$$C_s = \frac{P_s}{kT} \quad (7)$$

Combining Eqs. (3) to (7),

$$F_1 = h(C^* - C_o) \quad (8)$$

where $h = h_g/(k_{HL}kT)$, and represents a gas phase mass transfer coefficient written in terms of oxidant concentration in the solid. Thus, Eq. (8) defines the flux of oxidant from the gas to the oxide surface.

The flux of oxidant across the growing oxide layer is given by Fick's First Law

$$F_2 = -D_{eff} \frac{dc}{dx} \quad (9)$$

where the effective diffusion coefficient, D_{eff} , is used

because at present it is not clear what *the* diffusing species is (probably O₂, but O₂⁻, O⁻, and O have also been proposed), and x represents the distance into the oxide film from the SiO₂ surface. If quasi-steady state oxidation is assumed (*i.e.*, no accumulation of oxidant in the oxide), F₂ must be the same at any point in the oxide layer, so that dF₂/dx = 0. Therefore, Eq. (9) can be written

$$F_2 = D_{\text{eff}} \left(\frac{C_o - C_i}{X_o} \right) \quad (10)$$

where X_o represents the oxide thickness.

Finally, the flux of oxidant due to the oxidation reaction at the SiO₂/Si interface is assumed to be proportional to the concentration of oxidant at the interface, C_i. The proportionality constant is the surface reaction rate coefficient for oxidation, k_s

$$F_3 = k_s C_i \quad (11)$$

Under steady state conditions, F₁ = F₂ = F₃ = F; therefore, we can develop an expression for the concentration of oxidant reaching the silicon surface. The flux is

$$F_3 = F = \frac{k_s C^*}{1 + \frac{k_s}{h} + \frac{k_s X_o}{D_{\text{eff}}}} \quad (12)$$

The growth rate can now be described if the number of oxidant molecules incorporated into a unit volume of oxide is known. If this quantity is defined by θ, then the oxidation rate is

$$\frac{dX_o}{dt} = \frac{F_3}{\theta} = \frac{k_s C^* / \theta}{1 + \frac{k_s}{h} + \frac{k_s X_o}{D_{\text{eff}}}} \quad (13)$$

This differential equation can be solved if an initial condition is specified. To formulate the initial condition, it is useful to consider X_o consisting of two parts: an initial oxide layer X_i that might have been present on the silicon surface prior to the present oxidation step, and the additional oxide grown during the oxidation cycle. Such an approach makes the model general to multiple oxidations. The initial condition used is therefore X_o = X_i at t = 0.

Solution of Eq. (13) yields the general relationship for the thermal oxidation of silicon

$$X_o^2 + AX_o = B(t + \tau) \quad (14)$$

$$A \equiv 2 D_{\text{eff}} \left(\frac{1}{k_s} + \frac{1}{h} \right) \quad (14a)$$

$$B \equiv 2 D_{\text{eff}} \frac{C^*}{\theta} \quad (14b)$$

$$\tau \equiv \frac{X_i^2 + AX_i}{B} \quad (14c)$$

where τ is a constant (time units) that corrects for the presence of an initial oxide layer, X_i, or for an initial "rapid oxidation rate" in dry oxygen [6-12]. Eq. (14) can also be solved for X_o as a function of oxidation time, t.

$$\frac{X_o}{A/2} = \left(1 + \frac{t + \tau}{A^2/4B} \right)^{1/2} - 1 \quad (15)$$

It is useful to consider this expression in two limiting forms. At relatively long oxidation times or thick oxides, Eq. (15) reduces to

$$X_o^2 \equiv Bt \quad (16)$$

This represents the parabolic oxidation regime wherein the oxidation rate depends upon diffusion of oxidant through the growing oxide; B is the parabolic rate coefficient. For relatively short oxidation times or thin oxides, Eq. (15) becomes

$$X_o \equiv \frac{B}{A}(t + \tau) \quad (17)$$

Eq. (17) describes the linear or surface reaction rate controlled regime; B/A is the linear rate coefficient. As a result, Eq. (14) is often referred to as a linear-parabolic oxidation law.

Using the definitions (14a) and (14b), the semiquantitative dependence of the rate coefficients B and B/A on temperature (through h, k_s, and D_{eff}) and pressure (through C*) can be considered. Furthermore, the activation energy for the linear rate coefficient (B/A) at temperatures of 1000°C and above is ~2.0 eV for both dry O₂ and steam oxidation [1, 6]. This value is approximately equal to the Si-Si bond energy, which is consistent with the linear kinetics

TABLE 1

Oxidation Time (hr)	Oxide Thickness (μm)	
	(100)Si	(111)Si
1	0.0490	0.0700
2	0.0780	0.1050
4	0.1235	0.1540
7	0.1800	0.2120
16	0.2980	0.3390

regime controlling the oxidation by breaking a Si-Si bond on the silicon surface. By comparison, the activation energy for the parabolic rate coefficient B [1, 6] is higher for dry O₂ (~1.2 eV) than for steam (~0.8 eV). These results are consistent with values reported for diffusion of O₂ and H₂O through fused silica and suggest that the rate controlling step in the parabolic oxidation regime is diffusion of oxidant through the oxide film.

Although the above model is extremely useful for most oxidation regimes, it appears inadequate to describe the initial "rapid" oxidation rate observed in dry O₂ and the curvature of Arrhenius plots at temperatures below 1000°C. As a result, new models are being formulated, and additional experimental data are being generated [7-11].

EXAMPLE

A simple example can be used as a homework problem or can be incorporated into lectures or discussion sections to demonstrate the use of the general relationship for the thermal oxidation of silicon (Eq. 14).

Silicon wafers are thermally oxidized in dry oxygen at 1000°C, and the kinetic data shown in Table 1 are obtained by measuring the SiO₂ thickness grown on (100) and (111) crystal orientations of silicon.

- From the data in Table 1, determine the parabolic (B) and linear (B/A) rate constants via a graphical method for (100) and (111) silicon
- Discuss the comparison of the rate constants for these two orientations of silicon.

Solution

- Dividing Eq. (14) by X_o and rearranging yields

$$X_o = B \left(\frac{t + \tau}{X_o} \right) - A \quad (18)$$

This is the equation of a straight line; thus if X_o is plotted versus (t + τ)/X_o, the slope of the line is B and the intercept is -A. The parabolic (B) and linear (B/A) rate constants can therefore be determined by linear regression analysis. First, however, we need a value for τ, a correction factor for the initial "rapid oxidation rate" in dry O₂. Evaluation of τ is performed by extrapolating a plot of X_o versus t to zero oxide thickness. For these data, the extrapolation crosses the time axis at ~ -0.35 hr, so that τ is defined as 0.35 hr (this value can be given to the student as a constant).

Linear regression analysis of the oxidation rate data in the form of Eq. (18) gives

For (100) orientation

$$A = 0.196 \mu\text{m}, \quad B = 9.07 \times 10^{-3} \mu\text{m}^2/\text{hr}$$

so that

$$B = 0.0091 \mu\text{m}^2/\text{hr} \quad \text{and} \quad B/A = 0.0463 \mu\text{m}/\text{hr}$$

For (111) orientation

$$A = 0.105 \mu\text{m}, \quad B = 9.19 \times 10^{-3} \mu\text{m}^2/\text{hr}$$

so that

$$B = 0.0092 \mu\text{m}^2/\text{hr} \quad \text{and} \quad B/A = 0.0874 \mu\text{m}/\text{hr}$$

b. The two orientations of Si have essentially the same parabolic rate constant. Since B relates to the diffusion of oxidant through the amorphous SiO₂ layer, there should be no effect of B on silicon surface orientation provided that the oxide is the same in both cases.

The linear rate constant is larger for (111) than for (100) orientation. This observation correlates with the higher packing density of the Si (111) plane. Since the linear rate constant appears to be controlled by the reaction of oxidant with the Si surface, such differences are consistent with the atom density in the different planes.

SUMMARY

Thermal oxidation of silicon is an important step in the manufacture of silicon devices and integrated circuits. A general relationship describing the thermal oxidation process can be derived easily by considering fundamental chemical engineering principles. This expression can be used as an example to demonstrate the reduction of kinetic data obtained for silicon oxidation in undergraduate core chemical engineering courses.

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WORKING IN THE INTEGRATED CIRCUIT INDUSTRY

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THE INTENT OF THIS article is to introduce you to the work environment and the culture in the IC (integrated circuit) industry. This introduction to the work environment is necessary to adequately prepare you for making a career choice. In each of the paragraphs below, a statement of fact about the industry will be given and then discussed in terms of how it creates a culture or a unique work environment. A design process typical of the industry will be contrasted with chemical engineering design so that you can grasp the level of sophistication of the manufacturing environment. Lastly, the advantages of working in this industry will be highlighted.

In the IC industry, the product has an electrical engineering application, and thus the management and the majority of the employees are electrical engineers. Because electrical properties (film resistivity, electromigration properties, contact resistance, leakage current, dielectric constant, breakdown voltage, *etc.*) of materials directly relate to the material properties (grain size, contamination, stress, adhesion, alloy type, *etc.*), the second most frequently encountered employee is a material scientist. Only rarely does one find a chemical engineer in the IC industry. This distribution of employees results in a culture which considers process development and reactor design as extraneous to the primary function of the company. The most enlightened form of the industry recognizes that reactor conditions during film deposition contribute to the film properties, and the cause and effect relationships are correlated through orthogonal matrices. Because the average material scientist or

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electrical engineer has very little, if any, education in heat, mass, or momentum transport, in gas-solid kinetics or in reactor design, the whole problem of process design takes on the mystique of being a black art. A properly-educated chemical engineer in this environment can become an instant hero, if the stage is properly set, by applying his/her knowledge of reactor design to the manufacturing processes. But beware—any great opportunity comes with an equally great challenge.

The product which is being manufactured is not just one chemical which has been modified through a series of processes. It is a layered structure resulting from at least 100 sequential operations, each one with the potential to influence an earlier layer or a later layer. You will be working with 50-100 other engineers, each responsible for a different set of steps in the process of building an integrated circuit. Most of these people will be trained in chip design and failure analysis, but will generally be undereducated in process design. Compound this with the fact that the product you make is not visible to the naked eye. The best analogy is of one hundred blindfolded sculptors trying to recreate Michelangelo's statue of David while it sits on a rotating table. Success is determined by an artist at the end of the process deciding if it looks like the original. Failure analysis is a process of trying to determine which piece was sculpted poorly many layers and many rotations ago.

Because the chip yield is the only true measure of the viability of a new process, all proposed processes must be demonstrated upon a real product. In a development facility there may be only ten lots (25 wafers

The product . . . is not just one chemical which has been modified through a series of processes. It is a layered structure resulting from at least 100 sequential operations, each one with the potential to influence an earlier layer or a later layer.

each) every eight weeks that are available to all 100 process engineers for development purposes. This means that any one engineer may receive only two to five patterned test wafers every two months on which to test his/her ideas. Because process interactions are so strong, the best process developed on unpatterned wafers may yield horribly on the real patterned test wafers. The best process engineers strive hard to understand the interactions within their own process, whether it be an etch step, a deposition step, or photolithography, before receiving those very few and very precious test wafers. The clever process engineer also gets his/her hands dirty and learns the details of all the steps in creating films which will be contacting his or her film. This is a job best suited to experimentalists, and if you went through school attached only to a computer, you will find your work overwhelming. You better know when vacuum pump oil can contaminate wafers and how to run a scanning electron microscope.

An interesting result of the test wafer starved environment is an underground black market for test wafers within any facility. Imagine a product market in the 1200s where the people bartered their goods one at a time, and after a full day on the town square they had enough to live on for the next day or two. Any IC industry is a culture of 50-100 individuals networking furiously among themselves to obtain a few test wafers so that they can get their own jobs done and become heroes. Some individuals may operate through intimidation, others through bribing their friends with weekends on a family catamaran. Students simply won't need their speech classes or formal presentation skills—a much better background is in interpersonal relationships and in the art of negotiation or coercion 101.

