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Chemical Engineering Education**Volume 38****Number 1****Winter 2004****► EDUCATOR**

- 2 Chuck Eckert of The Georgia Institute of Technology,
William J. Koros

► DEPARTMENT

- 8 The University of Alabama,
C.S. Brazel, D.W. Arnold, G.C. April, A.M. Lane, J.M. Wiest

► LABORATORY

- 14 A Fluidized Bed Adsorption Laboratory Experiment,
Pamela R. Wright, Xue Liu, Benjamin J. Glasser
- 34 Nanostructured Materials: Synthesis of Zeolites,
Steven S.C. Chuang, Bei Chen, Yawu Chi, Abdelhamid Sayari
- 38 The Fuel Cell: An Ideal ChE Undergraduate Experiment,
Jung-Chou Lin, H. Russell Kunz, James M. Fenton, Suzanne S. Fenton

► CLASSROOM

- 22 On the Application of Durbin-Watson Statistics to Time-Series-Based
 Regression Models, *Thomas Z. Fahidy*
- 26 Teaching Electrolyte Thermodynamics,
Simão P. Pinho, Eugénia A. Macedo
- 54 Top Ten Ways to Improve Technical Writing,
John C. Friedly
- 64 Use of ConcepTests and Instant Feedback in Thermodynamics,
John L. Falconer
- 68 Rubric Development for Assessment of Undergraduate Research:
 Evaluating Multidisciplinary Team Projects,
James A. Newell, Heidi L. Newell, Kevin D. Dahm
- 74 Teaching Engineering Courses with Workbooks,
Yasar Demirel

► RANDOM THOUGHTS

- 32 Changing Times and Paradigms, *Richard M. Felder*

► CLASS AND HOME PROBLEMS

- 48 Incorporating Green Engineering into a Material and Energy Balance
 Course, *C. Stewart Slater, Robert P. Hesketh*

► LEARNING IN INDUSTRY

- 60 UOP-Chulalongkorn University Industrial-University Joint Program,
Santi Kulprathipanja, Ann Kulprathipanja

- 21 Positions Available

- 31 Book Review

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Chuck Eckert

of
*The Georgia Institute
of Technology*

WILLIAM J. KOROS
*The Georgia Institute of Technology
Atlanta, GA 30330*

Many people refer to Chuck Eckert as the “father of modern supercritical processing technology.” His work over three decades ago on solvation and reaction fundamentals under supercritical conditions helped reawaken chemical engineers to the opportunities within the supercritical state. This reawakening has blossomed into a rich subdiscipline that now encompasses much more than reaction and partitioning processes. Indeed, many of the most exciting topics now involve tailoring control of morphology of complex solids such as pharmaceuticals and polymers—items not initially envisioned even by Chuck.

Because he has had such a professional impact in chemical engineering, I was surprised by Chuck’s answer to my question, “What do you consider your most important contribution?” With a twinkle and wink of his eye, he pointed to a chart on his office wall. It comprised a “family tree” of individuals he has worked with through the years and who he felt he had positively affected. He said that the list symbolized his *real* life contribution—much better than any article or discovery could. He noted that most practical developments in the supercritical area were due to his students and their students and post docs long after they had left his direct supervision. The “family tree” that Chuck pointed to was prepared on the occasion of his selection as winner of the 1995 ACS Murphree Award. The award dinner, where the family



tree was presented to him, brought together many of Chuck’s former students, post docs, and colleagues who celebrated a career that had focused on coupled technical and personal mentorship for many individuals. This coupled contribution is truly his “signature” characteristic.

OVERVIEW

Chuck’s 39 years in academia include 24 years at the Uni-

versity of Illinois and 15 at Georgia Tech. During this period of time, he supervised an impressive 76 PhD dissertations and 65 additional MS theses. This pace continues, with another 10 PhD's still in progress. The names of his students are shown in Table 1.

While numbers don't tell the full story, they underline the truth in Chuck's perception that "people have been his proudest product." Ken Cox, a senior researcher at Shell Oil, has said, "There is no individual, outside my family, who has had such a major impact on my life. Strange thing is . . . he really is family! Many of the alumni from his research groups at Illinois and Georgia Tech form a close family for . . . Pappa Chuck!"

Another dimension of this picture is revealed by understanding the academic branches in the "family tree." Eighteen current or retired academics have worked with Chuck as either graduate students or post docs. Moreover, a probably incomplete list shows six "academic grandchildren" who have been educated by Chuck's direct academic descendents and who should also be added to the list to bring this academic branch up to at least 24.

Keith Johnston (UT Austin) says that "Chuck is totally dedi-

cated to the careers of his students." Similar sentiments come from Barbara Knutson (U. Kentucky): "Chuck develops both intellectual skills and people skills in his graduate students. He has acted as my coach, my mentor, and a cheerleader long after graduation, but most importantly, he is my friend. Chuck has succeeded in creating a close academic family." Joan Brennecke (Notre Dame), who won the 2001 ACS Ipatieff



Chuck accepts his "Family Tree: at the 1995 Murphree award dinner.

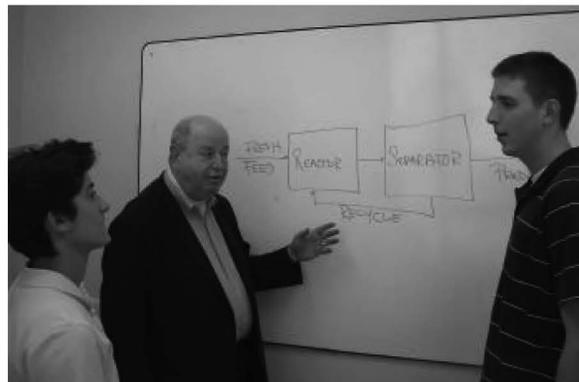
TABLE 1
Chuck Eckert's Graduate Advisees

<i>PhD Students</i>			<i>MS Students</i>	
K. F. Wong (1969)	W. T. Chen (1986)	H. Lesutis (2000)*	K. F. Wong (1967)	S. P. Brinduse (1981)
R. A. Grieger (1970)	S. W. Gilbert (1986)	K. West (2000)*	R. A. Grieger (1968)	W. T. Chen (1982)
S.P. Sawin (1970)	B. S. Hess (1987)	C. Wheeler (2001)*	L. D. Clements (1968)	T. K. Ellison (1982)
B. E. Poling (1971)	M. M. McNiell (1987)	K. Griffith (2001)*	S. P. Sawin (1968)	P. C. Hansen (1983)
R. B. Snyder (1971)	H. H. Yang (1987)	V. Wyatt (2001)*	L. G. Schornack (1969)	S. P. Singh (1983)
F. G. Clark (1973)	W. J. Howell (1989)	T. Ngo (2001)*	J. R. McCabe (1969)	C. T. Lira (1983)
J. H. Byon (1973)	D. M. Trampe (1989)	S. Nolen (2001)*	F. G. Clark (1970)	J. G. Van Alsten (1984)
J. R. McCabe (1973)	J. F. Brennecke (1989)	J. Hallett (2002)*	J. H. Byon (1970)	S. W. Gilbert (1984)
C. R. Hsieh (1973)	A. R. Hansen (1990)	J. McCarney (2002)*	C. R. Hsieh (1971)	M. M. McNiell (1984)
J. S. Smith (1975)	A. M. Karachewski (1990)	X. Xie (2003)*	K. P. Slaby (1971)	R. L. Matuszak (1985)
M. E. Paulaitis (1976)	M. P. Ekart (1992)	T. Chamblee (in progress)*	J. S. Smith (1972)	M. J. Hait (1985)
B. A. Newman (1977)	D. L. Tomasko (1992)	M.Lazzeroni (in progress)*	D. W. Wood (1972)	H. H. Yang (1985)
G.L. Nicolides (1977)	M. J. Hait (1992)*	R. Jones (in progress)*	P. E. Walter (1972)	J. H. Cordray (1986)
P. G. Glugla (1977)	D. B. Trampe (1993)	N. Maxie (in progress)*	R. H. W. Powell (1973)	W. J. Howell (1986)
C. W. Graves (1977)	B. L. Knutson (1994)	C. Thomas (in progress)*	A. I. Ness (1974)	D. M. Trampe (1987)
R. R. Irwin (1978)	D. Suleiman (1994)	J. Aronson (in progress)*	P. G. Glugla (1975)	J. F. Brennecke (1987)
A. Huss, Jr. (1978)	D. L. Boatright (1994)*	M. Janakat (in progress)*	C. W. Graves (1975)	A. R. Hansen (1987)
K. R. Cox (1979)	F. L. L. Pouillot (1995)	R. Weikel (in progress)*	A. Huss, Jr. (1976)	A. Karachewski (1987)
T. C. Long (1979)	K. P. Hafner (1996)	C. Pondy (in progress)*	R. R. Irwin (1976)	S. R. Alferi (1989)
P. K. Lim (1979)	J. Berkner (1996)*	L. Drauker (in progress)*	B. A. Scott (1976)	M. P. Ekart (1989)
E. R. Thomas (1980)	F. Deng (1996)*	E. Giambra (in progress)*	T. C. Long (1977)	D. L. Tomasko (1989)
K. Kondo (1981)	A. Dillow (1996)	J. Grilly (in progress)*	K. R. Cox (1977)	P. Katsikopoulos (1990)
M. M. Alger (1981)	B. L. West (1997)	E. Newton (in progress)*	L. A. Halas (1977)	R. K. Denton (1990)
K. P. Johnston (1981)	D. M. Bush (1997)		P. K. Lim (1977)	K. J. Hay (1991)
T. Stoicos (1982)	M. Vincent (1997)*		D. P. Deschner (1979)	D. Suleiman (1992)
D. H. Ziger (1983)	K. Chandler (1997)*		E. R. Thomas (1979)	K. Chandler (1995)
P. C. Hansen (1984)	J. Jones (1998)*		T. T. Oberle (1979)	R. Thompson (1996)
T. K. Ellison (1985)	N. Brantley (1999)*		K. P. Johnston (1979)	B. Eason (2001)*
J. C. Van Alsten (1985)	Z. Liu (2000)*		M. R. Anderson (1980)	D. Kass (in progress)*
C. T. Lira (1986)	J. Brown (2000)*		T. Stoicos (1980)	D. Taylor (in progress)*
			D. H. Ziger (1980)	

* Joint with C. L. Liotta



▲
Chuck with one of his undergraduate researchers.



▲
Chuck in class with some of his freshman students.



◀ **Charles Liotta and Chuck in one of their joint group meetings.**

Prize, said of her Ipatieff award symposium that “. . . it was the first time (and probably the only time) that the three most important men in my life were all in one room— my father, my husband, and Chuck! I think the continued care and mentoring is why the Eckert academic family has so many close ties.”

In addition to the mentor in Chuck, however, there is a major scholar who has produced well over two hundred archival journal articles, coauthored two books, and contributed twenty-one book chapters. One of his well-known coauthors, and his PhD research mentor, John Prausnitz (Berkeley) observed that, “Chuck communicates very well and encourages others by his enthusiasm and optimism. He thoroughly appreciates the importance of computers in research and education. In 1967, it was primarily *his* enthusiasm that convinced me to write with him (and two other graduate students) an early monograph on the use of computer calculations for multicomponent vapor-liquid equilibria—it was Chuck’s foresight and drive that accelerated the use of computers for applied thermodynamics in industry and education”.

Chuck’s contagious enthusiasm, tempered by a solid understanding of thermodynamics and thoughtful insights on

education, have made him attractive as an consultant and advisor. Moreover, strategically placed ex-students, knowing his catalytic capabilities have engaged him for services ranging from conventional analysis to the motivational aspects of education as well as research and its performance.

Chuck’s current research interests include

- *Molecular thermodynamics and solution theory*
- *Phase equilibria*
- *Supercritical fluid properties*
- *Applied chemical kinetics and catalysis*
- *Separation processes*
- *Environmentally friendly chemistry and processes*
- *Creation of novel materials*

Many of Chuck’s successes have resulted from his interest in “crossing the street” and collaborating with chemists. His work related to high-pressure reaction theory, the development of solvency models and development of new spectroscopic approaches typify this characteristic. In many respects, the chemistry aspects of problems are the greatest attractions for him.

Chuck’s approach involves a close coupling of experimental and theoretical attacks on problems. Prediction of limiting activity coefficients in water using a modified separation



Chuck with Aryn Teja and Ron Rousseau at a Georgia Tech reception in honor of Chuck's 1999 Walker Award.

of cohesive energy density coupled with actual measurement of these limiting coefficients illustrate the approach. The above work has provided important contributions to the understanding of “ordinary” liquids related to petrochemistry and even liquid metals. Another related, but still independent interest involves Chuck’s focus on spectroscopic techniques to study hydrogen-bonding systems—this initiative touches many areas in thermodynamics.

While the above work is well-known and highly note-worthy, probably Chuck’s best-known contributions relate to the gas-liquid critical region with particular reference to supercritical extraction and processing. With regard to the supercritical field, Pablo Debenedetti (Princeton University) notes that, “Since 1983, Chuck has, with unmatched regularity, made the key experimental observations and asked the truly important questions that other researchers in the field need to answer”. Indeed, in 1983, Chuck pioneered the measurement of solute partial molar volumes at infinite dilution in supercritical solvents. In addition to its practical importance, this ignited a large theoretical thrust across the field aimed at interpreting the provocative results he reported.

In 1988, Chuck introduced the use of spectroscopic techniques to study solvation in supercritical solvents. This pioneering work provided the first direct insights into the nature of solute-solvent interactions and the mechanisms of solvation under supercritical conditions. Focusing attention on short-range effects due to molecular asymmetry was a key advance. This theme has been developed by a huge number of subsequent researchers around the world

Still later, Chuck’s identification of the role of cosolvents in separations and supercritical processing marked another major contribution. The ability to design a solvent for a specific reaction or separation application through manipulation of process conditions or cosolvent type opened new possibilities and again stimulated many studies within the field.