Another interesting result from 50-100 people developing one invisible product with very strong process interactions is the "hot potato" syndrome. Imagine the case of shorts between metal lines on the chip's interconnect. Let's investigate where this failure mode might originate. It could be that conductive contamination was left during processing prior to metal deposition; or the metal itself may have an improper composition, making the etch difficult; or the photolithography process could be failing, leaving photoresist where it should not be; or the etch reactor may have changed its performance and is no longer clearing out the metal between the lines. These are the obvious possibilities. It could also be that the engineer in charge of oxide deposition (several layers ago) changed the process slightly, creating steeper sidewalls, and thus the etch can no longer clear metal

from under the new geometries. Who owns the problem? Clearly, the lab manager owns the problem, just like he/she owns all of the other problems in the clean room. It is too often the case that the lab manager is faced with a group of engineers, each claiming the problem belongs to another process group—thus the "hot potato" syndrome.

IC fabrication lines are very expensive to build and operate. Therefore, companies are forced to develop new processes on equipment producing the current product. The consequences of this constraint are profound. Hardware modifications are nearly always forbidden because they may interfere with current product yield. Remember that the hardware/process interactions are so poorly understood that any

Not only is there the obvious problem of making an inadequate tool (today's batch reactor) to create a new product (tomorrow's chip set), but there is the added problem of getting time on the production machines to run tests.

hardware change is viewed as potentially dangerous. The chip manufacturers do not consider themselves in the business of inventing processes and would rather work with a low-yielding piece of hardware than to modify it to optimize its performance. Imagine a sculptor making statues out of soap when the management decides to make statues out of metal. The sculptor now has to figure out how to sculpt metal with the same old tools because the production of soap statues must not be interrupted.

Not only is there the obvious problem of making an inadequate tool (today's batch reactor) to create a new product (tomorrow's chip set), but there is the added problem of getting time on the production machines to run tests. Today's product represents today's profit, and therefore production wafers take precedence over test wafers. Engineers have to find time for development without interfering with production. This creates another interesting situation: the art of bribing the machine operator off of the reactor for a while. (Once a chip set goes to production, it is handled almost exclusively by operators, not engineers.) Common tactics range from encouraging the operator to take long coffee breaks to designating the machine as "down," implying that it has hardware problems and is not suitable for production runs. Either method allows the engineer to process a batch of test wafers, and he/she works diligently trying to make the old tools fit the new need. Sometimes they are successful, but usually the IC industry is forced

to wait for new tools to be developed by equipment vendors.

Because the chip facilities view process development as the job of the equipment vendor, and the equipment vendor has no idea what the next generation of chips will look like, there exists a mismatch between the time a process is needed (now) and when the vendor can make a machine to fulfill this need (two years from now). The equipment companies are expected to produce the very best IC batch reactors with almost no capital investment from the IC industries. Not only is there no monetary support, but the IC fabrication engineers generally distrust equipment vendors because the last generation of batch reactors did not come with an adequate recipe for processing wafers. The vendors cannot find that optimum recipe because they do not have access to patterned wafers, which are the ultimate test of a process. In fact the IC fabs are very reluctant to help the vendor create the process because they don't want any information to leak out about the next generation of chips. As a consequence of this nearly adversarial vendor-IC fabrication facility relationship, the process becomes an orphan. The IC chip fabrication engineer is then faced with spending \$1.5 million on a piece of hardware (a batch reactor useful for one step of the 100-step process) with only a vague idea of the best operating conditions for his/her chip set.

There is usually a honeymoon period, albeit a short one, where the new machine belongs to a development engineer and not yet to production. In this window of one to three months, the development engineer is given *carte blanche* on the machine and some priority on obtaining test wafers. This is where six to eight years of chemical engineering buys leverage. The advantage is best understood by contrasting the textbook chemical engineering methods of process development with the methods currently used in the industry.

For the purpose of discussion, film properties and device behavior are termed "level 1" variables in this document, for they are the important surface properties dependent upon the local chemical environment present during growth (Figure 1). These level 1 properties are most directly related to the surface composition during growth, which in most cases is unmeasurable and only roughly predictable. The only exception to this is the measurement of surface composition during growth with Raman spectroscopy or *in situ* low energy electron spectroscopy, a technique requiring vacuum capabilities in the 10^{-10} torr range. The measurable variables which most directly affect film properties are the local gas composition, the wafer

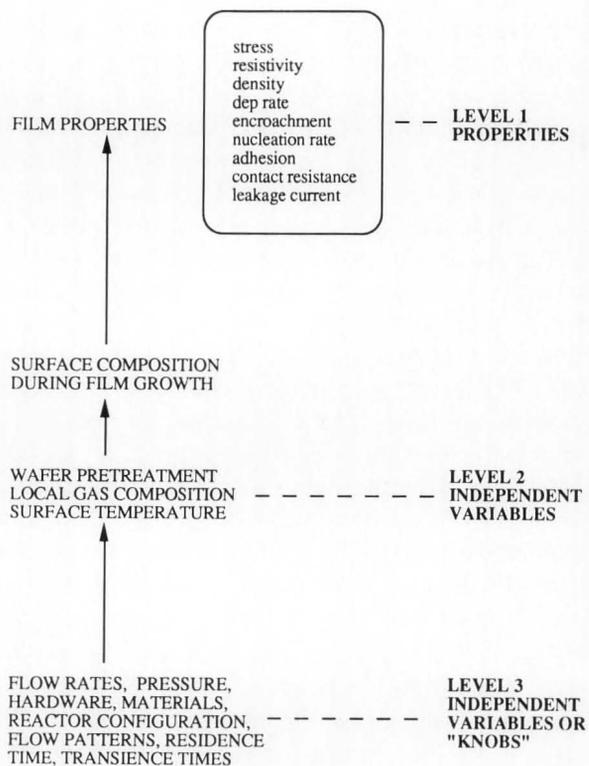


FIGURE 1. Variable chart

pretreatment, and the surface temperature—the local gas composition being that within a few mean free paths of the wafer surface. These variables are referred to as independent level 2 variables, for they control the level 1 dependent variables. Ultimately the level 2 variables are determined by the gas flow rates, pressure, reactor hardware, species residence times, reactor materials, transience times in the reactor, heating method, and other "reactor knobs." It has been the tradition in the IC industry to turn the level 3 reactor knobs in an orthogonal manner in order to determine the best conditions for running a piece of hardware. The level 1 properties are related to level 3 knobs by statistical correlations without any fundamental understanding of the processes involved. It is a perfect tool for engineers with an educational mismatch to the product they are expected to build. It is, for instance, how I would go about building a strong bridge since I am not trained in stress analysis.

This method of orthogonal experimental design is very well suited to processes where nothing is known about the behavior of the process and the hardware. Plasma processes, for instance, are so complex that they have traditionally qualified for this category. For processes which are dominated by chemical reactions with known kinetics (classical chemical vapor deposition), this method is not optimal. With a few heat and

mass balances, calculations of dimensionless groups, and an understanding of kinetics a skillful chemical engineer can often solve in an afternoon what a process engineer has been statistically correlating for man-months.

For demonstration purposes, let us contrast chemical engineering reactor design to orthogonal matrix design for a semi-batch reactor with no heat and mass transfer limitations (the most primitive case). As a chemical engineer, you are aware that the film properties are dominated by the local reactant concentrations and temperature. Any reactor design text will give the appropriate design equation, depending upon the Peclet number, for the reactor. Knowing the design equation, the kinetics, and the stoichiometry, the growth rate is perfectly predictable. Level 1 properties can then be related to the actual deposition environment given by the calculated level 2 variables.

If the kinetics are unknown, a chemical engineer is aware that the variables critical to film deposition are the local concentrations and surface temperatures. At this point the engineer can choose to determine the basic kinetics and create a predictive model, or more realistically he/she will be in an industrial situation that does not allow fundamental studies and will design an experiment based upon orthogonal matrices. The key in being efficient is in realizing that the engineering staff will have a more fundamental understanding of which variables actually control material properties if the matrix is built around level 2 variables (concentrations) rather than level 3 knobs (flow rates). This approach differs dramatically from the blind approach of most process engineers in the IC industry today.

Figure 2 is a plot of the operating conditions for performing an orthogonal matrix in flow rate space, the industry standard, for reactants A, B, and C. Fig-

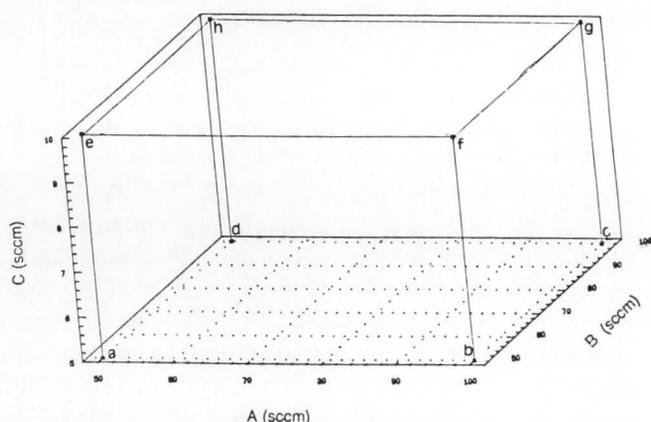


FIGURE 2. Orthogonal matrix in flowrate space for reactants A, B, and C.

ure 3 shows those same operating points plotted in concentration space when given a fixed surface area for deposition. As can be seen, in concentration space (the only one that really matters) the matrix is far from orthogonal. Interpretation of the experiments in terms of fundamentals is all but impossible. In fact it is no mystery at all that the industry has so much difficulty in converging on optimal processes.

The US IC industry is battling for survival against foreign competition. If it is to survive, it will have to develop a new strategy. We are already witnessing cooperation among competing industries and vendors in the form of Sematech. To really become an international leader, the US industry will have to launch itself out of the mode of empirical correlations and base its manufacturing processes upon science. This is the very heart of chemical engineering, and chemical engineering should therefore become the very center of the future of the IC industry. It is a waste of time to have fine circuit designers attempting to derive heat transfer relationships given in junior level chemical engineering textbooks, or attempting to define kinetics based upon pseudo-orthogonal matrices. It is our responsibility to use our knowledge and our tools to solve these problems efficiently and scientifically.

For chemical engineers, the IC industry is a gold mine of opportunity. Compared with the petroleum industry, the technical problems are easy. The processes operate at low pressure and moderate temperatures. Reactors often behave as mixed flow reactors because the diffusivities are so large. Pressure drops never exist. Processes are just as likely to be kinetically limited as mass transfer is limited. The reactions are often inorganic. One is usually limited to two

Continued on page 60.

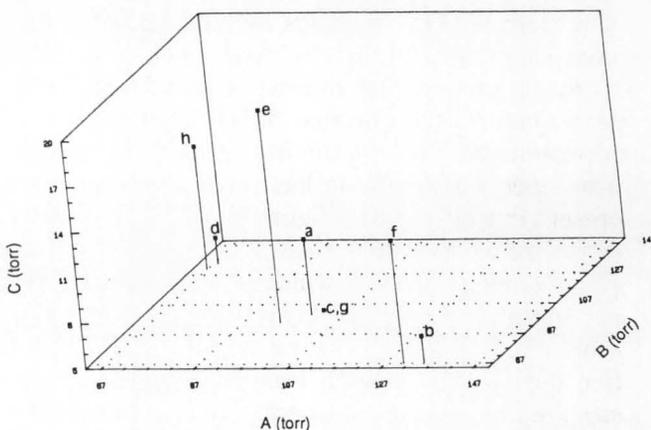


FIGURE 3. Operating points in Figure 2 plotted in partial pressure space, which is identical to concentration space when divided by the constant RT.

CHEMICAL VAPOR DEPOSITION EPITAXY ON PATTERNLESS AND PATTERNED SUBSTRATES

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THE ELECTRONIC MATERIALS processing curriculum at Purdue consists primarily of a one-semester course. The objective of this course is to provide chemical engineering students with the basic principles and practical aspects of the most advanced state of electronics processing. The main emphasis of the course is on fundamental processes especially useful for Very Large Scale Integration (VLSI) schemes [1].

About five weeks are devoted to epitaxy, which is a process by which material is deposited onto a crystalline substrate or seed, and the crystalline configuration is maintained. Two and one-half weeks are devoted to Vapor Phase Epitaxy (VPE) on patternless substrates, one week to VPE on patterned substrates typically known as Selective Epitaxial Growth (SEG), one week to doping profiles in epitaxially grown thin films, and one-half week to other kinds of epitaxy (*e.g.*, Molecular Beam Epitaxy (MBE), Plasma Assisted Chemical Vapor Deposition (PACVD)). The purpose of this paper is to focus on Chemical Vapor Deposition (CVD) epitaxy on patternless and patterned substrates in the manner in which it has been developed in our course over the past five years.

Journal articles play a very important role in many educational aspects of the CVD epitaxy on patternless and patterned substrates. A list of such journal articles typically used in class is presented at the end of this paper [7-23]. The rapid developments in the field preclude adequate discussion in a book, and in general there is very little discussion in books, if any, about CVD on patterned substrates.

First, the process of epitaxy is introduced and

About five weeks are devoted to epitaxy, which is a process by which material is deposited onto a crystalline substrate or seed, and the crystalline configuration is maintained.

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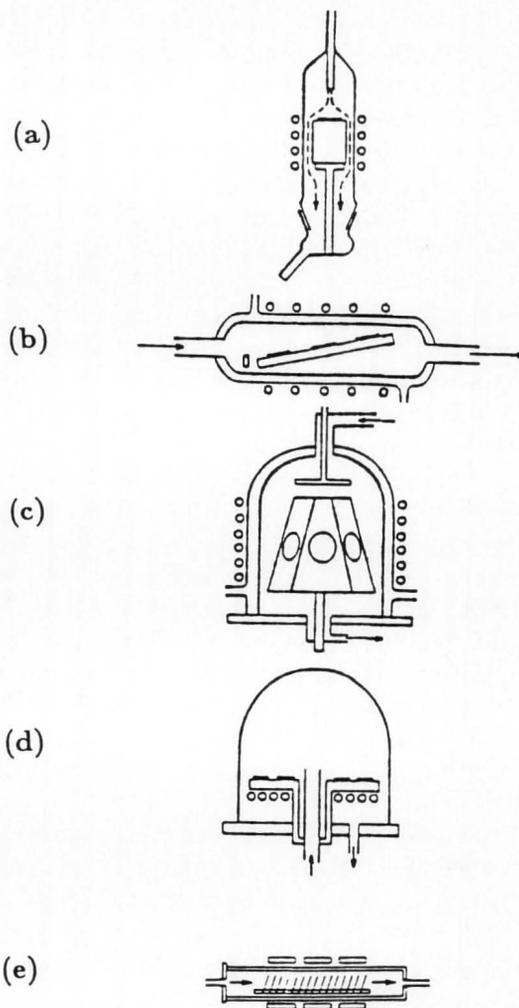


FIGURE 1. Schematic representation of (a) vertical, (b) horizontal, (c) barrel, (d) pancake, and (e) low pressure chemical vapor deposition epitaxial reactors.

classified into types (*e.g.*, VPE, MBE, PACVD, Solid Phase Epitaxy (SPE)) [2, 3, 6], and important features of epitaxy are briefly discussed. At the same time, some potential problems of epitaxy are briefly presented. Such problems with VPE, for example, can be autodoping, pattern shift, and pattern washout [2-4, 6].

CHEMICAL VAPOR DEPOSITION REACTORS

An introduction to different basic types of reactors

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used in the epitaxial thin film growth of electronic materials forms the first stage of our course. For VPE, five types of CVD reactors are discussed [2, 3, 6-11, 22] along with some recent reactor designs such as the Vapor Levitation Epitaxial (VLE) system [24] and the Epsilon One system [25]. They are the vertical (typically used in Metal Organic Chemical Vapor Deposition (MOCVD)), the horizontal, the barrel, the pancake, and the Low Pressure Chemical Vapor Deposition (LPCVD) reactors (see Figure 1). The LPCVD reactor has been increasingly used in reduced pressure epitaxy since problems associated with VPE, such as pattern shift, washout, and autodoping, have been remedied to a significant degree with low pressure epitaxy [11, 13, 14, 19].

The Epsilon One system is a one-wafer horizontal reactor with very low contact times between gas mixtures and substrates [25]. VLE uses growth vapors and carrier gas not only to provide reactants to a wafer surface but also to lift the wafer and keep it suspended above the growth apparatus during the epitaxial growth process [24]. PACVD reactor systems are also briefly presented. Throughout this section the emphasis is on discussing main features and potential advantages and disadvantages of the various systems used in electronic materials CVD.

CHEMICAL REACTIONS IN EPITAXY

Sources typically used in silicon (Si) or gallium arsenide (GaAs) epitaxy are presented next. Si and GaAs are the base semiconducting materials studied in the Purdue course on microelectronics processing, other materials being conceptually presented as rather simple extensions of these two base ones. Mass spectrometry and other gas phase analytical tools along with *in situ* substrate surface analysis techniques are shown to provide a means of understanding some of the chemical reactions that may occur during epitaxy. On the other hand, important chemical reactions during the pretreatment and preparation of a substrate surface are also discussed in detail. One example from silicon epitaxy is the process of removing all native oxide just before an epitaxial growth

step since device quality epitaxial thin film is, perhaps, the main objective of any epitaxial process.

In the context of SEG, only silicon epitaxy on patterned substrates is covered (see Figure 2). There has to be a higher degree of supersaturation for the nucleation of silicon on SiO_2 and Si_3N_4 as compared to that for nucleation on silicon surfaces. Thus, by keeping the supersaturation below a critical value it is possible to selectively deposit silicon on Si substrates masked by either silicon nitride or silicon oxide (*e.g.*, Figure 2). Crystal growth theories as discussed, for example, by Bennema and van Leeuwen [26] explain the initiation of growth by the adsorption of silicon at the growth interface. Adsorbed atoms form little clusters which are thermodynamically unstable until they reach a certain critical size. Thereafter it is energetically more favorable for them to remain in the solid phase than in the vapor phase [27]. The adsorption energy on foreign substrates is generally higher than that for Si. Thus it becomes possible to operate at a point where the nucleus size on the foreign material is held below the critical value, while nuclei of overcritical size can form on the silicon-growth interface. The process is a delicate balance between reasonable growth rates and polynucleation on the masking material, most often SiO_2 . The onset of nucleation on the mask is a function of temperature, pressure, mask material, and the Cl/Si ratio in the vapor phase.

Doping profiles in epitaxially grown thin films are presented from two points of view. First, an epitaxial

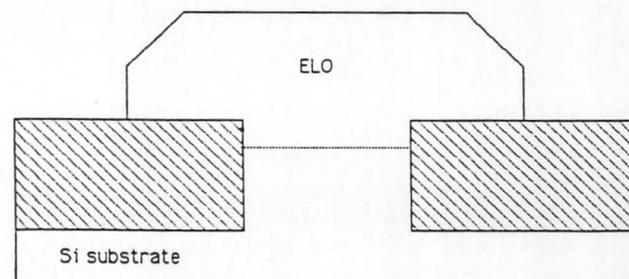
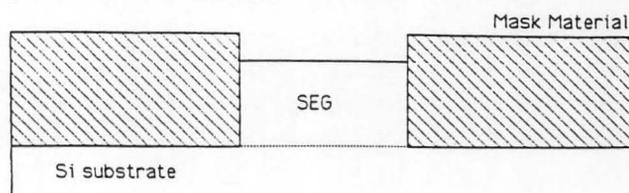


FIGURE 2. Selective epitaxial growth and epitaxial lateral overgrowth schematic cross sections.

layer doped with a desired element can be obtained with a cofeed of a dopant source along with other species of interest. In this case, additional chemical reactions, which include dopant species, have to be accounted for; these additional reactions can significantly affect the quality of growing doped epitaxial layers. Second, intrinsic epitaxial growth of, say, silicon on substrates with buried layers raises questions of doping a growing thin film with impurities coming from these buried layers through autodoping or out-diffusion [2, 3].

CHEMICAL EQUILIBRIUM—THERMODYNAMICS

Thermodynamic calculations of a CVD reaction system are discussed next. Such an analysis may provide important insights into several aspects of the system. Starting with a nonequilibrium inlet state, chemical equilibrium calculations can provide boundary values of operating parameters necessary for successful thin film growth and provide information on the response of the process to changes in operating conditions [7, 28]. Furthermore, the computation of equilibrium compositions with intentionally limited reactants may assist in the assessment of reaction mechanisms. In the course, students are presented with a computer program that allows quick equilibrium calculations of CVD reaction systems.

Thermodynamics calculations are also helpful for the pretreatment and preparation steps of substrates as well as for the growth of thin films doped with a desired impurity. However, in our course on microelectronics processing, the need for chemical equilibrium calculations is emphasized even more in the SEG of silicon on patterned substrates [29]. Nucleation on SiO_2 (or Si_3N_4) during SEG, silicon oxide (or nitride) degradation during SEG, and undesired impurities in SiO_2 (or Si_3N_4) films used for the patterning of a substrate are some of the many additional problems one does not have to worry about in CVD on a patternless substrate. Such issues are addressed in detail for the CVD of epitaxial silicon on patterned wafers.

KINETICS

The chemistry of CVD systems follows their chemical equilibrium calculations. Such chemistry is complex and usually involves surface and gas phase reactions [7]. With respect to gas phase reactions, two approaches are discussed. The first one includes experimental data from studies on individual gas phase reactions. The second approach is theoretical. Starting from basic data of all conceivable species and reactions in a given CVD reaction environment, one can

estimate rate constants from kinetic theory. Once this is done, dominating gas phase reactions can be determined at any set of CVD reactor conditions. It is emphasized in class that, typically, a combination of both approaches seems to be best. With such a conceptual understanding of gas phase reactions, particle formation (for example, during Si deposition from silane) can be reasonably well predicted. Thus, because particle formation in the gas phase can be detrimental to the quality of growing epitaxial thin films, the importance of gas phase chemistry and kinetics becomes clear.

On the other hand, it is pointed out that the role of gas phase reactions is becoming less important with decreasing CVD temperatures and partial pressures of the reactants. Therefore, in silicon SEG, which is typically carried out at reduced pressures and temperatures, many gas phase reactions are not expected to play an important role. Yet, both approaches discussed previously are also presented as thorough ways of accounting for gas phase reactions in CVD on patterned substrates.

When it comes to substrate surface reactions in CVD, it is pointed out that little is known even for epitaxial silicon deposition, which is perhaps the reaction system studied the most. Several difficulties in the understanding of CVD surface reactions are discussed. These are the typically unknown extent of gas phase reactions, the typically significant role of transport phenomena in the neighborhood of a substrate in particular (with the only exception perhaps of LPCVD epitaxial reactors), the potentially high levels of undesired impurities in the feed gases or in the reactor itself, the potentially high conversions of key reactants, and the possibility that some reactions may be very near their chemical equilibrium. It is mentioned that in a few studies, spectroscopic techniques have been utilized in CVD so that some surface reactions can be monitored. Although helpful, such studies are shown to provide more questions than answers.

In spite of our incomplete understanding of CVD surface reactions, a few reaction mechanisms for Si and GaAs growth are discussed in detail. Fairly widely acceptable gas phase and surface intermediates are used.

Naturally, the role of surface reactions in CVD on patterned wafers is presented as even more complex. In silicon SEG, there are two kinds of surfaces that any species is in contact with: the silicon seed windows area and the SiO_2 (or Si_3N_4) area. It is indicated to the students that, typically, silicon SEG in the seed windows is assumed to be similar to growth on patternless wafers; that is, the only potential contribution

coming from the oxide (or nitride) surface is assumed to be just surface diffusion close to the SiO_2 -Si interface. Yet, recent developments are shown to suggest that the oxide or nitride surface seems to participate to a much greater extent in the overall surface reaction scheme than thought before.

Also, what is usually called "kinetics of epitaxial growth" in several books and some journal articles [2-6] is discussed at the end. The above term includes mass transport in series with a truly kinetic step, the rate expression of which is assumed to be linear. Therefore, the final growth rate expression obtained involves an overall mass transfer coefficient along with a kinetic rate constant. Although such a growth rate expression may help in the understanding of diffusion controlled and surface reaction controlled deposition, it is emphasized that such an analysis is *not* the intrinsic kinetics of epitaxial thin film growth and that it simply provides an elementary, though clear, conceptual understanding of kinetically or mass transfer controlled processes in CVD systems.

CVD REACTOR MODELS—THIN FILM QUALITY

Today more than 70% of all fabricated integrated circuits employ epitaxy in one way or another. The requirements made on the quality of the epitaxially grown layers are stringent: less than $\pm 5\%$ thickness variation over a wafer and from wafer to wafer, less than $\pm 5\%$ doping nonuniformity and high growth rates to suppress dopant redistribution.