His broad and deep contributions to the chemical engineering literature were recognized in 1999 by the William Walker Award. *Chuck is shown in the photo above at an informal reception at Georgia Tech in his honor following his selection for the Walker Award.*

CONTRIBUTIONS TO THE COMMUNITY

Chuck’s contributions to his home institutions are discussed later, but his professional contributions to the broader community also deserve mention. In addition to

... Chuck notes [that] “Research is perhaps the best instructional tool that professors have at their disposal – the one-on-one creative interaction of real, unsolved problems is the best method of teaching and learning.”

membership in the American Institute of Chemical Engineers and The American Chemical Society, he is active in the International Association for the Advancement of High Pressure Science and Technology, the Association of Environmental Engineering Professors, and The International Society for Advancement of Supercritical Fluids. He has served on many National Science Foundation and National Research Council committees aimed at defining future directions in the thermodynamics area—especially for high pressure applications. Current and past service on the Editorial Boards of the *AIChE Journal*, *Industrial and Engineering Chemistry Research*, *Journal of Supercritical Fluids*, and *Fluid Phase Equilibria*, guarantees a steady flow of manuscripts to his desk

to review, which I sometimes find him pouring over when I visit his office.

In addition to presenting over 300 invited lectures, he has served in an almost-endless list of service capacities to our community. They range from the technical (Chairmanship of the International Symposium on Supercritical Fluids) to the time-consuming (AIChE, ABET Accreditation Committee), but all are aimed at enabling the functioning of our community.

A MIDWESTERN EDUCATED ON BOTH COASTS

Chuck grew up in St. Louis and attended MIT for his bachelor's and master's degrees, which he received in 1960 and 1961, respectively. He then crossed the country and earned his PhD from the University of California at Berkeley in 1964. He also did a postdoctoral stint in France, which began a lifelong affinity for that country that still results in frequent visits.

A DYNAMIC CAREER AT ILLINOIS

Chuck joined the faculty at the University of Illinois, Champaign-Urbana, in 1965 as an Assistant Professor. Rising through the ranks with promotions to Associate Professor (1969) and full Professor (1973), he was recognized for both his research and teaching contributions.

Chuck was also one of the pioneers in using computers for interactive education. He developed a number of educational

programs on the "Plato" system focused on this interactive concept—well ahead of most of the chemical engineering community. In 1973, he received the Alan P. Colburn award and in 1977, the ACS Ipatieff Prize. In 1983, Chuck was elected to the National Academy of Engineering for his

"Outstanding contributions leading to the selection of liquid metals and supercritical fluids as solvents in chemical reactors, and to improved understanding of the extreme conditions in such reactors." He has also received awards for distinguished teaching and leadership reflecting his contributions to diverse curriculum and strategic planning.

Chuck served at the Head of the Department at Illinois from 1980-86. Moreover, service to the community on ABET and numerous Steering

Committees made the years in the middle and late 1980s extremely busy.

Chuck recognized that poor communication skills were at least as serious a handicap for a typical BS ChE as not being able to solve complex equations. Again ahead of much of the community, he developed a highly successful "Chemical Engineering Communications" course dealing with oral as well as written technical communications skills. He "crossed the street" once more, this time to the English Department where he was able to assemble a team to deal with the full range of communications needs. Such courses are now fairly common, but twenty years ago, this initiative was viewed as "unusual" at best. His selection for an Alumni Professorship in 1985 reflected recognition for his innovations to deal with the full range of student needs.

A HUGE IMPACT AT GEORGIA TECH

Chuck moved to Georgia in 1989 and began a new supercharged career. He holds the J. Erskine Love, Jr., Chair in the School of Chemical and Biomolecular Engineering. He also holds the title of "Institute Professor," which is reserved for individuals who have had significant impact beyond their individual School bounds. Chuck serves as the Director of the Specialty Separations Center, which has a cross-disciplinary vision and goals to connect activities across the Tech campus.

Clearly, in the move to Georgia Chuck brought with him his ideas regarding the importance of excellence in research



Son Ted and daughter Lynn (Gasey) with Chuck at 1995 Murphree Award Dinner.

and teaching, and he has found a receptive environment at Tech. He was attracted by the Institute's collegiality, its opportunities for multidisciplinary work and partnerships with industry, and the opportunity to help promote the rapidly emerging program at Tech. He notes that, "The reality has far exceeded my expectations" with regard to the above opportunities.

From my own observations, and the comments of colleagues here at Tech, it is fair to say that the same sentiment is shared with regard to the payoff on expectations.

Arnie Stancell, a faculty colleague at Tech says, "I have had the pleasure of working with Chuck for ten years, and his enthusiasm for educating students is infectious. He is always working on ways to engage students in learning. He personally took on presenting a seminar course for freshman to introduce them to chemical engineering. He developed interesting problem sets illustrating applications of chemical engineering. He brought in speakers to discuss current societal problems that the chemical engineer can help solve. Chuck did not have to do this—he has won many honors and is highly respected. He did it because of a genuine passion for educating students and seeing them grow in their knowledge and understanding."

Indeed, Chuck's enthusiasm is infectious. His latest initiative is to promote research opportunities for undergraduates. Besides his full complement of graduate students, Chuck has opened his lab and made time to meet with undergraduates. Although always a part of his vision, the significantly expanded activity to involve undergraduates has caught the attention of faculty and administrators alike. The President's office at Tech has encouraged a broader participation by undergraduates and cited Chuck's "ahead-of-the-curve" leadership as exemplary. In his own words, Chuck notes, "Research is perhaps the best instructional tool that professors have at their disposal – the one-on-one creative interaction of real, unsolved problems is the best method of teaching and learning." The motivations for such a program are many, and include

- *Teaching fundamentals in ways that are more meaningful than contrived textbook problems, or sanitized cookbook laboratory experiments.*
- *Providing motivation, as the students are able to see the impact of their efforts on the real world. Students gain enthusiasm and self-confidence.*
- *Putting the students in close contact with PhD students, postdoctorals, and other high-level professionals; it demonstrates teamwork and motivates students to seek leadership roles in their professions.*
- *Providing a framework that permits students to gain more from their coursework.*
- *Providing a focus for students' understanding of the*

I left with the feeling that this duo could cook up more than enough ideas to keep a full industrial research center actively engaged if they were aimed at any particular problem.

profession, and helps them formulate meaningful plans for their futures – practice of the profession or graduate study.

- *Fostering creativity, where traditional courses tend to discourage it.*

In 2000, Chuck received a *State of Georgia Regent's Award* for his leadership in this regard.

THE ECKERT-LIOTTA TEAM

In addition to the institutional issues that helped attract Chuck to Georgia Tech, an important personal connection also encouraged the move. Charlie Liotta, an internationally well-known organic chemist in the Tech School of Chemistry, jokes that they built the School of Chemistry around him, since he has been there for 39 years. Chuck and Charlie became personally acquainted during numerous interactions as consultants for DuPont. Their hosts at DuPont would often team them together during consulting visits, and Chuck and Charlie eventually realized that there must be a message there. Indeed, their mutual technical interests and strengths were extremely complementary, and possibilities for collaboration were often discussed but never acted upon—until the opportunity for Chuck to move to Georgia Tech materialized. Ron Rousseau, Chairman of Chemical and Biomolecular Engineering at Tech, enlisted Charlie's active participation in recruiting Chuck in 1989, and the "dynamic duo" has been inseparable ever since. Together, they have published over fifty papers in the past fourteen years. Moreover, all of the most recent and current PhD and MS students that Chuck and Charlie supervise in both chemical engineering and chemistry are done jointly.

I have been lucky enough to participate in one of their weekly high-energy group meetings, and the intellectual intensity there was impressive. I left with the feeling that this duo could cook up more than enough ideas to keep a full industrial research center actively engaged if they were aimed at any particular problem.

Chuck indicates that much of the focus of their current research is on sustainable development and environmentally benign processing. This includes a variety of phase transfer catalysis-related projects, under supercritical and near-critical conditions. These topics integrate three long-time favorite subjects of Chuck's: phase equilibrium, high-pressure reactions, and supercritical partitioning. Based on the past experience, this will be a good area to expect future developments! □

The University of Alabama

C.S. BRAZEL, D.W. ARNOLD, G.C. APRIL, A.M. LANE, J.M. WIEST
The University of Alabama • Tuscaloosa, Alabama 35487-0203



Denny Chimes, one of the most recognizable features of the UA campus, framed by a dogwood tree in full bloom.

A sunny fall weekend in Alabama conjures up images of the storied traditions of The University of Alabama (UA): the aroma of Southern barbecue fills the air; alumni and students, as well as many others, descend on campus for a three-day tailgating party; many pay homage to the past by visiting the Paul “Bear” Bryant Museum, and crowds gather at Bryant-Denny stadium to cheer on the famed Crimson Tide. When the weekend passes, the visitors return to their normal lives in Tuscaloosa (home city to UA) and elsewhere, and the excitement of the big game is replaced by activities of the 20,000 students.

Set at the southern end of the Appalachians and bordered by the Black Warrior River, UA’s campus was established in 1831 and has seen many historic moments. Several buildings on campus survived the U.S. Civil War, and Governor Wallace’s stand in the schoolhouse door brings to mind a more ignominious past. Today, The University of Alabama provides a breadth of educational options for a diverse student body— from liberal arts and business to law, science, and engineering.

LIVING IN WEST CENTRAL ALABAMA

Tuscaloosa’s metropolitan area of 125,000 bustles with more than just University activities. About an hour’s drive west of Birmingham, Tuscaloosa is nestled in a forested area dotted with numerous recreational lakes. The spring and fall seasons are especially long and pleasant, inviting the outdoor enthusiast to participate in any number of pastimes. Tuscaloosa’s sister city of Northport is an active arts center that hosts the annual Kentuck festival each fall and numerous music and performing arts activities year-round. Local industries that employ our graduates include JVC America Inc., Hunt Oil Co.,

RadiciSpandex Co., Southern Heat Exchanger Corp., and Mercedes-Benz US International Inc.

The University of Alabama is central to the city of Tuscaloosa in both geography and spirit. It has an aesthetic appeal, with large grassy malls, tree-lined sidewalks, and campus buildings with stately Southern grace.

Sitting on the opposite side of campus from Bryant-Denny stadium, the Chemical Engineering Department is housed in the Tom Beville Building, one of the more recent additions to campus. It houses modern research laboratories, faculty offices, conference rooms, and interactive classrooms.

HISTORY AND GROWTH OF ChE AT UA

The College of Engineering at UA is the third oldest continuously operating engineering program in the country. Created in 1837, just six years after the formation of the University, the College remains an active and vital part of the University's higher education mission and solidifies the institution as the capstone for higher education in the State of Alabama. With nearly 15,000 undergraduate and 5,000 graduate students, UA is one of seven major PhD-granting institutions in Alabama. The campus is made up of eight colleges, with the College of Engineering representing about ten percent of the student population, but thirty percent of the honors students.

Established in 1910, the Chemical Engineering Department, like many others in the nation, originated out of a need for a degree that emphasized industrial aspects of chemistry. Its establishment was just one year after the inception of the American Institute of Chemical Engineers. The first UA chemical engineering degree was awarded in 1914.

During the early years, a professional degree was available to students in addition to the traditional BS and MS degrees. Then, in the early 1960s, the College of Engineering developed its PhD degree programs in response to the arrival of NASA and other research-intensive organizations in northern Alabama. The department awarded the first two PhD degrees in the College of Engineering in 1964.

Throughout the years, the changing face of the chemical industry has been reflected within UA's chemical engineering degree program. From highly practical BS and MS degree programs through the '60s and '70s, the department has evolved to keep pace with changes in industry and made sure that its ChE degree has retained relevance as student career choices have become more diverse. The mission of the Department has always been

UA's Chemical Engineering Department maintains an active role in the national curriculum reform efforts, striving to balance the important core concepts at the heart of chemical engineering with changing and emerging technologies.



UA chemical engineering graduates of 2003 stand along the stately stairs of the President's Mansion, one of a handful of buildings at UA to have survived the Civil War.

and remains to educate young professionals as translators of fundamental knowledge into viable solutions to problems that are technically, environmentally, sociologically, economically, and globally significant.

Today, UA's chemical engineering department comprises 230 undergraduate and 30 graduate students, along with a full-time staff of 18, including 12 professors. The program offers BS (since 1910), MS (since 1910), and PhD (since 1964) degrees

and annually graduates more than 40 undergraduates and eight graduate students.

UA students find employment in all areas of industry, from fine chemicals and consumer products to polymers and petrochemicals, or they pursue advanced study in graduate school, medical/dental school, or law school. Many undergraduates opt for minors or departmental certificates in areas such as business or environmental engineering. With more than thirty percent of its students graduating with honors, chemical engineering is a leader in the College and University for its diversity (more than forty percent women and fifteen percent minorities), its leadership, and its quest for excellence.

As one astute alumnus observed during a campus visit, although the Department's image has been transformed throughout the years, "the fundamental parts that made a chemical engineer in the 1960s remain as important for the chemical engineer in the new millennium." While this assessment shows the continued strength of a core chemical engineering degree, the Chemical Engineering Department continues to evolve to accommodate the new technologies that are just becoming visible on the horizon.

ChE FACULTY

There are currently 12 full-time, tenured, or tenure-track faculty in the Department. They include four full professors, three associate professors, and five assistant professors. Griffin serves as the Southeastern NIGEC Director and the State of Alabama EPSCoR Director. All faculty members are fully engaged in the instructional and research programs at the undergraduate and graduate levels. Collectively, the department has averaged more than \$2 million of externally funded awards over the last five years, resulting in a top-35 ranking for expenditures for chemical engineering research as compiled by NSF for the last three years (1999-2001). In addition, ASEE has consistently ranked the department among the top 50 chemical engineering BS-degree-granting institutions.

UNDERGRADUATE PROGRAMS

From a student's perspective, the Chemical Engineering Department offers several unique opportunities. Undergraduates get to know all of their professors during their four years on campus. As freshmen, the students take a one-hour introduction to chemical engineering course that focuses on informing students about career options, preparing them for problem solving, and building the camaraderie that grows between students during their time on campus. The AIChE student chapter actively involves the students in its meetings and outreach activities.