Selective epitaxy is even more sensitive to the variation of parameters than is epitaxy on patternless wafers; one has only a limited operating range in which nucleation on SiO_2 (or Si_3N_4) does not occur. Also, local depletion effects can significantly alter growth rates.

The basic continuity, momentum, energy, and mass equations of a comprehensive model of a CVD reactor are covered through the detailed modeling of a pancake reactor. Such equations in their general form apply to any type of reactor, the main variations being related to entrance effects and to whether natural convection plays an important role in a given CVD reactor system. Also, the special geometry and inlet and exhaust configurations of the reactor used have to be accounted for in a CVD reactor model. Gas phase chemistry is shown to be included in these modeling equations, whereas surface chemistry is accounted for through appropriate boundary conditions for a chosen CVD system. Important differences between cold-wall and hot-wall reactors are discussed in detail.

Results from the detailed model of a pancake reactor are presented in detail for patternless and pat-

terned substrates [30]. It is readily seen that one result of the solution of a detailed reactor model is an understanding of velocity, temperature, and species mass fraction profiles throughout the reactor of interest. Another result is predictions of the growth rate profiles on substrates.

Because of our incomplete understanding of CVD kinetics, it is emphasized that any CVD gas phase and surface chemistry should be tested in at least two different types of reactors. Furthermore, even within each reactor, wide regimes of operating parameters such as substrate temperature and reactor pressure are suggested for testing. However, even if such a model is able to predict all trends of thin film growth rate profiles quantitatively, it may not be able to predict other features such as defect density, surface resistivity, and quality of Si/SiO₂ interfaces that can characterize the quality of a grown thin film. The quality of a thin film grown in an epitaxial CVD system is also shown to be a fairly strong function of the quality of the substrate used, the purity of gases or other materials used, the impurities of the reactor itself, and the predeposition treatment. Film characterization after an epitaxial processing step is presented as an essential integrated part of any CVD on patternless or patterned substrates [2, 3, 6].

SELECTIVE EPITAXY

Specific focus on VPE on patterned substrates follows. SEG of silicon is presented as being most often carried out by employing an SiH_2Cl_2 -HCl system at reduced pressure and temperatures of about 800-1000°C [31-35]. SEG leads to structures exhibiting distinct faceting which depends on substrate orientation and seed window alignment relative to crystal planes. It is pointed out that (100) substrates and pattern alignment along [100] directions seem to give the best results for application purposes [36]. At reactor pressures greater than about 20 torr, SEG rates appear to depend rather strongly on the amount of exposed silicon area. However, a reduction of pressure below 20 torr or an increase of the reactor inlet ratio Cl/Si is shown to decrease such a loading effect. In a fabrication line it is indicated that both these remedies may be undesirable because they result in smaller growth rates.

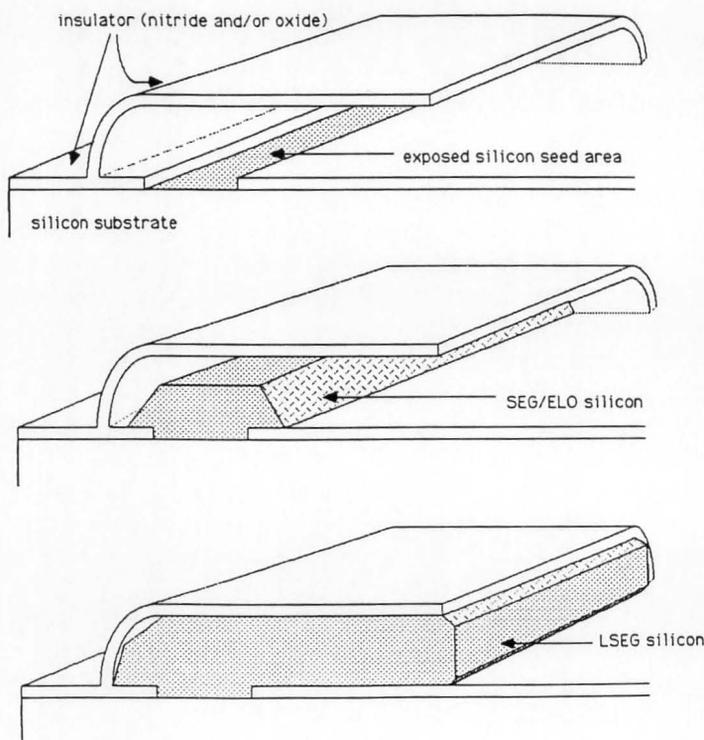
If the film is grown longer than necessary to fill the void created by the etching of the SiO_2 mask, it will not only grow vertically but horizontally as well (Epitaxial Lateral Overgrowth (ELO), Figure 2). This leads to a Silicon-on-Insulator (SOI) type structure which is very desirable from a device application point of view. Typical ratios of horizontal growth rates over

vertical ones, *i.e.*, aspect ratios, are pointed out to be about 1:1.

A different technique for growing epitaxial silicon over SiO₂ is also discussed [37]. Jastrzebski, *et al.* [37] report almost nucleation-free growth by growing without any HCl for a short time and then etching with HCl for about the same amount of time. These steps are repeated until the desired film thickness is achieved. The aspect ratio is about 1:1.

Large aspect ratios (much greater than 1:1) are shown to be of great interest for advanced dielectric isolation and the design of new three dimensional integrated circuits. One promising avenue for such a high aspect ratio is pointed out to be Lateral SEG (LSEG), which is depicted in Figure 3 [38]. The top structure is a cavity with prepared wing layers of different etched-rate materials and with a seed hole deep inside. In the center structure, selective growth extends up into the cavity and is technically ELO at this stage. As the top of the ELO meets the cavity ceiling, growth is now constrained to proceed only laterally, as shown in the bottom structure. This lateral growth is referred to as LSEG.

The importance of selective epitaxial growth in VLSI is stressed because it allows for novel device isolation techniques with higher densities as well as



Lateral selective epitaxial growth of silicon [38].

TABLE 1
Titles of Final Projects in CVD Epitaxy on
Patternless and Patterned Substrates

- Silicon on Insulators: A Focus on Epitaxial Lateral Overgrowth
- Solid Phase Epitaxy of Silicon
- GaAs Contacts: Theory and Practice
- Kinetics in the Vapor Phase Epitaxy of GaAs
- Recent Studies on the Kinetics of Epitaxial Silicon Growth
- Metalorganic Chemical Vapor Deposition of III-V Compounds
- Chemical Vapor Deposition of II-VI Materials
- Recent SOI Technologies
- Increasing the Throughput of High Electron Mobility Transistors Grown by III-V Molecular Beam and Chemical Beam Epitaxy
- Plasma Enhanced Chemical Vapor Deposition
- Silicon Epitaxial Growth Research at Purdue University: An Overview
- Silicon on Insulator Technologies

new device structures such as silicon on insulator arrangements [13, 14, 31-34, 38].

DOPING PROFILES IN EPITAXIAL LAYERS

Two potential problems associated with the doping profiles in such epitaxial thin films are addressed as being very important: autodoping (etchback) and solid state diffusion. Typically, a lightly doped epitaxial layer may have to be deposited on a heavily doped substrate with the same kind of dopant, or vice versa (*e.g.*, n- or n on n⁺, p- or p on p⁺). Also, for the formation of a pn junction, a p-doped epitaxial layer has to be deposited on an n-doped substrate or vice versa.

Autodoping is discussed first in detail. Etchback is shown to result in sharper transitions from the dopant concentration level in a substrate to the dopant level in the growing epitaxial layer, as substrate temperature or reactor pressure decreases. Simple semi-empirical models are developed for autodoping. These models are shown to be able to predict trends like the ones just mentioned as well as a shift in the position of the pn junction delineated by the two layers [2]. Comprehensive models of autodoping are briefly presented. Furthermore, although increased etchback is pointed out to be technologically undesirable, it is demonstrated that autodoping may be a very useful tool in determining velocity profiles just above a susceptor in some CVD reactors (*e.g.*, a pancake reactor).

Solid state diffusion is presented next. Although redistribution of the dopants because of diffusion during epitaxial growth of a (doped) thin film may not be very important compared with the redistribution that takes place during subsequent processing, a simple

model for solid state diffusion is discussed. This model is shown to result in a graded junction between substrate and epitaxial layer and in a shift of the pn junction delineated by the two layers. This shift, though, seems to compensate for the junction lag due to the autodoping effect. The intensity of solid state diffusion effects is shown to depend on the substrate temperature during epitaxy, the duration of this step, and the magnitude of solid state diffusivities at standard conditions. Also, a brief discussion of redistribution of dopants due to diffusion during subsequent processing is presented.

FINAL PROJECTS

After a brief coverage of other kinds of CVD epitaxy, such as PACVD, the last stage is a final term paper. Each student works on his/her own project after choosing a topic. Within such projects, students are expected to critically review any existing literature and to present their own "innovative ideas" in improving or developing various CVD epitaxial processes.

Topics in the chemical vapor deposition epitaxy on patternless and patterned substrates covered in the past four years are listed in Table 1.

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THE IMPEDANCE RESPONSE OF SEMICONDUCTORS

An Electrochemical Engineering Perspective

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CHEMICAL ENGINEERS working in the field of electronic materials are not normally concerned with processes taking place within the semiconductor. Most direct application of chemical engineering principle is seen in the analysis of the growth of semiconductors in the gas phase (CVD or MOCVD) or in the liquid phase (crystallization, Czochralski crystal growth, and Bridgman growth). Application of chemical engineering principles to these processes is not easy but is direct because the species of concern are not electrically charged. In contrast, the species within the semiconductor (*e.g.*, electrons, holes, ionized electron donors or acceptors) are charged, and proper analysis of processes taking place within the semiconductor requires that this electrical charge be treated.

Since ions in electrolytic solutions are also charged, the principles learned in the application of transport phenomena, reaction engineering, and thermodynamics to electrochemical systems can be applied almost directly to the study of semiconductor devices. Here, these principles are applied to interpret the impedance response of semiconducting electrodes.

BACKGROUND

Impedance techniques can be applied to semiconductors to identify the electronic structure, *i.e.*, the distribution of states within the semiconductor bandgap. A simplified schematic representation of the band structure is shown in Figure 1. Electrons can be excited from the valence or bonding orbitals to the conduction band by receiving thermal or electromagnetic (illumination) energy. The species formed by this excitation are electrons (in the conduction band) and holes (absence of an electron in the valence band). Both species are charged (electrons have a negative charge and holes have a positive charge) and can move in response to concentration or potential gradients.

The minimum energy required to excite an electron from the valence band to the conduction band is the bandgap energy. In the ideal semiconductor, electrons cannot exist at energy levels between the valence and conduction energies. In real materials, electronic states within the band gap can exist due to the presence of impurities (carbon, oxygen,

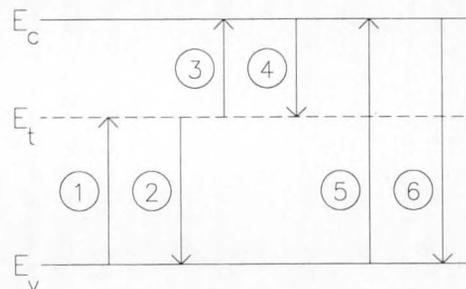


FIGURE 1. Generalized reaction scheme showing electronic transitions between the conduction band edge with energy E_c , the valence band edge with energy E_v , and a defect level with energy E_t .

and chromium are examples) or of dislocations, vacancies, or other lattice defects. These states can be electron donors or electron acceptors. Donor species are those which become positively charged when an electron is released, while acceptors become negatively charged when an electron is added. Because these species are charged, the distribution of electrical potential can be affected. Inter-band electronic states can be undesirable since they facilitate electronic transitions which can reduce the efficiency of electronic devices. In some cases, inter-band states are intentionally added when the added reaction pathways for electrons result in desired effects. Electroluminescent devices, for example, rely on emission of photons which takes place when electrons are transferred from the conduction band to an inter-band state in a large-bandgap semiconductor. The energy level of the states caused by introduction of the impurity determines the color of the emitted light. The impact of these states can be significant, even in concentrations that would seem to be very low by normal chemical engineering standards. There is, therefore, a need for developing new ways to evaluate the concentration, energy, and distribution of such electronic states.

A variety of techniques have been developed to study semiconductors which are based on impedance spectroscopy. We wish to focus here on a variant of electrochemical photocapacitance spectroscopy [1-5] in which the capacity of a reverse-biased electrode is measured as a function of the wavelength of incident sub-bandgap light. Let us note here that we really do not measure a capacity. Instead, we measure a periodic cell potential in response to a periodic current (or *vice-versa*) from which we calculate an impedance which has real and imaginary components. If we assume that this system behaves like an electrical circuit consisting of a capacitor and a resistor in series, we can, through regression techniques, obtain a value for a capacity and a resistance. The capacity obtained in this way is usually emphasized in this type of work since it can be easily related to the charge held in the semiconductor.

Since light of energy sufficient to cause an electronic transition will change the amount of charge held in a given

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state, changes in capacity at a given photon energy indicate the presence of states that allow transitions requiring that amount of energy. From this type of data we can obtain the energy levels of electronic states. The problem in this is that the largest contribution to the capacity is due to shallow level electronic states that are usually intentionally introduced as dopants. In fact, the change in capacity seen under illumination is (at best) proportional to the square root of the ratio of the defect concentration to the dopant concentration. This means that the technique of Haak and Tench [1-4] can be applied to semiconductors with a large defect concentration as compared to dopant concentration, but provides an unacceptable low signal to noise ratio when the dopant concentration is moderately large. On the other hand, the real part of the impedance, normally ignored since it is so difficult to relate to physical parameters, is very sensitive to these defects as low frequencies. We wish to focus here on the application of electrochemical principles to the problem of identifying the relationship between the real part of the impedance response and the energy, concentration, and distribution of defects. We can do this through development of a mathematical model based on the principles used in analysis of electrochemical systems. The treatment presented here follows a qualitative description of the experimental technique and the methods usually used in its analysis.

IMPEDANCE TECHNIQUES

Impedance techniques involve perturbation of a steady-state condition by a sinusoidal current or applied potential

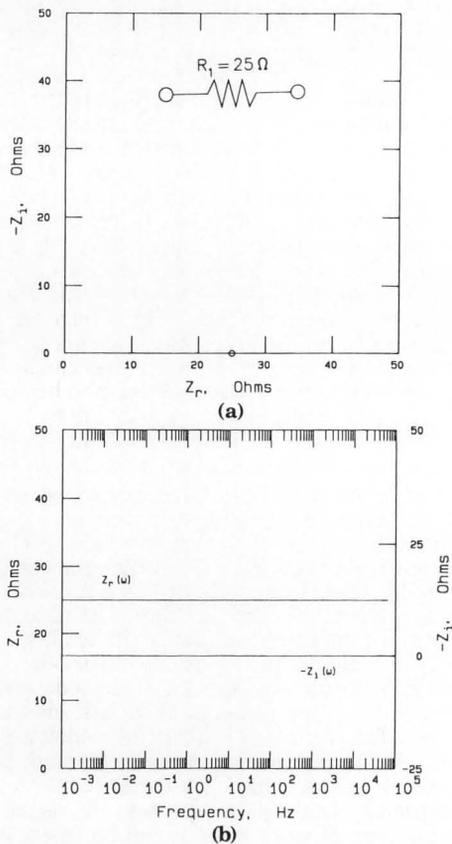


FIGURE 2. Impedance data for a system consisting of a resistor (with no capacitive component): a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

of low magnitude. A typical amplitude for an applied potential perturbation might be 10 mV, and the resulting sinusoidal current should have the same frequency, but may be shifted in phase. Thus the impedance, obtained by dividing potential by current, can be described as having real and imaginary components, *i.e.*,

$$Z = Z_r + jZ_j \quad (1)$$

A typical way to analyze impedance experiments is to compare the results to the impedance of simplified "equivalent" electrical circuits.

Equivalent Circuit Representations of Simple Systems

Electrochemists commonly present the resulting data in the form of an impedance plane plot ($-Z_j$ as a function of Z_r with frequency as a parameter). An impedance plane plot is given in Figure 2 for an electrical circuit consisting of a resistor. This is, of course, a very simple case. A Bode plot for this system (see Figure 2b) shows that the real part of the impedance is constant for all frequencies, and, since there is no phase shift, the imaginary part of the impedance is equal to zero. Thus, $Z_r = R$, and $Z_j = 0$.

The impedance data for a resistor and capacitor in series are given in Figure 3. The real part of the impedance is independent of potential, and the magnitude of the imaginary part is inversely proportional to frequency, *i.e.*, the highest values are seen at low frequencies. For this case: $Z_r = R_1$, and $Z_j = -1/\omega C_1$.

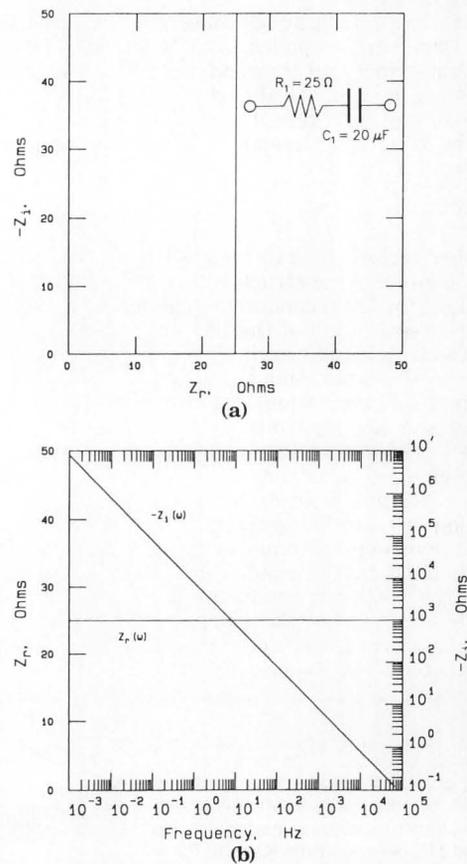


FIGURE 3. Impedance data for a system consisting of a resistor and a capacitor in series: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

Equivalent Circuit Representations for Electrochemical Systems

Simple electrochemical reactions at an electrode surface are often modeled in terms of the circuit shown in Figure 4. The resistance R_s is associated with the Ohmic resistance of the cell, the capacity is associated with the double layer capacity, and the resistance R_1 is related to the rate constant for the surface reaction. The impedance plane plot for this case is in the shape of a semicircle with the high frequency asymptote shifted from the origin by an amount equal to the solution resistance. Additional elements can be added to account for reactions proceeding in parallel or in series. A perfect semicircle is usually not observed experimentally, and a number of factors have been used to explain the observed depression of the semicircle. Roughening of the surface or growth of films during the course of an experiment can, in some cases, account for these observations. Mass transfer effects are also often important. These are treated by adding a Warburg element (see Figure 5). The impedance response of a Warburg element is a function of frequency and is derived by solving the convective diffusion equation for a given geometry to obtain the frequency dependent concentrations of reactants at the electrode surface. See reference 6 and chapter 9 in reference 7 for more discussion on the application of impedance techniques to typical electrochemical systems.

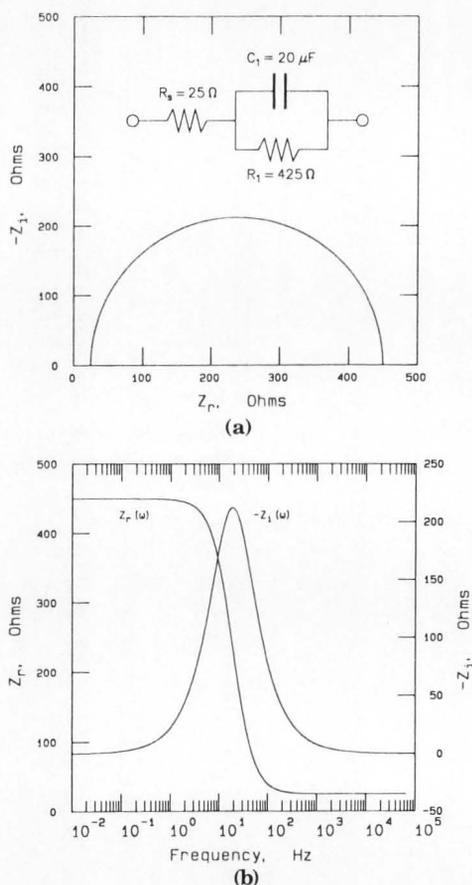


FIGURE 4. Impedance data for a system consisting of a resistor in series with the parallel combination of a capacitor and a resistor: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

An Equivalent Circuit Representation for Defects in Semiconductors

The fifth case considered here is that of a second resistor and capacitor in series added in parallel to the capacitor of Figure 3. The resulting impedance data are shown in Figure 6. The magnitude of the imaginary part of the impedance is largest at lower frequencies, and the impact of the added circuit components is seen at lower frequencies. The real and imaginary components of impedance, based on the equivalent circuit given in Figure 6, are

$$Z_r = R_2 + \frac{C_1^2 R_1}{(C_1 + C_2)^2 + \omega^2 (C_1 C_2 R_1)^2} \quad (2)$$

and

$$Z_j = -\frac{C_1 + C_2 + \omega^2 C_1^2 C_2 R_1^2}{\omega(C_1 + C_2)^2 + \omega^3 (C_1 C_2 R_1)^2} \quad (3)$$

respectively.

If the experimental system behaves like a given electrical circuit, nonlinear regression techniques could be used to obtain values for the resistor and capacitor components in that circuit. If the electrical circuit chosen does not account for all aspects of the data, *e.g.*, if the circuit of Figure 3 is used to model the data shown in Figure 6, the circuit components will be functions of frequency. Note that the circuits given in Figures 3 and 6 do not allow passage of direct cur-

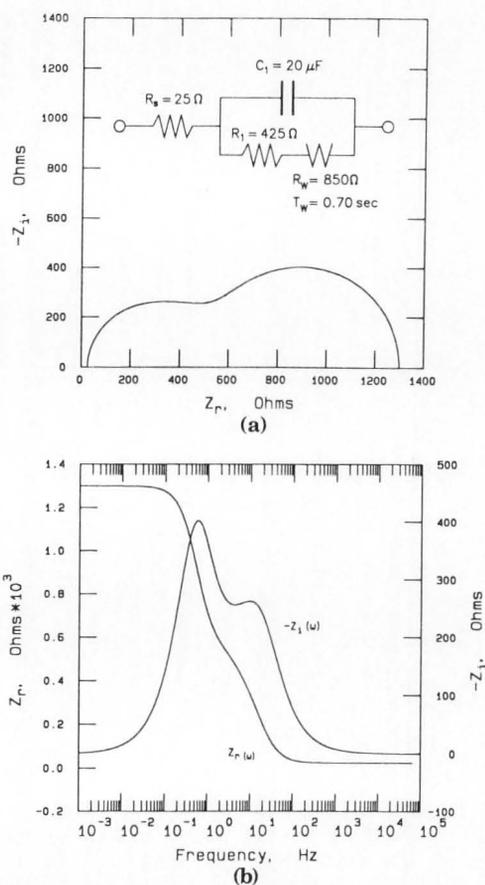


FIGURE 5. Impedance data for a system consisting of a resistor in series with the parallel combination of a capacitor and a resistor and Warburg element in series: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

rent. This corresponds to an ideally polarized or completely blocking electrode. To allow passage of direct current, a resistor in parallel to the other elements would be added as was done in Figures 4 and 5.