Chemical Engineering Faculty at The University of Alabama



Gary C. April, Department Head
University Research Professor
Ph.D., Louisiana State University, 1969
large system modeling • biomass conversion



David W. Arnold
Professor, Undergraduate Coordinator
Ph.D., Purdue University 1980
coal-water fuels • soil remediation



Christopher S. Brazel
Assistant Professor
Ph.D., Purdue University 1997
molecular design of polymer systems
• *drug delivery*



Eric Carlson
Associate Professor
Ph.D., University of Wyoming, 1986
numerical modeling of permeable media



Peter E. Clark
Associate Professor
Ph.D., Oklahoma State University, 1972
rheology of non-Newtonian fluids



Robert A. Griffin
Cudworth Professor; Director, Environmental Inst.
Ph.D., Utah State University, 1973
environmental • soil remediation



Duane T. Johnson
Assistant Professor
Ph.D., University of Florida, 1997
interfacial phenomena • magnetic dispersion technology
• *nonlinear dynamics*



Tonya M. Klein
Assistant Professor
Ph.D., North Carolina State University, 1999
chemical vapor deposition for electronics



Alan M. Lane
Professor
Ph.D., University of Massachusetts, 1984
catalysis • colloids



Stephen M.C. Ritchie
Assistant Professor
Ph.D., University of Kentucky, 2001
advanced membrane structures for environmental separations



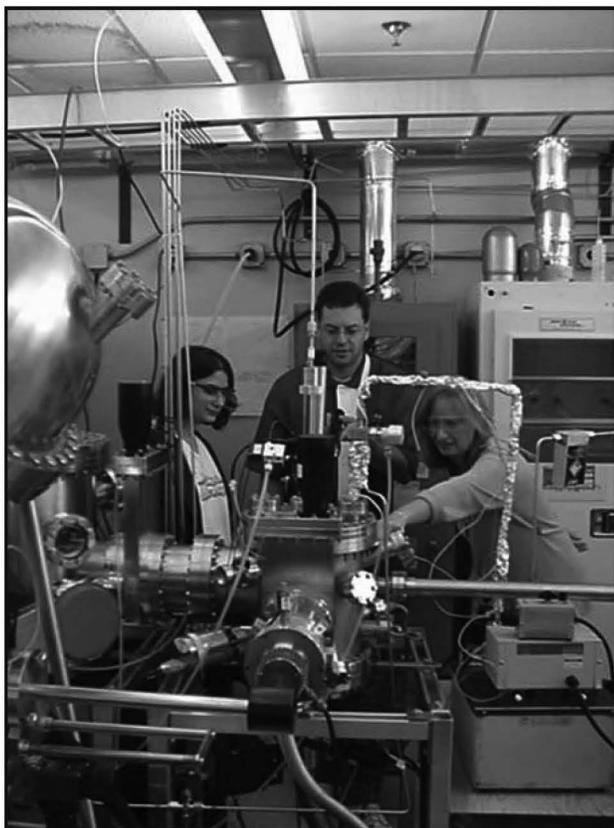
C. Heath Turner
Assistant Professor
Ph.D., North Carolina State University, 2002
chemical reaction simulations



Mark L. Weaver
Adjunct Associate Professor
Ph.D., University of Florida, 1995
microstructural characterization and tribology of bulk and thin films



John M. Wiest
Associate Professor
Ph.D., University of Wisconsin, 1986
molecular rheology • transport phenomena



Dr. Klein (right) runs a chemical vapor deposition experiment with researchers in her laboratory.

The students form the heart of the department, and their enthusiasm for UA chemical engineering shows at times such as E-Day, where the students take the lead role in preparing tours, demonstrations, and discussions for prospective engineering students from high schools across Alabama. The AIChE group also has a tradition of hosting a friendly picnic with the AIChE student chapter from one of our rival schools, Mississippi State.

As students progress through the curriculum, they can take advantage of numerous educational opportunities. Nearly thirty percent of the students are involved in cooperative education. Involvement in undergraduate research has increased significantly in the past five years, with more than one-third of the students working in a chemical engineering research lab.

The chemical engineering curriculum is centered around the traditional chemical engineering courses in material and energy balances, thermodynamics, and reaction and transport phenomena. The students also take advanced elective courses, two of which are technical—an advanced chemistry and an advanced chemical engineering course. The availability of engineering electives in chemical engineering has increased substantially with the influx of new assistant professors in the past five years. Four new junior/senior/graduate student electives have been taught for the first time at



Dr. Lane (also known as the blues guitarist Doobie 'Doghouse' Wilson) gets his class involved in the Reynolds' Rap.

UA since 2000. Two additional electives can be selected from nearly anything offered on campus; students simply have to justify their selection by describing how the course will aid their careers. With the wide availability of courses at UA, many choose to fill these electives with business classes, biology courses, foreign languages, environmental engineering classes, or undergraduate research.

Summer Lab

One of the unique educational experiences at UA comes in the early summer after completion of the junior year. "Summer lab" is a five-credit-hour course that is perhaps the most intense unit operations laboratory in the country. Lab is in session from 8 a.m. to 5 p.m., Monday through Saturday, for five weeks. It is taught in May to early June each year to avoid scheduling conflicts and distractions for the students. If you were to ask an undergraduate about summer lab, you would likely get one of two answers: "It's scary, the time commitment is overwhelming," or "It was the most significant event during my time at UA." The first statement represents what summer lab looks like to the freshmen, sophomores, and juniors, while the attitude shifts as seniors realize that the intense working environment not only pulls together the theory they have learned in other chemical engineering courses, but also prepares them for their careers.

By working in teams of three-to-five students, the students gain valuable experience with team dynamics while they work on five different experiments led by three to four professors. The experiments change from year to year. Teams receive short assignments composed of one-paragraph statements at the first lab meeting on the first Saturday. After an extensive safety review, they are released to write proposals, determine equipment to be used, and perform preliminary work. The students must prepare a proposal that is approved by the faculty for each experiment, followed by two days to build and run the experi-

. . . the department has evolved to keep pace with changes in industry and made sure that its ChE degree has retained relevance as student career choices have become more diverse.

ment, to compile and submit a technical report, and to present their results.

During the work, each group meets with the instructor to discuss experimental strategies and give progress reports. These meetings are designed to simulate an industrial setting; they are informal and may last as long as two hours. Team members answer questions on all aspects of the experiment at the proposal meeting. The challenge to create an acceptable proposal rests on the team and often requires several drafts. Great emphasis is placed on the proposal so the students understand what they are doing in lab and can get meaningful results. The instructors are heavily involved in supervision of the experiments.

Undergraduate Honors Program

A relative newcomer to the undergraduate curriculum is an honors program specifically for chemical engineering students. The requirements to join it match that of the University Honors College, and the courses carry through the junior and senior year. This curriculum requires a total of twelve hours of honors classes, with at least six hours in chemical engineering. Honors forum classes are taught at two levels: sophomore level (beginning of ChE curriculum) and junior/senior level. The forum subject rotates from semester to semester, with different instructors delving into recent developments in chemical engineering, such as "Engineering the Hydrogen Economy" and "Bionanotechnology." The honors co-op and internship program allows advanced students to work with industrial mentors and to earn honors credit upon presenting project findings to faculty. Industrial recruiters have shown marked enthusiasm about the honors co-op program, and we will learn more as UA's chemical engineering honors program matures.

GRADUATE EDUCATION AND RESEARCH

The department has offered graduate degrees in chemical engineering since 1914. The emphasis has shifted over the



The Tom Beville building, home to chemical engineering at UA.

last decade from masters to doctoral degrees. This has been accompanied by an increase in externally funded research from just under \$1 million to more than \$3 million in 2003. The laboratories and graduate student offices were custom designed by the faculty when the building was constructed in 1994.

A hallmark of our research program is collaboration with chemists, physicists, biologists, mathematicians, and other engineers in a variety of

campus-wide research centers. The Center for Materials for Information Technology (MINT) was established in 1990 in response to JVC's 1986 decision to locate a magnetic tape manufacturing facility in Tuscaloosa, as well as a large concentration of the data storage industry in the Southeast. Chemical engineering faculty (Arnold, Johnson, Klein, Lane, Weaver, Wiest) joined other faculty in science and engineering to earn an NSF Materials Research Science and Engineering Center grant in 1994 (the first ever in the Southeast) with renewals in 1998 and 2002. The emphasis is on developing new materials for high-density data storage and spintronics.

Mercedes-Benz located their only US-based production facility in Tuscaloosa in 1993, manufacturing the M-class SUV here. Honda, Hyundai, Nissan, Toyota, and the supporting industrial suppliers followed soon after, making the region a center for automobile manufacturing. UA supports this industry through the Center for Advanced Vehicle Technology, in which the multidisciplinary fuel cell research group plays a leading role. With a focus on materials, chemical engineering faculty (Lane, Wiest, Turner, Klein, Ritchie, Weaver) are developing new catalysts for hydrogen production and fuel cells.

A microelectromechanical systems (MEMS) laboratory was established in 2002. Initial work by Klein and collaborators focuses on the microfabrication of gyroscopes. They recently won an NSF grant to incorporate MEMS technology into the undergraduate program.



A sophomore demonstrates complex viscosity properties to high school students on E-Day.



Charlotte Nix runs a demonstration of environmental hazards of oil contamination for Project ROSE. The audience included high school students and their parents who were visiting the UA campus for E-Day.

A long-standing departmental emphasis on environmental research is now complemented by the university's Center for Green Manufacturing. Major projects have included waterborne magnetic inks (Lane, Arnold), biomass conversion (April), soil remediation (Arnold), and benign solvents and additives for the polymer industry (Brazel).

The mining and petroleum industries remain a vital part of the Alabama economy and are served by Carlson (subsurface modeling) and Clark (complex rheology). Clark was recently honored as a Society of Petroleum Engineers Distinguished Lecturer. He presented invited lectures throughout the U.S. during the 2002-2003 academic year.

The department is particularly proud of its NSF CAREER award recipients. Mark Weaver has been studying multilayer thermal barrier coatings since 1999, addressing the influence of thermal exposure on the interfacial microstructure. Tonya Klein began her work in the fall of 2003 on plasma-enhanced, atomic layer deposition, which is an advancement of traditional chemical vapor deposition.

The strong collaborations among chemical engineering faculty, their colleagues across campus, and the industries we serve result in a fun and exciting atmosphere in which to conduct truly cutting-edge research.

OUTREACH PROGRAMS

Among the various outreach activities of the Department, Project ROSE (Recycled Oil Saves Energy) stands out in both statewide impact and longevity. Project ROSE, under the direction of Gary April, has been running successfully for 27 years. It involves both a public awareness arm and activities to aid local communities in Alabama in collecting used motor oil for reclamation and recycle. Outreach to school groups includes environmental models to explain the effects of point source and non-point source contamination on ecosystem management. Project ROSE is run by two chemical engineering staff members: Ms. Sheri Powell and Ms. Charlotte Nix, who conduct demonstrations throughout the state. Project ROSE recently celebrated its active presence in all 67 Alabama counties.

THE FUTURE

UA's Chemical Engineering Department maintains an active role in the national curriculum reform efforts, striving to balance the important core concepts at the heart of chemical engineering with changing and emerging technologies. We are forging new relationships with the biological sciences department on campus and continue to expand our research programs through collaborations within and beyond the Tuscaloosa campus. Ultimately, our commitment to education is expressed in the opportunities afforded our students and the careers of our graduates.

ROLL TIDE ! □

A FLUIDIZED BED ADSORPTION LABORATORY EXPERIMENT

PAMELA R. WRIGHT,* XUE LIU, BENJAMIN J. GLASSER
Rutgers University • Piscataway, NJ 08854

There are a variety of pedagogical and motivational advantages in exposing students to real process equipment in a laboratory course.^[1] There is also a need, however, to use simple laboratory experiments in order to help students better understand basic principles learned in their coursework. Therefore, it is often advantageous to start students off with simple experiments where the connection to basic principles is obvious and then move on to more challenging and complex systems that resemble real-world situations.

A fluidized bed adsorption process provides a somewhat unique opportunity for students to carry out a series of experiments (on one piece of apparatus) that steadily approaches the real process equipment. The series starts with a study of bed expansion in a fluidized bed, goes on to residence time distribution measurements, and ends with a study of a bioseparation in a fluidized bed. This allows students to build upon ideas they have already learned in fluid mechanics, mass transfer, separations, and reaction engineering. The experiment was developed in the Department of Chemical and Biochemical Engineering at Rutgers University and forms part of the Process Engineering Laboratory course for seniors.

PROCESS OVERVIEW

Advances in biotechnology have resulted in the production of a multitude of therapeutic proteins by mammalian, bacterial, and yeast fermentations. The global market for therapeutic proteins used in the treatment of cancer and AIDS, as well as growth factors and monoclonal antibodies for diagnostic applications is rising. Current work on genomics and proteomics is likely to make it easier to discover new therapeutic proteins, which will in turn lead to an increase in the production of proteins.

At the same time, primary recovery and purification of the protein from the fermentation broth continues to be a significant limiting factor in the overall economics of therapeutic protein production. Therefore, bioseparations is a critical step both from a processing and research point of view. In fact, as

much as 80% of the production costs for many proteins can be incurred during product isolation and purification.^[2] For example, therapeutic proteins such as interferons and interleukins are considered high-value proteins with a price of \$1,000,000 per gram or more.^[3] Product concentrations in a typical feed stream are low, between 10^{-2} and 10^{-6} mg/L, and much of the high manufacturing costs can be attributed to recovery time and product losses across each step of the purification process.^[4] In addition, the final purified product must often be greater than 99.9% pure, with less than 10 pg per dose of nucleic acids and endotoxins.^[5]

In the biotechnology and pharmaceutical industries, ion exchange chromatography (IEC) is the most widely used operation for purification of proteins. The operation typically involves a packed bed of resin particles or adsorbent beads that selectively adsorb the target protein. After the resin par-



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Xue Liu received his BS and MS from Tsinghua University (China). Currently he is a PhD student at Rutgers University. His research is in the field of gas-particle flows in fluidized beds and risers.



Benjamin J. Glasser is Associate Professor of Chemical and Biochemical Engineering at Rutgers University. He earned degrees in chemical engineering from the University of the Witwatersrand (BS, MS) and Princeton University (PhD). His research interests include gas-particle flows, granular flows, multiphase reactors, and nonlinear dynamics of transport processes.