The electrical circuit given in Figure 6 is especially relevant to our system because it describes the behavior of an ideally polarized semiconductor electrode that contains a reasonable concentration of inter-band defects. In the high frequency limit,

$$Z_r = R_2 \quad (4)$$

and

$$Z_j = -\frac{1}{\omega C_2} \quad (5)$$

This behavior is more easily seen in a logarithmic impedance plane plot as shown in Figure 7. This type of plot emphasizes the high frequency data at the expense of the low frequency asymptote. The high frequency limit obscures the influence of the defects and yields the same result as would be obtained for a resistor and capacitor in series. For this reason, experimental data are frequently taken at high frequencies (greater than 10 kHz is usually sufficient). The defects, represented by C_1 and R_1 , have a major influence at low frequencies, *i.e.*,

$$Z_r = R_2 + \frac{C_1^2 R_1}{(C_1 + C_2)^2} \quad (6)$$

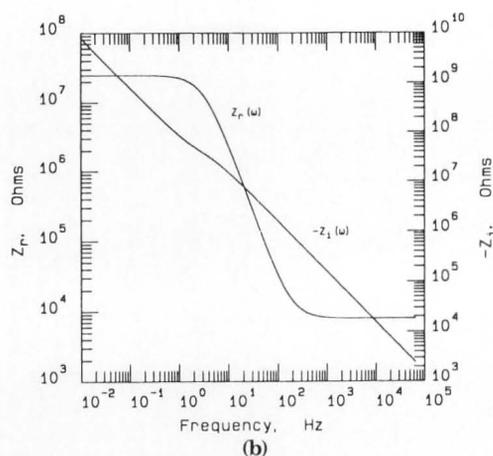
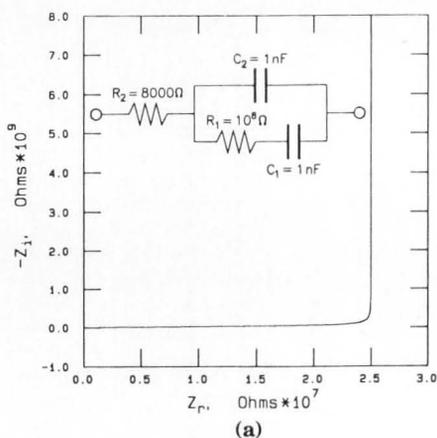


FIGURE 6. Impedance data for a system consisting of a resistor in series with the parallel combination of a capacitor and a resistor and capacitor in series: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

and

$$Z_j = -\frac{C_1 + C_2}{\omega(C_1 + C_2)^2} \quad (7)$$

The imaginary part of the impedance tends toward $-\infty$ while the real part of the impedance is shifted from the bulk resistance by a constant which includes the time constant associated with the defects $R_1 C_1$ and an averaged capacity $(C_1 + C_2)^2 / C_1$. This interpretation of the circuit elements is based, to a large extent, on the results of the mathematical model presented in subsequent sections.

We can compare these idealized cases to experimental results. Impedance plane plots are presented in Figure 8 with potential as a parameter for an n-GaAs electrode in contact with a mercury pool [8]. The logarithmic plot was used to emphasize the behavior at the high frequency limit. Linear regression of these data with Eqs. (2) and (3) yields frequency-independent values of circuit components which correspond to the solid line. The component values do vary with applied potential, and, if illumination had been used, the component values would vary with the photon energy of the illumination. The problem we face is how to tie these component values to physical characteristics of the semiconductor. One way to gain this intuition is to develop models for the system based on treatment of transport phenomena

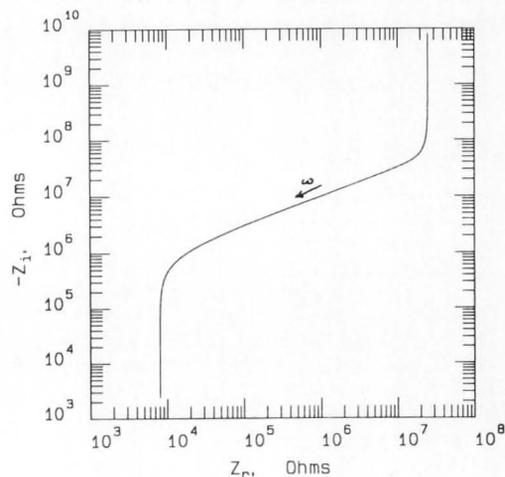


FIGURE 7. Impedance data for the system of Figure 6 consisting of a resistor in series with the parallel combination of a capacitor and a resistor and capacitor in series.

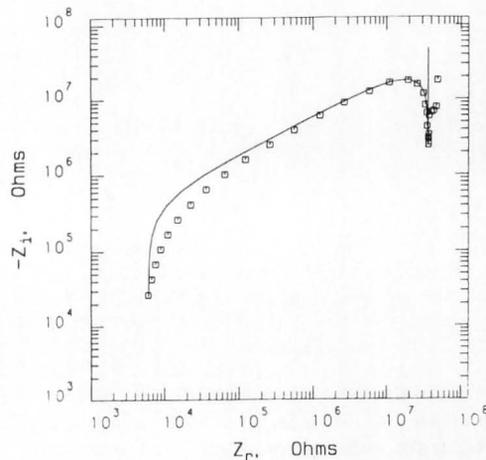


FIGURE 8. Impedance plane plot for a semi-insulating n-GaAs electrode in contact with a mercury pool [8].

and reaction kinetics and to compare the results of these models to those from the equivalent electrical circuits.

THEORETICAL DEVELOPMENT

Development of mathematical models for the impedance response of semiconducting systems generally takes place in two steps: development of a steady-state model followed by development of a model treating the sinusoidal perturbation of voltage or current about the steady-state values. Since the species of interest have a charge associated with them, we need to include treatment of electrical potential as well as concentrations. Thus, the electrostatic potential and the concentrations of electrons, holes, and ionized defect states become dependent variables for this system. The shallow-level doping species are usually assumed to be completely ionized at room temperatures and thus contribute to a fixed concentration of charge. Parts of the development presented here are given in references 9, 10, 11, and 12. References 13 and 14 provide good background to general aspects of semiconductor physics, and 15 provides a good mathematical foundation for electrochemical engineering.

Mass Transport Expressions

The electrochemical potential μ_i of a given species i can arbitrarily be separated into terms representing a secondary reference state μ_i^0 , a chemical contribution, and an electrical contribution, *i.e.*,

$$\mu_i = \mu_i^0 + RT \ln(c_i f_i) + z_i F \Phi \quad (8)$$

where c_i is the volumetric concentration of species i , f_i is the activity coefficient, z_i is the charge number, and Φ is a potential which characterizes the electrical state of the system and can be defined in many ways. This treatment is entirely analogous to the definition of chemical potentials as used for electrically neutral systems. In fact, the usual chemical potential is recovered for the case where z_i is equal to zero.

The flux N_i of species i is governed by the gradient of the electrochemical potential, given in one dimension by

$$N_i = -u_i c_i \frac{d\mu_i}{dy} \quad (9)$$

where u_i is the mobility of species i . If the semiconductor is nondegenerate, the electron and hole activity coefficients f_i can be considered to be constant, and Eq. (8) can be substituted into Eq. (9) to give the dilute solution transport expression

$$N_i = -D_i \frac{dc_i}{dy} - u_i z_i F c_i \frac{d\Phi}{dy} \quad (10)$$

where the transport properties D_i and u_i are related through the Nernst-Einstein equation; *i.e.*,

$$D_i = RT u_i \quad (11)$$

From Eq. (10), the fluxes of electrons and holes are driven by concentration and potential gradients. This distinction is a result of the separation of the chemical and electrical contributions given in Eq. (8). If desired, degenerate semiconductor conditions can be modeled by calculating the value of the activity coefficients f_i for electrons and holes (*e.g.*, [16] and [17]). The flux expression for species i is constrained by the equation of continuity, *i.e.*,

$$\frac{\partial c_i}{\partial t} = \frac{\partial N_{yi}}{\partial y} + G_i \quad (12)$$

Usually inter-band defect states are considered to be immobile; the rate of change of the concentration of ionized inter-band states is equal to their (position-dependent) rate of production, G_i .

For most electrochemical systems, the separation of charge associated with interfacial regions can be treated simply as contributing to rate constants associated with electrode kinetics. This is not appropriate for a semiconductor because this separation of charge is integral to the operation of electronic devices. Poisson's equation,

$$\frac{\partial^2 \Phi}{\partial y^2} = -\frac{F}{\epsilon_{sc}} [p - n + N_d - N_a] \quad (13)$$

can be used to relate the electrostatic potential Φ to the charge held within the semiconductor. The scaling length for this system, found by making the governing equations dimensionless, is given by the Debye length,

$$\lambda_{sc} = \left[\frac{\epsilon_{sc} RT}{F^2 (N_d - N_a)} \right]^{1/2} \quad (14)$$

The term $(N_d - N_a)$ includes the charge associated with partially ionized mid-bandgap acceptors (which may be a function of applied potential) as well as the completely ionized dopant species (which may have an arbitrary distribution, but is usually assumed to be independent of operating conditions).

Kinetic Expressions for Electronic Transitions

Calculation of a rate expression for G_i requires the choice of a kinetic framework. In this work, electrons are allowed to pass between the conduction band (with energy E_c), the valence band (with energy E_v), and the inter-band species (with energy E_t). A general scheme for the various electron transitions associated with this approach are shown in Figure 1. With these representations, the rates of the electronic transitions between the various energy levels can be described by applying mass action principles (*e.g.*, [13]) to give

$$r_1 = k_1 c_d^+ \quad (15)$$

$$r_2 = k_2 (c_d^t - c_d^+) p \quad (16)$$

$$r_3 = k_3 (c_d^t - c_d^+) \quad (17)$$

$$r_4 = k_4 c_d^+ n \quad (18)$$

$$r_5 = k_5 \quad (19)$$

and

$$r_6 = k_6 np \quad (20)$$

where k_i is the rate constant of reaction i , c_d^+ is the concentration of positively charged, inter-band donor species, c_d^t is the total concentration of inter-band donors, n is the electron concentration, and p is the hole concentration.

In the absence of inter-band states, generation of electrons and holes occurs through band-to-band mechanisms. The rate of electron generation is given by

$$G_{e^-} = k_6 (n_i^2 - np) \quad (21)$$

where the two righthand terms represent thermal generation ($k_6 = k_6 n_i^2$) and recombination, respectively, and n_i is termed the "intrinsic concentration" (a physical property equal to the concentration of electrons and holes in the "ideal" undoped semiconductor). The constraint that the rates of generation and recombination are equal provides that $np = n_i^2$ under equilibrium conditions. In the presence of inter-band states, the net rate of production for electrons (and holes) is given by

$$G_{e^-} = k_6 \left[1 + \frac{k_2 k_4 p}{k_6 (k_3 + k_2 p)} \right] (n_i^2 - np) \quad (22)$$

Again, at equilibrium, the rates of generation and recombination are equal and $np = n_i^2$.

Use of the above six kinetic expressions requires selection of the six rate constants (or three rate constants and three equilibrium constants) associated with these expressions. This apparently arbitrary selection can be approached by deriving equilibrium expressions to relate the rate constants for the reversible, homogeneous reaction pairs explicitly in terms of the energy differences between the valence band, inter-band species, and the conduction band, *i.e.*,

$$E_{12} = \frac{k_1}{k_2} = N_v g \exp \left[\frac{F(E_v - E_t)}{RT} \right] \quad (23)$$

$$E_{34} = \frac{k_3}{k_4} = \frac{N_c}{g} \exp \left[\frac{F(E_t - E_c)}{RT} \right] \quad (24)$$

and

$$E_{56} = \frac{k_5}{k_6} = N_c N_v \exp \left[\frac{F(E_v - E_c)}{RT} \right] \quad (25)$$

where E_{ij} is the equilibrium constant for reaction pair ij , g is the degeneracy associated with the inter-band state, N_c is the conduction band density of states, and N_v is the valence band density of states. These expressions were derived by assuming thermal equilibrium and substituting standard statistical expressions for electron, hole, and defect concentration in terms of energy level. The numerical value for g is determined by the electronic character of the state, *e.g.*, $g = 4$ for electron acceptors and $g = 2$ for electron donors [14].

Parameter variation studies can be further simplified by the assumption that the rate constants are interrelated such that, given energy levels for the electronic states, all rate constants can be obtained from a single rate constant. For example, the relationship,

$$k_4 = k_2 \left(\frac{E_{12}}{E_{34}} \right)^{\frac{1}{2}} \quad (26)$$

was obtained by assuming that changes in the free energy of reaction associated with varying the energy of an electronic state are distributed equally between the activation energies for the forward and the reverse directions. This is similar to the standard approach used to separate the free energy of an electrochemical reaction into chemical and electrical terms. The symmetry factor in this application is assumed to have a value of $1/2$ (*e.g.*, [15]).