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ticles become filled with protein, the feed to the column is stopped and an eluent buffer is passed through the column in an elution step. This leads to the product being released into the eluent buffer, and the end result is that the product is typically concentrated 10X to 40X.

Generally, the fermentation broths contain suspended solids, *e.g.*, cells or cell debris that would clog a packed bed. To prevent this, feedstocks are usually clarified by filtration or centrifugation before the chromatographic separation in order to remove the cell debris. Fluidized or expanded bed adsorption has increasingly become an alternative method of interest for adsorption of proteins from feedstocks containing cells.^[6,7] In this process, a bed of adsorbent beads is expanded or fluidized by the upflow of liquid, leading to large voids between the adsorbent beads and allowing cells and cellular debris to pass through the bed without becoming trapped. As a result, fluidized bed adsorption eliminates the need for the expensive operations of filtration and centrifugation.

Another advantage that fluidized bed adsorption has over a packed bed is enhanced mass transfer, which can lead to increased process yields.^[8] This means that for a given pressure drop across the bed, the fluidized bed can in principle achieve a higher rate of protein removal. For these reasons, this technology is increasingly being applied as a downstream separation technique in the pharmaceutical and biotechnology industries. At the present time, the technique has been used for the recovery of recombinant proteins from mammalian cell culture and *E. coli* fermentation broths.^[9-11]

Karau, *et al.*,^[12] defined expanded bed adsorption as a subset of fluidized bed adsorption that specifically addresses situations with low superficial velocities close to the minimum fluidization velocity. For most resins, the expression “expanded bed adsorption” is applicable only to bed expansions of less than two times the settled bed height. In this article, adsorption is investigated at bed expansions of two to four-

... it is often advantageous to start students off with simple experiments where the connection to basic principles is obvious and then move on to more challenging and complex systems that resemble real-world situations.

and-one-half times the settled bed height. Thus, the expression “fluidized bed adsorption” is used to emphasize that we are investigating protein adsorption for a large range of bed expansions, including high expansions.

The basic process of fluidized bed adsorption includes the application of feed through the bottom of a column filled with resin, as illustrated in Figure 1. Initially, the resin is settled, but the upward feed flow results in suspension or fluidization of the resin bed. Product in the feedstock adsorbs to the resin while nonproduct solid material (*e.g.*, cell debris) washes out with the spent feed. Subsequent washing with a buffer further removes nonproduct solid material that may remain associated with the resin. Product is then recovered by introducing an eluent buffer (salt solution) through the top of the column. To minimize process volumes, elution is usually conducted in the packed-bed mode where the product is concentrated 10X to 40X. After elution, the resin can be cleaned and regenerated for repeated use.

To determine the bed expansion characteristics, study the effects of liquid velocity and bed expansion on the flow hydrodynamics, and identify the dominant mechanistic features in a fluidized bed adsorption column, the laboratory course is divided into three parts: bed expansion characterization, tracer studies, and adsorption of protein. Each of the three experiments involved in this project requires approximately four hours of work and is carried out in a single afternoon. Experiments are finished in three weeks, and the project write-up is due in the fourth week. Before the first day of each lab, students are required to read the introduction section from the laboratory manual for that week’s experiments as well as related materials in the library.

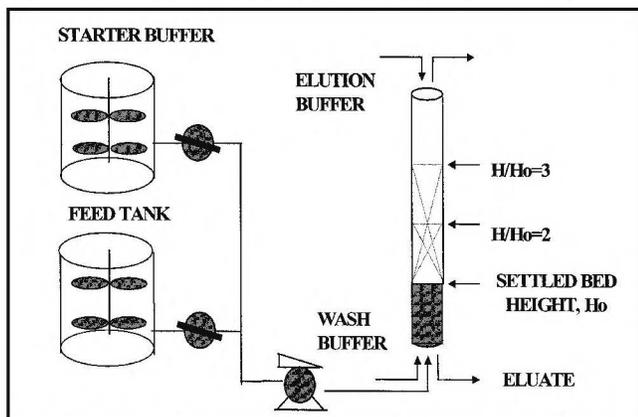


Figure 1. Schematic of normal operating mode of fluidized bed adsorption process.

EXPERIMENTAL EQUIPMENT AND MATERIALS

The laboratory equipment consists of a Streamline 50 expanded bed adsorption column (Pharmacia Biotech, Piscataway, NJ), a peristaltic pump, an in-line UV sensor, and a UV analyzer. A schematic of the experimental setup is shown in Figure 2 (next page), with the principal components listed in the caption. The column is constructed of a borosilicate glass tube, 5 cm in diameter and 100 cm long. The normal operating pressure is less than 0.5 bar, but the column can withstand pressures up to 1 bar. The column should not be operated above 1 bar pressure or without liquid.

The column is supported by a stainless steel mounting for

protection and contains an adsorbing resin. The minimum resin loading is 200 mL or 10 cm settled height; the maximum loading is 600 mL or 30 cm settled height. The resin is retained by a stainless steel 60-mesh screen at the base of the column. A peristaltic pump is used to pump fluid into the base of the column through a stainless steel distributor plate with 12 equally spaced 1-mm holes. The distributor plate is mounted in the base of the column below the screen and it and the screen are held in place with rubber gaskets. The column is equipped with a moveable rod piston fitted with a 60-mesh screen to retain the resin at high flow rates or high expansions. During operation, the piston is moved just above the expanded bed height to minimize head space. Spent charge is pumped out through the piston and fed to an in-line UV sensor (Wedgewood Technology, San Carlos, CA).

The signal from the sensor is analyzed by an UV analyzer at 280 nm. The resin used in the experiment is Streamline SP (Pharmacia Biotech, Piscataway, NJ), which is a cation exchange resin with a particle radius range from 45 to 178 μm . A Malvern Mastersizer X was used to determine that the average particle radius is 89 μm , with a particle-size distribution that is approximately Gaussian with a skewness of 0.878. Streamline SP has been used previously in several fluidized bed adsorption applications, and its hydrodynamic and expansion properties are well characterized.^[10,13,14] The average particle density is 1.18 g/mL. Each particle is composed of a crystalline quartz core, covered by 6% cross-linked agarose. The dynamic binding capacity reported by the manufacturer is 70–85 mg/mL for most proteins. Bound proteins inside the particle remain attached at one adsorption site until they are eluted.

The protein lysozyme (EC 3.2.1.17, Sigma Chemical Company, St. Louis, MO) was selected as an adsorbing species since it is relatively inexpensive, well-characterized, and easily assayed by spectrophotometric methods. Most importantly, it adsorbs and desorbs readily from Streamline SP resin.

Lysozyme is a globular protein with hydrolytic enzyme properties. It is nearly spherical, with dimensions of 4.5 x 3 x 3 nm.^[15] The molecular weight is 14,600 and the isoelectric pH is 10.7 to 11.3.^[16] This high isoelectric pH allows adsorption by cation exchange resins at a wide range of pH values. A point worth mentioning is that the use of protein is not, in principle, necessary for this experiment. One could do a much less expensive experiment by changing the protein adsorption into an ion exchange experiment—for example, exchanging Na^+ from a NaCl solution. We believe, however, that stu-

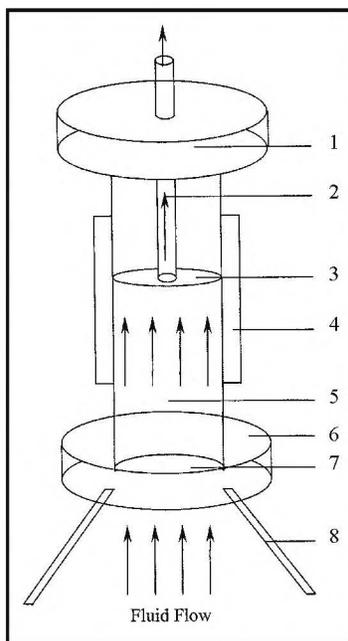


Figure 2. Fluidized bed adsorption column.

1. Top flange
2. Adapter rod piston
3. Adapter distributor and net
4. Stainless steel mount
5. Glass column
6. Bottom flange
7. Column distributor and net
8. Stand

dents benefit from being exposed to a bioseparation and working with a real protein and a commercial resin.

EXPERIMENTAL PROCEDURE

Column Setup • Before experiments, students are required to familiarize themselves with the standard operating procedure for operating the Streamline 50 expanded bed adsorption column. The procedure is

- The first step is to remove the adapter from the column. The purpose of the adapter is to minimize the head space above the resin particles during fluidization. To push out the adapter from the column, use the hydraulic pump to pump water into the base of the column at a pump setting of 2 (150 mL/min). The adapter rises. Stop pumping when the adapter sits in the upper flange at the top of the column. Then remove the domed nuts and washers on the lid, raise the lid, and remove the piston and adapter plate. Once the piston and adapter have been removed, reverse the pump to decrease the level of water in the column to approximately 30 cm.

- Prepare an adsorbent-water slurry with deionized water. To maintain the dynamic

binding capacity, the adsorbent should always remain wet—by no means should it ever be isolated via filtration. Quickly pour the slurry into the column. Resuspend any adsorbent remaining in the container with deionized water and pour this into the column. If aggregates of air-adsorbent remain floating on the liquid surface, they need to be removed or pushed down into the liquid. Allow the resin to settle and add more resin if necessary to obtain desired settled bed height. Fill the column to the rim of the glass tube with deionized water.

- When the column is secure in the steel mounting assembly, carefully tilt the adapter and insert it into the column so that one side of the gasket on the adapter net is in the water-filled column. Without trapping air under the net, carefully put the adapter into a vertical position. Slowly push the adapter down until the gasket can be seen under the upper flange. When the adapter is firmly seated in the column, push down the lid and replace the washers and domed nuts. Fill the space above the adapter with deionized water.

- To lower or raise the adapter, pump deionized water into the column side connector (above the adapter) or into the base of the column at a pump setting of 2 (150

mL/min). Stop the pump when the adapter is at the desired height in the column. Once the resin is in the column and the adapter height has been set, the column is ready for operation.

Bed Expansion Characterization • The first step prior to starting adsorption is to characterize the bed expansion as a function of linear velocity and viscosity in a nonadsorbing system with 200 mL of resin in the column. Viscous and non-viscous fluids are pumped into the base of the column at four different linear velocities. The expanded bed height is measured at each velocity to obtain expansion plots and Richardson-Zaki plots.^[17] This information is used to compare fluidization conditions with published results and also to identify desirable conditions for adsorption studies.

In this experiment, students are divided into three groups and each group carries out experiments with a fluid of different viscosity. The groups share their data at the end of the experiment in order to increase the amount of data each group has to analyze. Group A performs experiments using a 0.05 mol/L sodium acetate buffer solution with 0% glycerol and a sodium acetate buffer solution with 5% glycerol. Group B performs experiments with a 0.05 mol/L sodium acetate buffer solution with 0% glycerol and a sodium acetate buffer solution with 15% glycerol. Group C uses a 0.05 mol/L sodium acetate buffer solution with 0% glycerol and a sodium acetate buffer solution with 30% glycerol. The fluid viscosity is measured by a viscometer. The experimental procedure is

- Record the pump setting and allow ten minutes for the bed to stabilize. The flow rate is determined by the volume collected per unit time (mL/min). Once the flow rate is known, the linear superficial velocity is just the flow rate divided by the cross-sectional area.

- After ten minutes has passed, read off the stabilized expanded bed height. The McCabe equation below determines the fluidized bed porosity:^[18]

$$\frac{H}{H_0} = \frac{(1 - \epsilon_0)}{(1 - \epsilon)} \quad (1)$$

where ϵ_0 is the voidage of the particles in settled bed mode, H_0 is the settled bed height, H is the expanded bed height, and ϵ is the expanded bed porosity. A value of $\epsilon_0 = 0.4$ was measured for the particles in settled bed mode.

- After the experiment, students can plot the logarithm of the linear superficial velocity versus the logarithm of the expanded bed porosity. The slope of this line is the Richardson-Zaki coefficient.^[17]

Tracer Studies • To characterize the internal flow hydrodynamics and axial mixing of Streamline SP resin, tracer studies are performed using a 0.25% acetone pulse to determine the dispersion and residence time distribution (RTD) characteristics of the system as a function of bed expansion. The

[This] experiment also provides an opportunity for students to carry out a series of experiments that increases in complexity and approaches the real process equipment.

acetone is added into the sodium acetate buffer as well as the various percentage glycerol buffer solutions. The acetone at the column outlet is monitored by the UV analyzer at 280 nm for a given degree of bed expansion, which is determined by the liquid velocity corresponding to each fluidized bed height. Students can obtain this information from the *Bed Expansion Characterization*. A positive step signal is used to obtain residence time distributions by the F-curve method.^[19] Measurements associated with the positive step signal lead to an F-curve. The data in the F-curve is then differentiated to obtain the C-curve. Values for the variance (σ_B^2) of the C curve are used to calculate the mean residence time in the expanded bed, axial dispersion coefficient (D_{ax}), and the number of theoretical plates (N). In the interest of saving time, only one run per a given flow rate is carried out. The experimental procedure is

- After recording such information as pH, temperature, flow rate, and the characteristics of the solution, students should move the adapter approximately 1 cm above the desired expansion height. A large gap (or large head space) above the resin may lead to a region of pure fluid above the resin, and this will affect the residence time distribution measurements. Start the recorder/UV-monitor and allow it to warm up for 20 minutes or more. Prior to expansion, two 20-L carboys need to be set up. One should be filled with sodium acetate buffer solution and the other should be filled with tracer (0.25% acetone in sodium acetate buffer solution). Air bubbles should be evacuated from the lines before expansion. Once the adapter is in position, bed expansion can be started by introducing the buffer solution. When the bed is fully expanded at the test flow rate, note the expanded bed height from the calibrated column and continue pumping buffer. At this time, zero the UV sensor. After this is done, unclamp and bleed the tracer line and clamp the buffer line.

- At the instant tracer is introduced, begin to record the time and UV readings from the sensor. UV recordings should be taken every 30 seconds in the beginning, until an increase in activity is noticed, at which point readings should be taken every 15 seconds. Continue to take readings approximately 5-10 minutes after the UV readings have leveled off.