Similar expressions can be developed for band-to-band recombination, *i.e.*,

$$k_2 = k_6 \left(\frac{E_{56}}{E_{12}} \right)^{\frac{1}{2}} \quad (27)$$

The use of Eq. (27) to relate the homogeneous, band-to-band rate constant k_6 to the corresponding inter-band constants k_2 (and k_4) is equivalent to assuming that the reaction cross section is the same for recombination through trap sites as it is for direct band-to-band recombination. This assumption could easily be relaxed to account for enhanced rates of recombination through trap sites.

In the case where solar illumination is applied to the semiconductor, the expression for the optical generation of electrons under solar illumination is

$$G_{e^-, \text{opt}} = q_0 \gamma m \exp(-m\gamma) \quad (28)$$

where γ is the fraction of incident photons with energy greater than the bandgap E_g , m is the band-to-band absorption coefficient, and q_0 is the solar flux. Similar expressions apply for sub-bandgap illumination; however, treatment of optical excitation by light with photon energies smaller than the bandgap requires expressions for the effective absorption coefficient. Such expressions can be found in the literature (*e.g.*, [18]) for the absorption coefficient m corresponding to the transition of electrons from inter-band acceptor states to the conduction band. This absorption coefficient is a function of the inter-band state energy, the photon energy, and the concentration of ionized states. Absorption of sub-bandgap illumination is negligible for the usual values of semiconductor thickness, inter-band species density, and absorption coefficients. This allows the effects of sub-bandgap illumination to be included as a modification of the rate constants in the expressions for r_1 and r_3 .

Impedance Modeling

A system whose time response $y(t)$ to a perturbation $x(t)$ can be described by the expression

$$\begin{aligned} b_0 \frac{d^n y(t)}{dt^n} + b_1 \frac{d^{n-1} y(t)}{dt^{n-1}} + \dots + b_n y(t) \\ = a_0 \frac{d^m x(t)}{dt^m} + a_1 \frac{d^{m-1} x(t)}{dt^{m-1}} + \dots + a_m x(t) \end{aligned} \quad (29)$$

is defined as a *linear* system. One characteristic of such a system is that a perturbation of the form $x(t) = \cos(\omega t)$ will result in a response of the form $y(t) = \cos(\omega t + \theta)$. This behavior is also observed for nonlinear systems if the amplitude of the perturbation is small enough that a first-order Taylor series expansion about the steady state is appropriate.

Experimental impedance measurements are evaluated using this theory since the current response to a sinusoidal applied potential is also sinusoidal. The important restrictions are that the system be stationary, that the system response be driven by the imposed signal, and that the imposed voltage perturbation be sufficiently small that the system can be described by Eq. (29). If these conditions are not violated, all variables of the system will take the form

$$\mathbf{x} = \bar{\mathbf{x}} + (\tilde{\mathbf{x}}_r + j\tilde{\mathbf{x}}_i) \exp(j\omega t) \quad (30)$$

where $\bar{\mathbf{x}}$, $\tilde{\mathbf{x}}_r$, and $\tilde{\mathbf{x}}_i$ are functions of position, but are independent of time. This means that impedance measurements are usually made in the region where the voltage perturbation is small enough for the system to be linear, yet large enough to give a significant signal to noise ratio. For a current density given by

$$\mathbf{i} = \bar{\mathbf{i}} + \tilde{\mathbf{i}}_r \exp(j\omega t) \quad (31)$$

the concentration of electrons is given by

$$\mathbf{n} = \bar{\mathbf{n}} + (\tilde{\mathbf{n}}_r + j\tilde{\mathbf{n}}_i) \exp(j\omega t) \quad (32)$$

Similar expressions are used for potential and the concentrations of holes, ionized electron acceptors, and ionized electron donors. In the above equations, an overbar represents the steady-state value, and a tilde represents the perturbation value. The actual concentration or potential at a given point in time and space is given by the real part of the expressions given above. The approach described here has

been used to model the impedance response of semiconductors in the absence of inter-band states [19, 20] and in the analysis of electrochemical systems (*e.g.*, [21-24]).

The above expressions are substituted into the governing equations which are solved sequentially for the steady-state and the sinusoidal steady-state portions, respectively. The impedance can be resolved from the calculated potential variation across the space charge region into real and imaginary components according to

$$Z_r = \frac{\Delta\bar{\Phi}_r}{\bar{i}_r} \quad (33)$$

and

$$Z_j = \frac{\Delta\bar{\Phi}_j}{\bar{i}_r} \quad (34)$$

respectively.

Steady State Boundary Conditions

The governing equations are initially solved under the steady-state condition, subject to the boundary conditions

$$\bar{N}_p = 0, \quad \frac{d\bar{\Phi}}{dy} = 0, \quad \text{and} \quad \bar{i} = 0$$

at the semiconductor-current collector interface (ohmic contact), and

$$\bar{N}_n = 0, \quad \bar{\Phi} = 0, \quad \text{and} \quad \frac{d\bar{\Phi}}{dy} = -\frac{q_{sc}}{\epsilon_{sc}}$$

at the semiconductor-electrolyte interface (ideally polarizable contact). These conditions are appropriate for a semiconductor-mercury contact or for a semiconductor-electrolyte contact where the electrolyte is chosen so that no chemical reaction occurs.

Sinusoidal Steady State Boundary Conditions

The time-dependent equations are solved for the response to a superimposed sinusoidal current by introducing expressions for the dependent variables (such as Eq. (32)) into the governing equations and linearizing around the steady state solution obtained in the previous step. Appropriate boundary conditions for the impedance calculations are given by

$$\bar{N}_{p,j} = \bar{N}_{p,r} = 0, \quad \bar{p}_j = \bar{p}_r = 0, \quad \text{and} \quad \bar{n}_j = \bar{n}_r = 0$$

at the semiconductor-current-collector interface, and by

$$\bar{N}_{n,j} = \bar{N}_{n,r} = 0, \quad \bar{\Phi}_j = \bar{\Phi}_r = 0, \quad \frac{d\bar{\Phi}_j}{dy} = \frac{\bar{i}_r}{\epsilon_{sc}\omega}, \quad \text{and} \quad \frac{d\bar{\Phi}_r}{dy} = 0$$

at the semiconductor-electrolyte interface. Again, these conditions are consistent with an ideally polarized electrode where the superimposed current acts only as a charging current.

Numerical Method for Solution

The solution of the coupled differential equations is non-trivial, and a complete solution requires use of a computer. The results of this type of numerical solution are presented elsewhere [11, 12]. The point here is to emphasize that the apparently complex behavior associated with transport and reaction processes within the semiconductor in response to a sinusoidal perturbation of current or applied potential can

be described by a straightforward application of principles learned in the study of electrochemical systems.

Analytic Expressions Used for Analysis of Experimental Data

Analytic solutions to the above equations have been developed that are valid in the high frequency limit. These solutions are based on integration of Poisson's equation coupled with assumption of equilibrium concentration distributions. The relationship between the applied potential and the R-C series capacitance was derived by Mott and Schottky (see, *e.g.* Joffe [25]) in the late 1930's to be (for an n-type semiconductor)

$$\frac{1}{C^2} = \frac{2\left(V + \frac{RT}{F}\right)}{\epsilon F(N_d - N_a)} \quad (35)$$

This is the well-known Mott-Schottky relationship.

Deviations from straight lines in Mott-Schottky plots, are frequently attributed to the influence of potential dependent charging of surface or bulk states. While deviations can also be attributed to non-uniform dopant concentrations, this interpretation is supported by analytic calculations of the contribution of defects to the space charge as a function of applied potential (*i.e.*, [26-27]).

CONCLUSIONS

The principles learned in the study of mass transport, thermodynamics, and heterogeneous and homogeneous kinetics associated with electrochemical systems can be applied directly to the transport and reaction processes that take place within a semiconductor. The theory of dilute solutions is generally appropriate, and values for needed parameters can be obtained through application of statistical thermodynamics.

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NOTATION

Roman Characters

- c_i concentration of species i , cm^{-3}
- C space charge capacitance calculated from an R-C series circuit, F/cm^2
- ΔC Change in C from a chosen reference level, F/cm^2
- D_i diffusivity of species i , cm^2/s
- E_a inter-band acceptor energy, eV
- E_c conduction band energy, eV
- E_d inter-band donor energy, eV
- E_f Fermi energy, eV
- E_g bandgap energy, $E_c - E_v$, eV
- E_{jk} equilibrium constant for reversible reactions j and k
- E_t Energy of generalized inter-band trap species, eV
- E_v valence band edge energy, eV
- f_i activity coefficient for generalized species i
- F Faraday's constant, 96487 C/equiv.
- g degeneracy of inter-band species
- i current density, mA
- j $\sqrt{-1}$

k_j rate constant for species j
 m absorption coefficient, cm^{-1}
 n electron concentration, cm^{-3}
 n_i intrinsic carrier concentration, cm^{-3}
 N_c effective density of conduction band states, cm^{-3}
 N_d doping concentration, cm^{-3}
 N_v effective density of valence band states, cm^{-3}
 N_{y_i} molar flux of species i , $\text{mol}/\text{m}^2 \cdot \text{s}$
 r_i rate of reaction of species i , $\text{mol}/\text{cm}^3 \cdot \text{s}$
 R universal gas constant, $8.314 \text{ J}/\text{mol} \cdot \text{K}$
 R resistance associated with a given electrical circuit, Ω
 t time, s
 T absolute temperature, K
 u_i mobility of species i , $\text{m}^2/\text{V} \cdot \text{s}$
 V applied potential, referenced to flatband, V
 \bar{x} steady state symbol for variable x
 \tilde{x}_r real component of the perturbation in variable x
 \tilde{x}_j imaginary component of the perturbation in variable x
 y distance from interface, cm
 z_i charge number for species, i
 Z complex impedance, $\Omega \cdot \text{cm}^2$

Greek Characters

ϵ permittivity, Farad/cm
 θ phase angle, rad
 λ Debye length, cm
 μ_i electrochemical potential of species i , J/mol
 μ_i^0 reference electrochemical potential of species i , J/mol
 Φ electrostatic potential, V
 $\Delta\tilde{\Phi}$ change in the real or imaginary portion of the potential across the semiconductor sample, V
 ω frequency, s^{-1}

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STOCHASTIC MODELING OF CHEMICAL PROCESS SYSTEMS

Part I: Introduction

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A STOCHASTIC SYSTEM is a system evolving according to probabilistic laws as opposed to deterministic laws. In practical terms this implies that given a system in a certain measurable state, the evolution of the system through other possible states can only be predicted in terms of a probability. We are thoroughly familiar with deterministic systems whereby, for example, knowledge of the initial position and momentum will allow us to exactly determine the future position.

Imagine a system for which knowledge of the initial conditions only allows us to predict the future position with a certain probability. Such a system would seem to go against the scientific belief of strict determinism. For our purposes, however, we can assume that although in principle it may be possible to make strict deterministic statements about the behavior of

any physical system, such statements would require exact and complete knowledge about the initial conditions and the external forces acting on the system. Since such exact knowledge is often beyond us, the reality as we perceive it may be represented best by stochastic models. This philosophy is in line with current theories involving deterministic chaos where a small error in the value of the initial conditions produces an enormous error in later predictions about the process (see, *e.g.*, reference 1).

Consider, for example, a bubbling fluidized bed. Theoretically, it is possible to exactly predict the sizes and positions of bubbles at each moment in time. However, the prediction would be dependent upon the initial conditions since the bubbles do not occur with exactly the same positions and sizes each time a fluidized bed is started up. Such a system appears to us to be stochastic, and thus we speak of the random coalescence and movement of the bubbles. This is equivalent to stating that although in principle we may be able to understand the mechanism of coalescence for two or three isolated bubbles in a deterministic manner, we are unable to extend the deterministic model to accurately predict the behavior of a large swarm of bubbles. Therefore, we resort to a model involving random movement and coalescence. Nevertheless, it is important to note that neither the deterministic nor the probabilistic mode of modeling excludes or negates the utility of the other. Indeed, while the deterministic model may be intractable for large complicated systems, the basic knowledge it provides about the dependence of the rate constants appearing in the probabilistic model on system parameters is invaluable. Both modes of modeling should be seen as working hand-in-hand, providing complementary understanding of complicated systems. An example of this aspect can be found in the recent work of Muralidhar and Ramkrishna [2] in modeling coalescence efficiencies.

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Numerous chemical process systems lend themselves to a stochastic description due to their inherent complexity and fluctuating nature. Examples of such systems can be found in dispersed phase flow, turbulence, solids mixing, and in many other chemical engineering fields of study.