- Then clamp the tracer line and re-open the buffer line. Record this time and continue to record UV readings in 15-30-second intervals until the readings go

down to approximately zero.

■ Every group should do three expansions that include 2X, 3.3X, and 4.5X the settled height.

Adsorption of Protein • After examining particle fluidization and axial dispersion characteristics of the resin, dynamic adsorption capacities are measured for the resin to assess mass-transfer effects under different hydrodynamic conditions. To identify the dominant mechanistic features of the fluidized bed adsorption system, the fluidization studies should be designed to isolate mass-transfer effects from hydrodynamic effects. This can be accomplished by frontal analysis of breakthrough curves to determine dynamic adsorption capacity of the resin under varying conditions of linear velocity, viscosity, and axial dispersion. The experimental procedure is

■ Prior to experimentation, several initial steps should be performed. The resin should be washed with 10 L of a 1-mol/L NaCl solution at a pump setting of 1.5 (100 mL/min). This expands the bed and allows for proper cleaning of the resin. Following the salt solution wash, 20 L of deionized water should be introduced into the column with a pump setting of 1.5 (100 mL/min). This removes the salt as well as other impurities that are introduced while the resin is sitting immobile in the column. The conductivity of the outlet should be checked to ensure all the salt has been removed by obtaining a conductivity reading of less than 5 mS. If the conductivity is too high, continue washing the resin with another 10 L of deionized water. Equilibrate the resin with 20 L of a 0.05-mol/L sodium acetate buffer solution at a pH of 5. If the resin is not equilibrated to the buffer, inaccurate data will be obtained for the adsorption. Prior to experimentation, additional buffer solution (20 L) as well as protein solution (10 L) should be prepared, and the UV sensor should be allowed to warm up for 20 minutes to obtain accurate readings for concentration. Then zero the UV sensor using 0.05-mol/L sodium acetate buffer.

■ Before starting the experiments, a sample of the protein solution should be introduced into the UV sensor to obtain an initial concentration reading. This is the C_0 value. The desired breakthrough concentration (usually 10 to 30% of initial concentration) is the breakthrough percentage multiplied by the initial concentration.

■ For operation of the column, the following procedure should be followed. From the *Bed Expansion Characterization*, students have a direct correlation between pump setting, linear velocity, and expanded bed height. Due to the expense of the protein, only one adsorption is carried out for each group. Group A uses a 2X expansion, Group B uses a 3.3X expansion, and Group C uses a 4.5X expansion. The lines to the column

should be bled prior to introducing any fluid into the column, and the lines from each solution must be void of air bubbles. The buffer solution should be introduced first in order to obtain a stable bed height.

■ Once this is achieved, the protein solution can be introduced. Record UV readings at 1-minute intervals until increased activity in the UV output is noticed. Then take UV readings at 30-second intervals until C/C_0 of 0.15 has been reached. This point is defined as column breakthrough, which is the point of reduced binding capacity. In most commercial applications, the adsorption is discontinued at a point where the exit concentration is 10% to 15% of the inlet feed concentration, to prevent unacceptable product losses. In this study, 15% has been used. Once breakthrough is achieved, the time should be recorded as well as the buffer volume.

■ After the above procedure has been finished, unclamp the buffer solution line and clamp the protein solution line. At this point, 10 L of a 1-mol/L NaCl solution at pH 5 should be introduced into the column at a pump setting of 1.5 (100 mL/min) to recover the protein. After that, 20 L of deionized water should be introduced into the column at a pump setting of 1.5

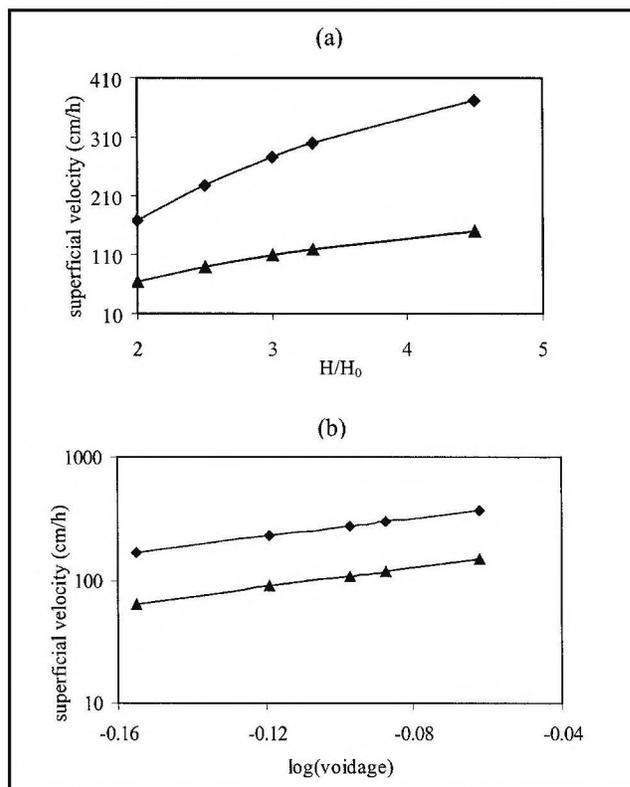


Figure 3. The characteristics of the bed expansion. (a) Plot of H/H_0 versus linear velocity in the buffer solution without glycerol (◆), and with 30% glycerol (▲). (b) Richardson-Zaki parameter plots in the buffer solution without glycerol (◆) and with 30% glycerol (▲).

(100 mL/min) to rinse the column and resin.

RESULTS AND DISCUSSION

Bed Expansion Characterization • The effects of fluid velocity and viscosity on the bed expansion can be seen in Figure 3. As would be expected, an increase in viscosity leads to a larger expansion for a given superficial velocity (see Figure 3a). Richardson and Zaki^[17] observed that if the log of the voidage was plotted versus the log of superficial fluidization velocity, a linear relationship is obtained. A correlation was developed and is generally called the “Richardson-Zaki equation,” written as

$$\frac{u_s}{u_t} = \varepsilon^{(n+1)} \quad (2)$$

where n is the Richardson-Zaki number, u_s is the superficial velocity, and u_t is the particle terminal velocity, which is a function of particle density, fluid density, particle diameter, and fluid viscosity. In the fluidized bed system, u_t can be seen as a constant. In order to compute the Richardson-Zaki number, n , one can plot the logarithm of linear velocity versus the

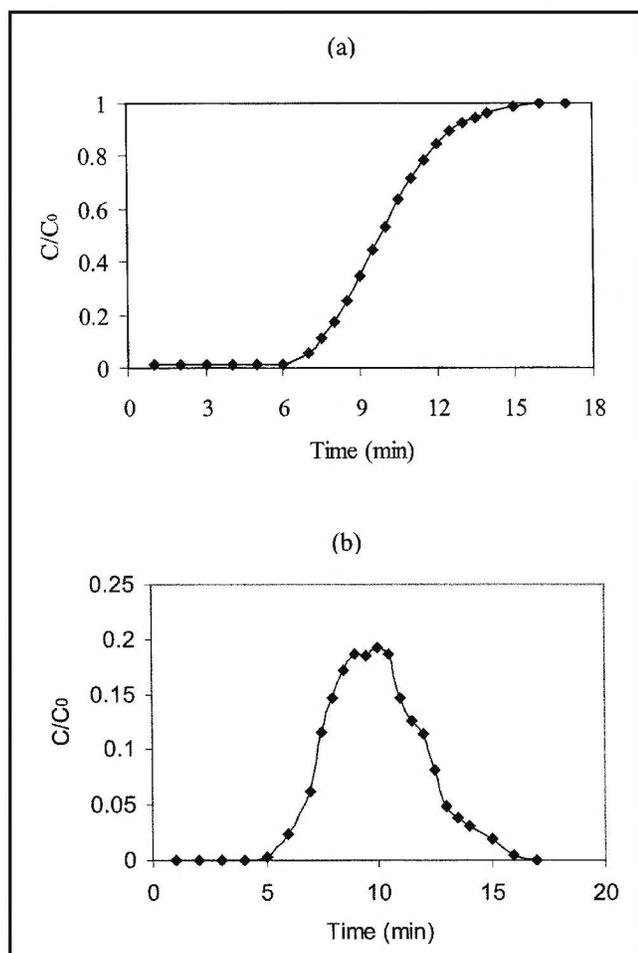


Figure 4. Acetone tracer curves for Streamline SP at an expansion of $H/H_0 = 2$ in 50 mol/L NAOAC buffer solution. (a) F-curve; (b) C-curve

logarithm of fluidized bed porosity. One should get a straight line with slope $n+1$. The Richardson-Zaki number is a function of the ratio of particle diameter to column diameter. Since the resin and the column are not changed during experiments, the Richardson-Zaki number should be the same for the different buffer solutions, as can be seen in Figure 3(b). Although the fluid viscosity does not change the Richardson-Zaki number, it does affect the bed expansion, as shown in Figure 3(a).

Tracer Studies • To characterize the internal flow hydrodynamics and axial mixing of Streamline SP, tracer studies are performed at different bed expansions. Good reproducibility is generally obtained from three trials at each condition and the standard deviation is generally less than 5% for each parameter. Figure 4 shows typical acetone tracer curves for Streamline SP at an expansion of $H/H_0 = 2$ in 0.05 mol/L NAOAC buffer. Axial dispersion coefficients are obtained from the variance, σ_θ^2 , in the C-curve as follows:^[12]

$$D_{ax} = (u_s H \sigma_\theta^2 / 2) \quad (3)$$

where H is the height of the fluidized bed and u_s is the superficial linear velocity. σ_θ^2 can be calculated in the following way:^[19]

$$t_{mean} = \left[\left(\int_0^\infty t C dt \right) / \left(\int_0^\infty C dt \right) \right] \quad (4)$$

$$\sigma^2 = \left[\left(\int_0^\infty (t - t_{mean})^2 C dt \right) / \left(\int_0^\infty C dt \right) \right] \quad (5)$$

$$\sigma_\theta^2 = (\sigma^2 / t_{mean}^2) \quad (6)$$

where C is the concentration of the tracer at time t . These quantities can be evaluated by making use of the following numerical integration formulas:

$$t_{mean} = \left[\left(\sum C_i t_i \Delta t_i \right) / \left(\sum C_i \Delta t_i \right) \right] \quad (7)$$

$$\sigma^2 = \left[\left(\sum (t_i - t_{mean})^2 * C_i \Delta t_i \right) / \left(\sum C_i \Delta t_i \right) \right] \quad (8)$$

where the data is divided into time intervals of Δt_i and C_i is the concentration of tracer at time t_i .

Once the value of σ_θ^2 and D_{ax} has been calculated, the Peclet number and the number of theoretical plates can be determined from

$$Pe = (u_s H / \varepsilon D_{ax}) \quad (9)$$

$$N = 1 / \sigma_\theta^2 \quad (10)$$

The axial dispersion coefficients for Streamline SP in buffer without glycerol at the expansion of 2X and 3.3X are computed to be $1.8 \times 10^{-6} \text{ m}^2/\text{s}$ and $7.27 \times 10^{-6} \text{ m}^2/\text{s}$, respectively. When 30% glycerol is added, axial dispersion is relatively unchanged at $H/H_0 = 2$, but lower linear velocities are required to obtain this same degree of expansion. For the fluid-

ized bed system, the Peclet number, which is the ratio of the convective transport to the dispersive transport in the expansion, can be used to quantify the extent of deviation from plug flow in the column.^[18] In true plug flow, the Peclet number approaches infinity. For completely mixed flow, the Peclet number approaches 0. In this study, the Peclet number ranges from 40 to 80, indicating a small deviation from plug flow.

Adsorption of Protein • For these experiments, the frontal analysis of breakthrough curves has been used to determine the effect of axial dispersion on adsorption in an expanded bed. The breakthrough curves are shown in Figure 5. To facilitate direct comparison of breakthrough, the adsorbed concentration, q , is normalized with respect to the equilibrium capacity q_0 and plotted as q/q_0 versus C/C_0 . As discussed earlier, breakthrough is defined as $C/C_0 = 0.15$ or at 15% of the feed concentration, C_0 . Results from RTD and frontal analysis are shown in Table 1 together with the q/q_0 values at breakthrough (*i.e.*, the q/q_0 value corresponding to $C/C_0 = 0.15$). Here the average residence time for each condition is defined as

$$\tau = \varepsilon H / u_s \quad (11)$$

When the expanded bed height is 2 times the settled bed height, the bed porosity, ε , is approximately 0.7. Under these conditions, the linear velocity is 168 cm/h, and q/q_0 is 0.97 at breakthrough. The addition of 30% glycerol resulted in an increased bulk phase viscosity and a linear velocity of only 64 cm/h is required to expand the bed to twice the settled height. Under this condition, breakthrough occurs at $q/q_0 = 0.86$ even though the residence time is significantly higher than for the buffer-only case. When Streamline SP is expanded to 3.3 times the settled height in buffer at 300 cm/h, q/q_0 decreases to 0.68 at breakthrough. The residence time does not change, but the axial dispersion increases compared to the case where $H/H_0 = 2$. Therefore, since the residence time is relatively constant, early breakthrough is likely due to increased axial dispersion.

When 30% glycerol is added, the expanded bed height increases to 4.5 times of the settled height at a reduced linear velocity of 150 cm/h, and a longer residence time than that for the $H/H_0 = 2$ expansion in glycerol is obtained. Here, breakthrough occurs even earlier at a q/q_0 value of 0.54 due to a 6-fold increase in axial dispersion. The shape of the breakthrough curves for Streamline SP resin under the conditions presented here is of interest as well. The breakthrough curves are all relatively sharp except for the condition of $H/H_0 = 4.5$ with 30% glycerol. In this case, a gradual breakthrough curve is obtained, indicating that a low level of lysozyme is bled through the column before breakthrough is established. In an actual application, this would amount to product loss.

These results suggest that a macroporous resin such as Streamline SP is best used for low viscosity feedstocks applied at intermediate linear velocities since dynamic capacities are severely reduced with higher viscosity feedstocks. It

should be mentioned that the particles used for this study were not elutriated, and so a wide particle size distribution was used for all cases (as supplied by the resin manufacturer). The effect of particle size distribution on breakthrough in fluidized bed adsorptions was investigated recently by Karau, *et al.*^[12] In their study, they found that particles with a wide size distribution would reduce axial dispersion compared to a narrow particle size distribution. The work described here could be extended by sieving the resin into narrow fractions and carrying out experiments to confirm the results of Karau, *et al.*

The results of this work also suggest that to maximize throughput with minimal product losses, the operation could be divided into two steps. Initially, one could operate at very high expansions until the onset of breakthrough due to high axial dispersion. At this point the particles are not saturated. Thus, the linear velocity can be reduced to decrease the bed height to a regime where only intraparticle or film mass transfer effects dominate. Adsorption could continue at this smaller expansion with a corresponding longer residence time and reduced axial dispersion until the point of breakthrough. Further experiments could be carried out to confirm this hypothesis.

CONCLUSIONS

This paper describes an experiment that exposes students

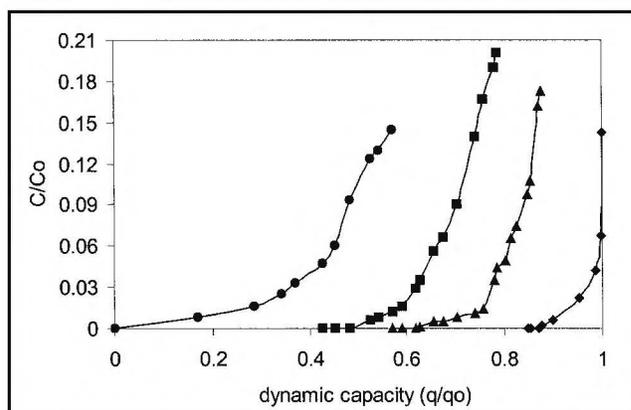


Figure 5. Breakthrough curves for Streamline SP.

- ◆ $H/H_0 = 2$, 0% glycerol and $u_s = 168$ cm/h
- $H/H_0 = 3.3$, 0% glycerol and $u_s = 300$ cm/h
- ▲ $H/H_0 = 2$, 30% glycerol and $u_s = 64$ cm/h
- $H/H_0 = 4.5$, 30% glycerol and $u_s = 150$ cm/h

TABLE 1
Results of Frontal Analysis with Streamline SP

Buffer (% glyc)	H/H_0	u_s (cm/h)	D_{ax} (m^2/s)	q/q_0	ε	τ (min)
0%	2.0	168	1.80×10^{-6}	1.00	0.70	5.0
0%	3.3	300	7.27×10^{-6}	0.75	0.82	5.4
30%	2.0	64	1.08×10^{-6}	0.86	0.70	13.1
30%	4.5	150	6.27×10^{-6}	0.57	0.87	15.7

to the basic principles of fluidized-bed operation and protein adsorption. Feedback from students who have worked on the laboratory experiment has been very positive. They have particularly enjoyed working with a real protein and a commercial resin (that needs to be handled with care).

In the experiment, students study the relation of the linear velocity and the buffer viscosity to the expanded bed height by simple bed operation, the flow hydrodynamics of the bed expansion system by tracer studies, and the protein adsorption characteristics by frontal analysis of breakthrough curves. In this way they are forced to put together concepts they have learned in separate courses in fluid mechanics, mass transfer, separations, and reaction engineering. The fluidized bed laboratory experiment also provides an opportunity for students to carry out a series of experiments that increases in complexity and approaches the real process equipment.

NOMENCLATURE

H	fluidized bed height (cm)
ϵ	fluidized bed porosity
n	Richardson-Zaki number
u_s	superficial velocity (cm/h)
u_t	particle terminal velocity (cm/h)
N	theoretical plate number
D_{ax}	axial dispersion coefficient (m ² /s)
t	time (s)
τ	average residence time
Pe	Peclet number
C	concentration (mol/L)
q	adsorbed concentration (mol/L)

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ON THE APPLICATION OF DURBIN-WATSON STATISTICS TO TIME-SERIES-BASED REGRESSION MODELS

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A fundamental tenet in (linear) regression analysis is that errors associated with a model must be random and independent from observation to observation in an experiment, with expectation (or mean value) zero. Various aspects of residual behavior are routinely discussed in modern texts on probability and statistics. The distribution of

$$e_k = y_k - \hat{y}_k; k = 1, \dots, n$$

should show a random scatter when plotted against

$$x_k, y_k, \text{ or } \hat{y}_k$$

as abscissa.

If the statistical experiment involves observations in a time sequence, and the error at time instant t_k is influenced by the error at the immediately previous time instant t_{k-1} , the resulting “influential carryover”^[1,2] violates the error-independence criterion. The errors may be negatively or positively correlated.

The technique introduced by Durbin and Watson^[3] more than fifty years ago is a popular and straightforward test for the existence of autocorrelation in time-series analysis (*e.g.*, in forecasting). Only a small number of textbooks on probability and statistics intended for engineering and natural sciences treats this subject matter, however.

The purpose of this article is to demonstrate the application of the Durbin-Watson (DW) technique to regression analysis concerning chemical engineering processes where the “regressor”^[4] sequence occurs as a time series. Regression problems of this kind appear routinely in reaction kinetics/chemical reaction engineering, applied transport phenomena, process control, and engineering economics and plant design, thus touching all major domains of the undergraduate curriculum.

The DW technique is illustrated by two examples. The first is related to decisions concerning the order of a chemical reaction. The second illustrates its usefulness in determining if a regression model is statistically admissible, and as such, is of major interest to chemical (and other) engineers.

BRIEF THEORY

Given the general first-order autoregressive process^[5]

$$Y_k = \beta_0 + \sum_{i=1}^{p-1} \beta_i x_{k,i} + e_k \quad k = 1, \dots, n \quad (1)$$

where the errors are assumed to obey the first-order autocorrelation

$$e_k = \rho e_{k-1} + u_k \quad (2)$$

with $|\rho| < 1$, and independent random u_k belonging to the normal distribution with zero mean and variance ρ^2 . The regressor set $\{x_n\}$ contains observations obtained at consecutive time instants t_1, t_2, \dots, t_n . In the case of correlated errors, the variance of each error term is given by

$$\sigma^2(e_k) = \frac{\sigma^2}{1 - \rho^2} \quad (3)$$



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and the covariance of adjacent errors is

$$\sigma^2(e_k; e_{k-1}) = \rho\sigma^2(e_k) \quad (4)$$

To test the null hypothesis $H_0: \rho = 0$ against an appropriate alternative hypothesis H_1 , the Durbin-Watson statistic

$$D = \frac{\sum_{k=2}^n (e_k - e_{k-1})^2}{\sum_{k=1}^n e_k^2} = \frac{\text{SSED}}{\text{SSE}} \quad (5)$$

is computed and compared to upper (d_U) and lower (d_L) limits of D , as a function of observation size, in critical tables.^[3,5,6] The decision scheme is given in Table 1.

The D -statistic is related to the Lag 1 autocorrelation^[5,7] coefficient of residuals defined as^[5]

$$r_1 = \frac{\sum_{k=2}^n e_k e_{k-1}}{\sum_{k=1}^n e_k^2} \quad (6)$$

by the simple relationship

$$D = 2(1 - r_1) \quad (7)$$

which is particularly useful for $n < 15$ since critical tables do not extend outside the $15 \leq n \leq 100$ range. If the inequality $|r_1| > 2/\sqrt{n}$ stands, the independence of errors is in serious doubt. The size of observations in the first example is sufficiently large to use critical tables, whereas tables cannot

be used in the second example.

EXAMPLE 1

Kinetics of the Bromination of Metaxylene

The rate equation written in terms of bromine concentration

$$\frac{dc}{dt} = -kc^m \quad (8)$$

has the rate constant $k \approx 0.1 \text{ (dm}^3/\text{mol)}^{1/2} \text{ min}^{-1}$ and apparent order $m = 1.5$ at 17°C .^[8] As can be seen from Table 2 (next page), the errors do not appear to be correlated, since the DW-statistic D is larger than d_U values at levels of significance α .

If we assume for the sake of argument, however, that the decomposition is first order ($m = 1$), the test results depend on the selected level of significance. Since R^2 , R_{adj}^2 , and the residual distributions (not shown) are not appreciably different, the model carrying $m = 1.5$ is a better fit.

This conclusion is also supported by the 95% confidence intervals for the true regression parameter b_0 : (-0.6494; 0.3079) when $m = 1.5$ and (-3.6478; -2.01306) when $m = 1$; in the second case, the correct value of zero does not even fall into the interval

What happens if the decomposition is assumed to be of zero order? With $m = 0$ in Eq. (8), the bromine concentration would be a linear function of time. The $c = \beta_0 + \beta_1 t + \text{error}$ model would have the sample regression parameters $b_0 = 0.25849$ and $b_1 = -0.004119$, with $R^2 = 0.857$ and $s_e^2 = 0.00724$ (including the $t = 63.00$; $c = 0.0482$ observation pair, lost by the rate-averaging process discussed in Ref. 8). Since $\text{SSE} = 0.03558$ and $\text{SSED} = 0.02419$, however, the DW statistic $D \approx 0.7$ is less than the d_L values shown in Table 2, indicating a positive correlation between errors. The residual distribution also being parabolic (*i.e.*, definitely non-random), the postulation of zero-order kinetics would be statistically most questionable, apart from its physical improbability.

EXAMPLE 2

Effect of Temperature/Humidity Index on the Level of Pollution

The level of pollution as a function of the temperature/humidity index, recorded on ten consecutive days at a certain location^[9] are shown in Table 3. The problem assignment in Ref. 9 is to determine if the data are suitable for a linear re-

TABLE 1
Decision Schemes in the DW Statistical Test

Note: Rejection of H_0 is a statistically stronger result than failure to reject it.

Test Hypotheses	Criterion	Decision
$H_0: \rho = 0; H_1: \rho > 0$	$D < d_L$	Reject H_0 in favor of H_1
	$D > d_U$	Fail to reject H_0
$H_0: \rho = 0; H_1: \rho < 0$	$(4-D) < d_L$	Reject H_0 in favor of H_1
	$(4-D) > d_U$	Fail to reject H_0
	$d_L \leq D \leq d_U$	Inconclusive
	$d_L \leq (4-D) \leq d_U$	Inconclusive

gression analysis.

Table 4 illustrates that increasing the degree of the polynomial is not particularly effective, inasmuch as the adjusted R^2 values indicate that even at best, only about 65% of the variations in the pollution index are explained by variations in the temperature/humidity index. The error variances are also very similar.

The residual distribution in all three cases is reasonably random, and the numerical values of the Lag 1 autocorrelation coefficient magnitude are well below the numerical value of $2/\sqrt{10} = 0.632$. The errors appear to be unrelated.

It is instructive to note that the power relationship $Y = \beta_0 x_1^\beta$ would not yield a better fit with a nonlinear $R^2 = 0.690$ (linearization yields $\ln(b_0) = -5.77981$ and $b_1 = 1.52312$; the residual distribution is quasi-random).

FURTHER COMMENTS ON THE DURBIN-WATSON TECHNIQUE

If the DW-statistic falls into the inconclusiveness zone, "remedial measures" for autocorrelation may be applied: addition of independent variables, transformation of variables, the Cochrane-Orcutt procedure, and the Hildreth-Lu procedure. The discussion of these techniques is beyond the scope of this paper and may be

TABLE 3
Pollution as Function of Temperature/Humidity Index
 x - temperature/humidity index; Y - coded pollution level

Day k	1	2	3	4	5	6	7	8	9	10
x °F	77	95	30	45	85	50	65	60	63	82
Y	1.5	4.0	0.5	1.4	2.0	0.8	2.5	2.0	1.7	2.8

TABLE 2
Application of DWT to the Kinetics of Metaxylene Bromination.
Experimental data are taken from Ref. 8, Table 3.1.1.

k	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
t_k	0	2.25	4.50	6.33	8.00	10.25	12.00	13.50	15.60	17.85	19.60	27.00	30.00	38.00	41.00	45.00	47.00	57.00
x_k	0.3150	0.2812	0.2555	0.2353	0.2153	0.1980	0.1852	0.1713	0.1566	0.1465	0.1295	0.1107	0.0942	0.0799	0.0736	0.0692	0.0615	0.0518
y_k	16.44	13.56	11.48	11.68	9.11	8.00	7.73	7.71	5.87	4.06	3.64	3.23	2.79	2.10	1.55	1.35	1.25	1.18

t_k : observation time (min)

x_k : mean bromine concentration (mol/dm³)

y_k : mean rate of reaction - $10^3 \Delta c/\Delta t$ (mol/dm³ min)

	$Y = \beta_0 + \beta_1 x^{1.5} + \text{error}$	$Y = \beta_0 + \beta_1 x + \text{error}$
b_0	-0.170746	-2.830640
b_1	94.494843	57.830640
R^2	0.987	0.977
R_{adj}^2	0.986	0.976
s_c^2	0.3054	0.5305
SSED	8.54756	9.86520
SSE	4.88721	8.48330
D	1.749	1.162
Decision on errors	Not correlated at $\alpha=0.01; 0.025; 0.05$	$\alpha = 0.01$: Not correlated $\alpha=0.025$: No conclusions $\alpha=0.05$: Borderline positive correlation

Critical values of the DW statistic at $n = 19^{(3,5)}$

α	d_L	d_U
0.05	1.16	1.39
0.025	1.03	1.26
0.01	0.90	1.12

found elsewhere.^[10]

The DW technique may not indicate autocorrelated errors associated with a second-order autoregressive pattern

$$e_k = \rho_1 e_{k-1} + \rho_2 e_{k-2} + u_k \quad (9)$$

and hence it is not robust against incorrect model specifications.

Alternative tests of autocorrelation include the Theil-Nagar procedure^[10,11] and the Olmstead-Tukey, Mann-Kendall, Hotelling-Pabst, and von Neumann tests summarized briefly by Powell.^[6] To the author's knowledge, the Durbin-Watson technique is more widely used.