At this point we wish to carefully distinguish between the deterministic models mentioned above, which allow an exact determination of the behavior of the system, and macroscopic models, which are also deterministic but are volume-averaged over the exact deterministic equations. Macroscopic models, therefore, are deterministic models involving variables such as overall temperature and concentration. In contrast, the exact deterministic or so-called microscopic models deal with the position and momentum of individual molecules. The exact relationship between these two domains is the subject of study of statistical mechanics. Although the stochastic models considered in this paper are less detailed than microscopic models, they are more detailed than the macroscopic models describing only the average behavior of a system. Thus, our desire to arrive at an accurate formulation of the stochastic model necessitates a close scrutiny of the mechanisms underlying the kinetic behavior of the process. In fact, a multitude of stochastic models corresponds to any given macroscopic model. Hence, the *ad hoc* addition of fluctuating terms to a macroscopic model is of relatively limited value if we wish to predict the effect of changing operating conditions on the higher moments of the probability distribution of the random variables.

BRIEF HISTORY

Numerous chemical process systems lend themselves to a stochastic description due to their inherent complexity and fluctuating nature. Examples of such systems can be found in dispersed phase flow, turbulence, solids mixing, and in many other chemical engineering fields of study. Research efforts in these areas have been reported extensively. For example, by using probabilistic methods, coalescence and breakage in dispersed phase systems have been studied by Valentas and Amundson [3], Ramkrishna and Shah [4], Ramkrishna [5], and Bajpai, Ramkrishna and Prokop [6], among others. Stochastic modeling of mixing and chemical reactions has been reported by Krambeck, Katz, and Shinnar [7], King [8], Pell and Aris [9], Mann and O'Leary [10], and Nauman [11], as well as work done by Fan and co-workers [12-14], and others. A fluidized-bed reactor is a notable example of a stochastic system with the random generation and coalescence of bubbles leading to pressure and density fluctuations. Stochastic mod-

els for fluidized beds have been discussed by Bukur, *et al.* [15], Shah, *et al.*, [16], Ligon and Amundson [17, 18], and recently by Fox and Fan [19].

RATIONALE FOR STOCHASTIC ANALYSIS AND MODELING

The incorporation of stochastic analysis and modeling into the repertoire of our profession is a matter of great urgency. Indeed, the need for a monograph or textbook on this subject is noted in a list compiled by Bird [20] and published in this journal. Devising appropriate stochastic models for chemical process systems, however, can be difficult. Construction of valid models requires the proper determination of the source of fluctuations and the mechanisms by which they evolve. The fact that relatively little interest has been shown for stochastic analysis and modeling of chemically reacting systems rests most likely with the nature of the internal fluctuations; such systems contain roughly the Avogadro number of molecules. A well-known result of statistical mechanics states that the number of density fluctuations are of the order of \sqrt{N} where N equals the total number of molecules in the system. The implication is that, in terms of concentration, the fluctuations are negligible with respect to the mean value equations and thus will be of little concern in the macroscopic description of chemical reactions. This result may be satisfying to the physicist who wishes to build a unified theory of matter based on molecular dynamics, but it is usually of little practical value to the chemical engineer modeling an actual chemically reacting system.

Visible or detectable fluctuations do exist in countless process systems, but their roots are not to be sought at the molecular level. A fluidized bed, for example, often fluctuates violently. These fluctuations obviously do not stem from the transfer of individual molecules among different phases in the bed; they stem from the transfer of relatively large entities, *e.g.*, clusters of particles and bubbles. It is well known that the bubbles can be modeled as entities which randomly enter into the bed, coalesce in it, and leave from it. Thus, the importance of properly identifying the source of fluctuations for a successful description of their impact on the system is obvious. Stochastic models based on independent molecular processes will show that the fluctuations are negligible in large systems, while a stochastic model based on mechanisms

involving, for example, bubble interactions will yield significant fluctuations.

From the stochastic model of a chemically reacting system, the more familiar kinetic expressions found in the chemical reaction engineering literature can be derived by calculating the average numbers of molecules of each species and expressing these in terms of continuous variables. The latter is of course possible and quite accurate since the number of molecules in any system is usually very large—it is on the order of the Avogadro number. As noted earlier, the variance of the numbers of molecules of each species will be of the order of the mean number of molecules. Consequently, when working in terms of molar concentration, the standard deviation will be several orders of magnitude smaller than the mean concentration. The

From the discussion . . . it should be clear that the stochastic model is more fundamental in nature than the deterministic rate equations of chemical kinetics or, in general, macroscopic models.

probability distribution of the random variables will then approach a delta function centered at the mean or average concentration for a system containing a large number of independent particles. In the statistical physics literature, this limit is often referred to as the thermodynamic limit. In this limit it is possible to describe the system in terms of the thermodynamic variables of chemical concentration and temperature instead of more fundamental quantities such as position and momentum.

From the discussion presented thus far it should be clear that the stochastic model is more fundamental in nature than the deterministic rate equations of chemical kinetics or, in general, macroscopic models. However, we are justified in using the deterministic rate equations when the number of molecules in the system is extremely large. In general, we can say that stochastic population balances for large numbers of independent entities almost always reduce to the deterministic mean value rate expressions. Nevertheless, in all cases, the stochastic model represents a fundamentally more basic description of the physical behavior of the system. It recognizes the existence of the individual members of the population and their ability to undergo change at random times.

For relatively small populations the random nature of the changes in the population numbers can be quite significant. For example, the change in the number of bubbles of each size in a fluidized bed takes place rather quickly, resulting in the widely fluctuating behavior of this system. A detailed stochastic model of

the fluidized bed might include a stochastic population balance for the bubble phase from which other physically important quantities, *e.g.*, the total surface area of the bubble phase, could be derived and their random nature quantified [19, 21]. These observations, of course, carry over to dispersed phase systems in general where deterministic population balances are widely used (see, *e.g.*, Ramkrishna [22]).

STOCHASTIC MODELS AND THE MASTER EQUATION

An appropriate stochastic model should depict the details of the internal mechanisms generating the fluctuations and can be solved by means of a rational approximation technique when the resultant equations are non-linear or be amenable to numerical simulation. A general formulation possessing both of these qualities is known in the modern literature as the master equation (see, *e.g.*, van Kampen [23] and Gardiner [24]). The master equation was first introduced into the statistical chemistry literature as a method of deriving statistical mechanics from molecular dynamics (see, *e.g.*, Cohen [25]). In the ensuing years much work has been done to understand the nature of the solutions to the master equation. Numerous approximation schemes have been devised to solve nonlinear master equations [24]. Perhaps the most successful of these has been the system size expansion [23].

A stochastic formulation based on the Janossy density function can be found elsewhere [26, 27]. However, we prefer to work with the master equation formulation for several important reasons: (1) the master equation uses as random variables the numbers of entities or particles that are the natural variables when considering a population balance; (2) although the Janossy density function and the joint probability distribution in the master equation are theoretically interchangeable through a correct change of variables, the master equation is easier to formulate once the fundamental events that change the values of the numbers of entities in each state are known; (3) in contrast to the Janossy density function, there is a vast body of literature pertaining to the master equation wherein numerous solutions are discussed, rational approximation techniques are introduced, and statistics such as the first passage time and the probability of large fluctuations are derived (see, *e.g.*, van Kampen [23] and Gardiner [24] for partial lists of references and basic derivations, solutions, and approximation techniques); (4) the rates of transition for each possible event appearing in the master equation are exactly the quantities needed when performing a

Monte-Carlo simulation of the system; (5) the procedure to go from the master equation to a multivariate Fokker-Planck equation or to a stochastic differential equation is straightforward, thus opening the possibility of applying the large body of literature in these fields to problems involving the master equation; and (6) except for the limited work carried out with the Janossy density function in the chemical engineering literature, the master equation formulation is perhaps the most commonly used stochastic formulation for population balance problems in the current scientific literature.

Numerous physico-chemical systems have been studied through formulation of their master equations. In particular, various chemically-reacting systems have been thoroughly studied and numerous examples are available in the literature [23, 24, 28, 29]. Nicolis and Prigogine [28] discuss stochastic methods for reaction-diffusion systems and non-equilibrium statistical mechanics with an emphasis on self-organization in nonequilibrium conditions. Oppenheim, *et al.* [29] present an interesting and useful compilation of basic papers on stochastic methods in chemical physics. Van Kampen [23] discusses in detail the effects of internal and external fluctuations in chemically reacting systems, while Gardiner [24] has collected many examples of nonlinear chemical reactions in both lumped and distributed systems. These authors and others have also dealt with the effects of fluctuations on the so-called "critical slowing down" in chemical systems and with other random effects and have presented methods for the stochastic treatment of mean passage time in bistable systems. While these systems are well documented in the statistical physics literature, the results have made little headway into chemical engineering.

Many chemical process systems are governed by nonlinear equations; this, in turn, implies that the stochastic model should also be nonlinear. This complication naturally leads to a coupling between the moment equations describing the population. It is then no longer possible to find the moments of the probability distribution of the random variables by solving an independent equation for each moment. To solve these equations, approximation techniques need to be introduced. Common *ad hoc* assumptions of independence between random variables or formulation of the higher-order moments as products of lower-order ones are of limited value. Instead, a rational expansion technique where the magnitude of higher-order terms can be controlled is clearly preferable. This technique will allow us to uncouple and solve the equations for lower order moments and then to use them in the

Part II of this series will be concerned with the derivation and solution of the master equation. The System Size Expansion will also be outlined . . .

coefficients of the equations for higher order moments while minimizing the error introduced through the approximation procedure. The System Size Expansion is such an approximation technique for the master equation [23].

Part II of this series will be concerned with the derivation and solution of the master equation. The System Size Expansion will also be outlined and used to find approximations for the moments and correlation functions of the random variables. For illustration the master equation will be applied to the modeling of a chemically-reacting system in the final part, Part III. It will be demonstrated that fluctuations in a large population are extremely small compared to the mean value and thus can often be ignored.

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DEPARTMENT: Arizona

Continued from page 6.

with a tendency for high quality. Many of the early PhD graduates, for instance, went on to become professors and administrators at major universities.

Since the majority of graduate students in a developing program were in the MS degree program, they were very closely supervised and generally produced publication-quality work. Many have gone on to important positions: three are company vice presidents; one is a director of overseas development; and several are heads of company divisions of various types. Several others pursued PhDs at other universities and have entered academia or research and development.

As mentioned before, the PhD/MS student ratio has recently increased to a level that will ensure a high rate of PhD graduates in future years. It appears that the department is beginning to achieve its early objectives for the graduate program. In terms of doctoral students, the department has been long on quality but short on quantity. Now that graduate enrollment has reached the desired level, we are focusing our efforts on maintaining quality in both graduate and undergraduate programs. □

WORKING IN THE IC INDUSTRY

Continued from page 41.

phases: gas and solid. Because of problems with particulates, liquids have been all but eliminated from the clean room. The reactors are small, and a batch of product can be held in one hand. Reaction times are on the order of minutes rather than days, so the turnaround is fast. Process control is simply a matter of using *in situ* diagnostics to predict the endpoint of an etch or deposition step. Compared with the difficulties of death, mutation, complex organic chemistry, living membranes, and mass transfer limitation typical of bio-engineering, the challenges of the IC industry are controllable. The problems are straightforward, but they generally require experimental solutions. There is enough work to be done to keep surface scientists occupied for several decades. Not only do the problems require experimental solutions, but the chemical engineer who lacks knowledge of device physics is just as handicapped as the electrical engineer with his/her ignorance of continuum mechanics. The need for a cross-disciplinary education cannot be overemphasized.

In conclusion, if you have the people skills to run for congress, the patience to spend a day in a junior high school, the perseverance to climb Mt. McKinley, the hands-on skills to keep dual Weber carburetors perfectly tuned on a 1960 Porsche, and the desire to help an industry which is vital to our national security and economy, consider obtaining a graduate degree in IC processing and joining a US IC company. □

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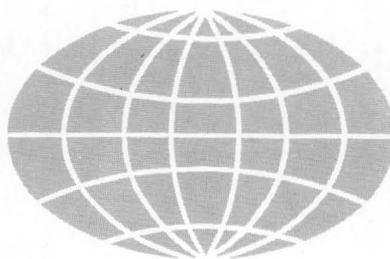
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