CONCLUSIONS

Owing to the relative ease of its use, the inclusion of the Durbin-Watson technique in a probability and statistics course is well advised for the undergraduate chemical engineering curriculum. It is somewhat surprising that the technique is treated only by a small number of engineering textbooks, notably the ones cited in this paper. Routine teaching of the technique would further emphasize for students the importance of error structure analysis and help counteract their often-demonstrated inclination to assign inflated significance to the R^2 parameter.

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Useful discussions with Dr. Tom Duever of the Department of Chemical Engineering are hereby gratefully acknowledged.

NOMENCLATURE

- b_i sample regression parameters, *i.e.*, least-squares estimators of true regression parameters β_i , $i = 1, \dots, p$
 c concentration

- D Durbin-Watson statistic (Eq. 5)
 d_L, d_U lower and upper level bounds, respectively, in critical tables of the Durbin-Watson statistic
 e error (or residual), defined as the difference between the observed and regressed value of the dependent variable
 k rate constant (Eq. 8)
 m reaction order (Eq. 8)
 n length of the time series and size of the observation set
 p size of the regression polynomial (simple linear: 2; quadratic: 3, etc.)
 R^2 coefficient of determination; R_{adj}^2 its adjusted value, defined as $1 - [SSE/(n-p)]/[SST/(n-1)]$
 r_1 Lag 1 autocorrelation coefficient (Eq. 6)
 s_e^2 sample error variance, defined as $SSE/(n-p)$
 t time; t_k the k -th instant in the time series
 u random variable (Eq. 2)
 x independent variable (regressor)
 Y dependent variable; \hat{Y} regressed dependent variable

Greek Symbols

- α level of significance in hypothesis testing
 β_i true population regression parameters, $k = 1, \dots, p$
 σ^2 true (population) variance
 ρ true (population) correlation coefficient

Special Symbols

- SSE sum of the squared errors (Eq. 5)
 SSEd sum of the squared error differences (Eq. 5)
 SST total sum of squares in regression theory

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TABLE 4
Application of DWT to the Pollution Problem of Example 2.
Data are taken from Ref. 9

	<i>Simple linear model</i>	<i>Quadratic model</i>	<i>Cubic model</i>
b_0	-0.80347	0.36495	-6.62620
b_1	0.041771	0.001023	0.395176
b_2	-	3.2274×10^{-4}	-6.470×10^{-3}
b_3	-	-	3.644×10^{-5}
R^2	0.684	0.700	0.766
R_{adj}^2	0.644	0.614	0.649
s_e^2	0.364	0.395	0.359
SSEd	6.4739	6.0833	3.7614
SSE	2.9144	2.7654	2.1568
D	2.221	2.200	1.744
$ r_1 $	0.110	0.100	0.128

TEACHING ELECTROLYTE THERMODYNAMICS

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Electrolyte solutions can be found in many natural and industrial processes. Some examples are the absorption of acid gases, such as carbon dioxide, for removal from effluent gas streams, avoiding atmospheric pollution;^[1] the fractional crystallization processes in which several salts are separated as pure phases from a multicomponent mixture; for the production of fertilizers such as ammonium phosphate, ammonium nitrate, or potassium sulfate;^[2] for extractive distillation using salt as the extractive agent;^[3] and for precipitation of globular proteins from an aqueous solution by the addition of salts.^[4]

It is not surprising that during the last few decades, much attention has been devoted to experimental and theoretical studies in this area. At the undergraduate level, however, most of the thermodynamics courses still do not consider these types of mixtures, and as a result the students are not given enough insight into the differences when compared to nonelectrolyte thermodynamics. Nevertheless, several authors have recognized this gap, and recent editions of the books by Prausnitz, et al.,^[5] and Tester and Modell^[6] include chapters totally devoted to the thermodynamics of electrolyte solutions.

Electrolytes are usually classified according to their degree of dissociation in solution: those undergoing a total dissociation into cations and anions are called strong electrolytes, while the ones that participate in different chemical reactions, such as ion association, are called weak electrolytes. This classification has no definite boundaries because the degree of dissociation depends on, among other things, the type of solvent and solute concentration. For instance, zinc iodide is a strong electrolyte in water only if the concentration is lower than about 0.3 molal.^[7]

In this paper, the thermodynamic description of a strong electrolyte solution is illustrated by calculations on the freezing point depression of strong electrolytes in water, emphasizing the differences between electrolyte and nonelectrolyte thermodynamics. In this way, students can gain some knowl-

edge on the physical chemistry of electrolyte solutions.

THE IDEALITY IN ELECTROLYTE SOLUTIONS

Freezing point depression is a colligative property that depends on the number of solute particles but not on its nature. If we consider a solution of a solvent 1 in which a solute A is dissolved, the freezing point depression is defined as the difference between the melting temperature of the pure solvent, T_m , and the freezing temperature of the mixture, T_f ($\Delta T = T_m - T_f$). This last temperature is lower than the melting point of the pure solvent. It is interesting to observe how the freezing point changes with the amount of solute added to the solvent. The simplest equation for the freezing point depression, which is familiar to the students in a chemical thermodynamics course, can be written as^[8]

$$\Delta T = T_m - T_f = \frac{RT_m^2}{\Delta H_f(T_m)} x_A \quad (1)$$

where ΔH_f is the enthalpy of fusion at T_m , R is the ideal gas constant, and x_A is the solute mole fraction.

The different performance obtained, using Eq. (1), in the



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calculation of ΔT for nonelectrolyte and electrolyte solutions can be easily compared. The relative percent deviations obtained for the representation of freezing point depression for aqueous solutions of D-fructose, ethylene glycol, NaCl, and AgNO_3 , can be seen in Figure 1. Despite the fact that the maximum mole fraction is around 0.01, for the NaCl and AgNO_3 aqueous solutions the deviations are much more pronounced than for the nonelectrolyte systems, with errors higher than 4% even at very low concentrations ($\approx 5 \times 10^{-4}$). It should be mentioned that for those calculations, $\Delta H_f(T_m) = 6010.0 \text{ J/mol}$ and $T_m = 273.15 \text{ K}$ were used.^[9]

One main assumption in the derivation of Eq. (1) is that the solute is very dilute and forms an ideal solution. When, for instance, NaCl is dissolved in water, the solution essentially contains sodium and chloride ions. At this point it is important to call the students' attention to the different nature of forces depending on the kind of solutes: the ions interact with each other through coulombic potential, which varies as $1/r$. For neutral solute molecules (nonelectrolytes) such as D-fructose, the interactions vary something like $1/r^6$. So the interaction between ions in solution is effective over a much greater distance than the interaction between neutral solute particles and, unlike what happens in nonelectrolyte solutions, even in very dilute solutions the long-range nature of the electrostatic forces between the ions is responsible for strong deviation from ideal behavior. Thus, while Eq. (1) is widely used for nonelectrolyte solutions, it cannot give reliable results for electrolyte solutions since they are ideal at concentrations too low to produce a measurable ΔT .

Figure 1 is a fine way of showing students the different perspective that should be taken regarding the concept of ideality at high dilution in electrolyte and nonelectrolyte solutions. Another important difference that arises in the thermodynamics of electrolytes is the concentration scale used. In electrolyte, it is common to use the molality scale instead of the mole fraction scale. Moreover, in order to properly account for the number of solute particles in solution, due to the dissociation of the electrolyte, the mole fraction of solute A used in Eq. (1) should be calculated as

$$x_A = \frac{\nu n_A}{\nu n_A + n_1} \quad (2)$$

where n_A and n_1 are the solute and solvent mole numbers, respectively, and ν is the sum of the stoichiometric coefficients

of the anion and the cation.

THE DEBYE-HÜCKEL THEORY AS THE PATH FOR NON-IDEALITY IN ELECTROLYTE SOLUTIONS

So far, the students have learned that, for electrolyte solutions, assuming ideality may introduce significant errors in the calculation of the properties of the solution, even at high dilution. Thus, in order to obtain trustworthy values of ΔT , corrections to the ideal behavior should be introduced using the activity coefficient. From the thermodynamic condition for equilibrium and after some reasonable assumptions, it is possible to obtain^[8]

$$\ln \gamma_1 x_1 = \frac{\Delta H_f(T_m)}{R} \left(\frac{1}{T_m} - \frac{1}{T_f} \right) \quad (3)$$

where γ_1 is the solvent activity coefficient and x_1 is its mole fraction. Now, ΔT can be calculated by solving Eq. (3) for T_f .

Taking into account only the electrostatic forces, assuming ions to be charged points in a continuous medium of uniform relative permittivity, and using well-established concepts from classical electrostatics, Peter Debye and Erich Hückel^[11] derived the following expression for the mean ionic molal activity coefficient of an electrolyte (γ_{\pm}^*)

$$\ln \gamma_{\pm}^* = - \frac{A |z_+ z_-| \sqrt{I}}{1 + B a \sqrt{I}} \quad (4)$$

In Eq. (4), A and B are parameters related to the density and dielectric constant of the solvent,^[5,12,13]

and a is the so-called distance of closest approach between ions (usually taken as 4 Å), z_+ and z_- are the charges of the cation and the anion, respectively, and I is the ionic strength defined by

$$I = 0.5 \sum_{i=1}^{N_{\text{ions}}} m_i z_i^2 \quad (5)$$

being m_i the molality of the ion i and N_{ions} the number of types of ions in the solution.

The ionic strength is a very common measure of concentration in electrolyte solutions. In fact, it takes into account not only the concentration of the ion but also the magnitude of its charge. A big difference comes from the fact that using this model, the freezing point depression is now not only dependent upon the solute concentration, but also on its charges.

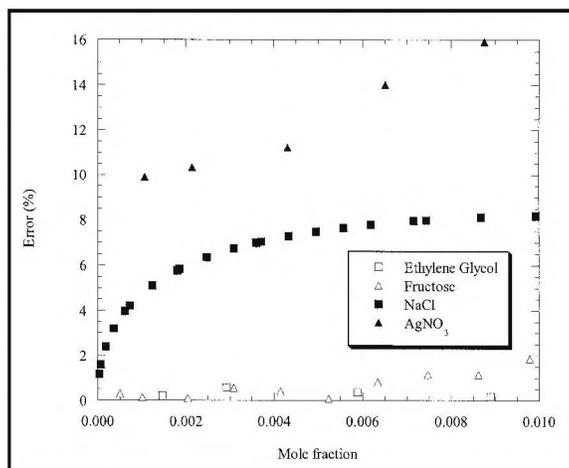


Figure 1. Comparison of the relative percentage deviations in the calculation of the ideal freezing point depression for aqueous nonelectrolyte and electrolyte solutions.^[9,10]

So the characterization of the electrolytes, in terms of its ions valences, is fundamental to establish differences that occur when applying the proposed methodology for the study of the freezing point depression of different types of electrolytes. Depending on the charge of the cation and the anion, the electrolytes can be classified as 1:1, 2:1, 1:2, 2:2, etc. For example, a 2:1 type has a cation of double charge and an anion of unit charge.

From Eq. (4), taking into consideration the Gibbs-Duhem equation, the activity of the solvent can be calculated as

$$\ell n \gamma_1 x_1 = -M_1 v m \left(1 - A |z_+ z_-| \sqrt{I} \sigma(Ba\sqrt{I}) \right) \quad (6)$$

where M_1 is the molar mass of the solvent (kg/mol), and $s(y)$ is the function

$$\sigma(y) = \frac{1}{y^3} \left(1 + y - 2 \ell n(1 + y) - \frac{1}{1 + y} \right) \quad (7)$$

The full understanding of the thermodynamic concepts that makes possible the derivation of Eq. (6) from Eq. (4) is far beyond the scope of this paper, but it is important to refer to some of the most relevant points such as the definition of the activity coefficients in different concentration scales, the standard states and the normalization of the activity coefficients, and the need for defining mean ionic properties, which are calculated based on the properties of the ions.^[5-7] These concepts introduce significant changes to the nonelectrolyte thermodynamics and should be carefully discussed with the students.

Inserting the result for $\ell n \gamma_1 x_1$ given by Eq. (6) into Eq. (3), it is possible to obtain better estimates for ΔT in electrolyte solutions. Fixing $A = 1.130 \text{ kg}^{0.5}/\text{mol}^{0.5}$ and $B = 3.246 \times 10^9 \text{ kg}^{0.5}/(\text{m mol}^{0.5})$, obtained by using values of the solvent density and dielectric constant for water at 273.15 K,^[9] one can calculate, for comparison with the previous results shown, new values of ΔT for aqueous NaCl solutions.

The errors obtained assuming ideal behavior and using the Debye-Hückel equation are compared in Figure 2. Using this new methodology, the errors in calculated values of ΔT are only higher than 4% for

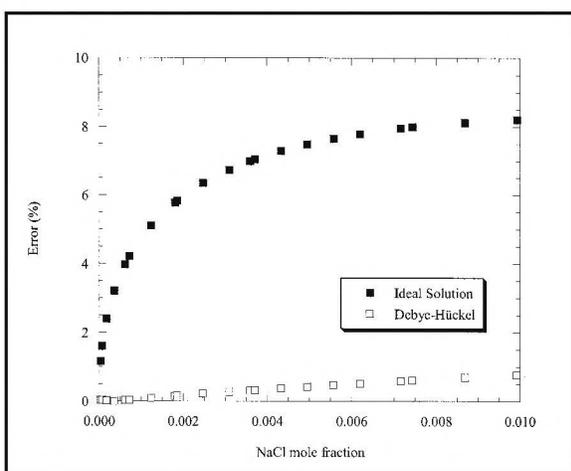


Figure 2. Comparison of the relative percentage deviations in the calculation of the freezing point depression: ideal behavior and the Debye-Hückel equation. NaCl/water system.^[9,10]

x_A around 0.05. In fact, the Debye-Hückel theory gives an exact expression for the activity coefficients of the electrolyte and of the solvent for very dilute solutions, and as can be seen, the errors for ΔT at very low solute mole fraction are near zero.

In Figures 3 and 4, the freezing point depressions are shown for different types of electrolytes at low molality in water assuming ideality and using the Debye-Hückel equation. In all cases the assumption of ideality agrees only with the experimental values at very low concentrations, and the molality range of applicability of this equation decreases as the valences of the ions increase. This is evident in Figure 3 since the ideal

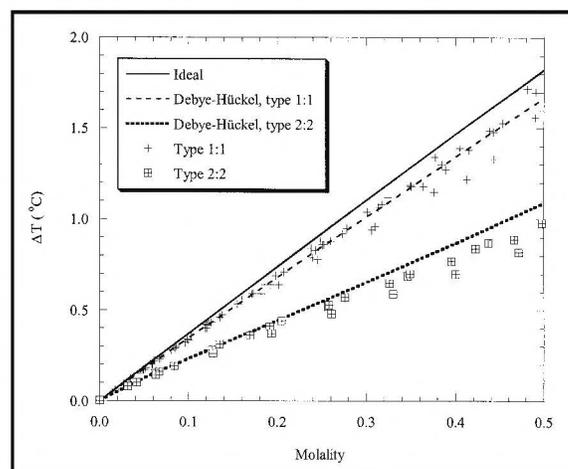


Figure 3. Comparison of the freezing point depression for 1:1 (HNO_3 , LiCl , NaCl , NaBr , NaOH , NaNO_3 , KCl , KBr , KI , KOH , KNO_3 , CH_3COOH , NH_4Cl , and AgNO_3) and 2:2 (MgSO_4 , MnSO_4 , ZnSO_4 , and CuSO_4) electrolytes:^[9,10] ideal behavior and the Debye-Hückel equation

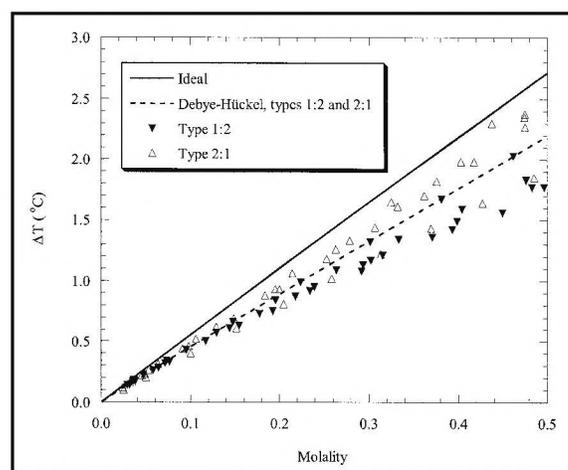


Figure 4. Comparison of the freezing point depression for 1:2 (Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, K_2CO_3 , K_2SO_4 , and $(\text{NH}_4)_2\text{SO}_4$) and 2:1 (BaCl_2 , CsCl_2 , MgCl_2 , SrCl_2 , and CaCl_2) electrolytes:^[9] ideal behavior and the Debye-Hückel equation.

curve in terms of molality is the same for 1:1 and 2:2 electrolytes, while the experimental data are different. The improvement observed upon using a simple model such as the Debye-Hückel model is even more evident for 1:2, 2:1, or 2:2 electrolytes than for 1:1 electrolytes. Nevertheless, the Debye-Hückel model allows more accurate calculation of the freezing point depression to higher concentrations for all types of electrolytes.

This brief discussion alerts the students to the changes that must be made for the description of electrolyte systems. Also, there can be significant differences when comparing the behavior of aqueous solutions of electrolytes of different valences, which is explored in the next section by extending the calculations to concentrated solutions.

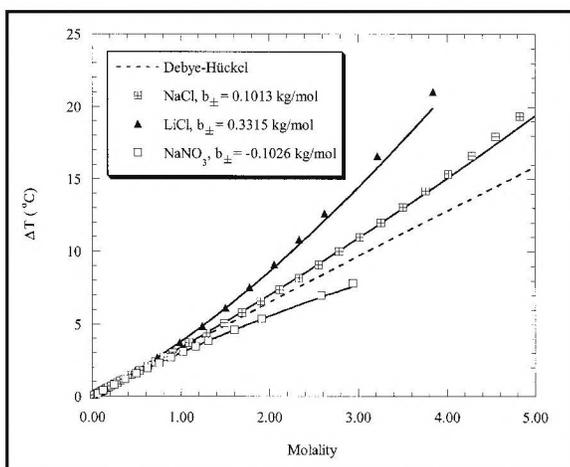


Figure 5. Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 1:1 electrolytes.^[9,10] Improvement to the Debye-Hückel equation.

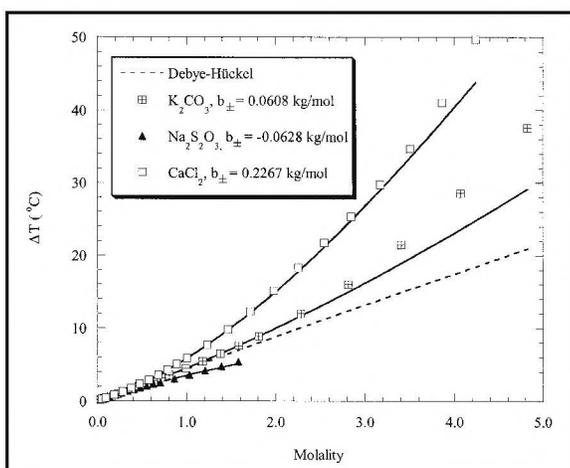


Figure 6 Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 1:2 or 2:1 electrolytes.^[9] Improvement to the Debye-Hückel equation.

EXTENDING THE FREEZING POINT CALCULATION FOR CONCENTRATED SOLUTIONS

The main assumption of the Debye-Hückel theory is that deviations from ideality are only due to electrostatic forces between the ions, which is physically reasonable at high dilution but unreal when the ionic concentration increases so the ions more closely approach each other and short-range forces become dominant. Guggenheim suggested the use of a power series in electrolyte concentration to better describe the physical chemistry of electrolyte solutions, leading to the virial expansion models. To do so, Guggenheim added a new specific electrolyte empirical interaction parameter (b_{\pm}), proposing the following equation for the mean ionic molal activity coefficient:^[13]

$$\ell_n \gamma_{\pm}^* = -\frac{A|z_+z_-|\sqrt{I}}{1+\sqrt{I}} + b_{\pm}I \quad (8)$$

From Eq. (8), the activity of the solvent is given by

$$\ell_n \gamma_1 x_1 = -M_1 v m \left[1 - A|z_+z_-|\sqrt{I} \sigma(\sqrt{I}) + \frac{b_{\pm}I}{2} \right] \quad (9)$$

It is interesting for the students to evaluate how this change makes possible a much better quantitative description of the freezing point depression at high concentrations. Thus, using an experimental value of the freezing temperature at a concentration around 1 molal, it is possible to obtain a value for the empirical parameter b_{\pm} . For instance, the experimental value for an aqueous NaCl solution of 0.90 molal is $T_f = 270.11$ K; from this, $b_{\pm} = 0.1013$ kg/mol is calculated. Now, combining Eqs. (3) and (9) makes it possible to study the usefulness of the equation proposed by Guggenheim for calculation of the freezing point depression.

Figure 5 presents a comparison between the Debye-Hückel and Guggenheim equations for the estimation of ΔT in aqueous solutions of electrolytes of type 1:1 at concentrations up to 5 molal. It can be easily observed that the use of the Guggenheim equation, with a new empirical parameter regressed from a unique experimental freezing point measurement, introduces a significant improvement in the representa-

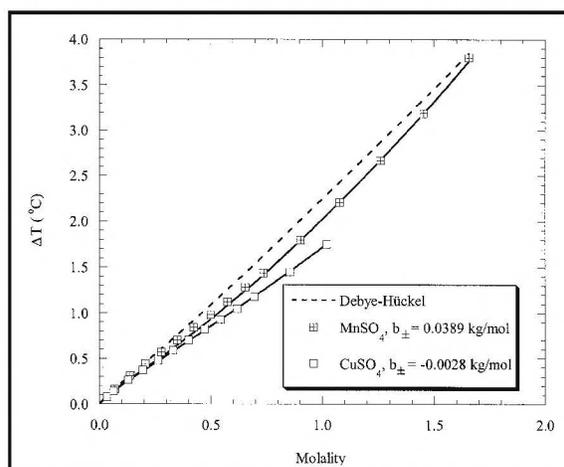


Figure 7. Analysis of the Guggenheim equation in the description of the freezing point depression of aqueous solutions with 2:2 electrolytes.^[9] Improvement to the Debye-Hückel equation.

tion of ΔT for all systems shown. Compared with the previous results shown for the NaCl/water system, the application of this equation results only in a percentage deviation higher than 4% for solute mole fraction around 0.15 (≈ 5 molal), which is a 3-times-higher concentration than the results achieved using the Debye-Hückel equation. The use of the Guggenheim equation for the systems of water/LiCl and water/ NaNO_3 shows an even greater improvement over the Debye-Hückel equation.

In Figures 6 and 7, the same kind of comparison is presented for, respectively, 1:2 and 2:1, and 2:2 electrolytes in water. The results obtained provide a very reasonable correlation of the experimental data and only for the system of water/ K_2CO_3 are there big discrepancies relative to the experimental results for solute mole fractions higher than 0.15 (≈ 3.4 molal), which is, nonetheless, a very good result. Moreover, the Guggenheim equation makes it possible to calculate a freezing point depression up to 40°C (CaCl_2 system, Figure 6).

Table 1 summarizes the deviations obtained in the representation of the freezing points of different aqueous electrolyte solutions. It gives a more comprehensive comparison between all methodologies considered here and the type of electrolyte. First, one sees that the deviations from ideality increase as the valences of the ions increase. The Debye-Hückel equation introduces improvements for all types of systems, which are especially evident for the 2:2 electrolytes. In that case, the maximum molality is much lower than in the other cases, and that is certainly a contributing factor in the big improvements obtained. Finally, it is important to stress that based solely on one experimental data point for each salt, a simple model like the Guggenheim equation makes it possible to calculate the freezing point for all systems with average error of about 2.10%.

Since colligative properties depend on the number of particles in solution, the freezing point data can be analyzed in terms of the physical chemistry of the electrolyte solutions. That is, it might give indications of the degree of dissociation, solvation, and ion-pairing. The students can also be asked to consider other hypotheses that could be made or improved for electrolyte solutions in the development of the models studies here, and further to consider more complex models such as the Pitzer model in the representation of thermodynamic properties of electrolyte solutions.

CONCLUSIONS

The differences that must be taken into account when study-

ing aqueous electrolyte systems rather than nonelectrolyte systems have been pointed out in this paper. Specifically, we have shown that even at very high dilutions, one must use the Debye-Hückel type limiting law to properly represent the freezing point depression. In this way, the students can compare the experimental data with values assuming the ideal behavior and using the Debye-Hückel equation. Finally, the

students are also challenged to understand the need for more elaborate expressions in the representation of that property at high concentrations. To do this, we suggest obtaining an empirical parameter of the Guggenheim equation using an experimental data of the freezing point depression at a concentration around 1 molal.

This simple analysis of electrolyte solutions is certainly a

nice starting point to motivate students to get some knowledge of electrolyte thermodynamics. It can be introduced in a thermodynamic or a physical-chemistry course, which could be even more attractive if it can be combined with a laboratory experiment for measurement of the freezing point depression of an aqueous electrolyte solution.

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TABLE 1
Comparison of Different Approaches for Calculation of the Freezing Point Depression in Aqueous Electrolyte Systems.

Salt Type	Data Sets	Maximum Molality	Error (%)		
			Ideal	Debye-Hückel	Guggenheim
1:1	14	5.1	10.00	6.89	1.19
2:1	5	4.2	22.51	18.56	2.77
1:2	6	4.8	34.55	13.59	2.71
2:2	4	1.7	81.85	11.86	4.02

The Pilot Plant Real Book: A Unique Handbook for the Chemical Process Industry

by Francis X. McConville

Published by FXM Engineering and Design, 6 Intervale Road,
Worcester MA 01602 <www.fxmttech.com> (2002)

Reviewed by

Ka M. Ng

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The pilot plant is indispensable in the development of chemical processes. Yet it is seldom covered in a typical chemical engineering curriculum, leaving it as one of the subjects that the graduate is supposed to learn “on the job.” The author suggests that this omission is a failure of today’s educational system. Given the importance of pilot plant, which can be viewed as one of the four elements of process development,[1] there is some truth in this assertion. At least this omission forgoes an opportunity to show the students how basic principles, experiments, know-how, experience, simulations, literature data, workflow, etc., come together in the development of products and processes.

If you are an educator, a process development chemist, or engineer, who shares McConville’s view that there is a gap in pilot plant education and practice, this book may be just what you want. It provides a lucid account of how chemical processes are transferred from the lab to the plant. The information often needed for pilot plant personnel is organized in a logical and readily accessible manner. This book is named a “Real Book”—McConville explains that just as young jazz musicians had to master the “Real Book,” a bootleg, photocopied collection of the great jazz standards with all the songs anyone needed to know in one place, this book has admirably achieved a similar objective for pilot plants, particularly those for the pharmaceutical industry.

Chapter 1 sets the tone by describing the role of a pilot plant. It contains a wealth of hints on factors to consider and things to do and not to do in scale-up, which is one of primary functions of a pilot plant. Some of the terms and jargon commonly used in pilot plant such as work-up, batch record, campaign report, equipment qualification, cGMP, and others are explained. Chapter 2 describes the key pieces of equipment and their operations in a typical pharmaceutical pilot plant. Consider the discussion on the reactor. It complements a chemical reaction engineering textbook in which reactor theory and kinetics is covered by focusing on the practical issues such as reactor types and configurations, selection criteria, raw material charging, sampling methods, reac-

tor cleaning, etc.

Chapters 3, 4 and 5 are concerned with liquid handling, heat transfer, and electrical instrumentation, respectively, all basic issues in a pilot plant. Solvents are covered in Chapter 6. It identifies the solvents useful for crystallization, and those limited for pharmaceutical use, as well as their physical and chemical properties. Binary azeotropes for some common solvents are also listed. These data are important for pilot plants because it is often possible to take advantage of them to improve the efficiency of drying and solvent exchange operations by distillation.

Compressed gases are covered in Chapter 7. Proper procedures for handling compressed gases, metering gases, using gas pressure regulators, installing a vacuum pump, etc., are described. Chapter 8 provides data on the properties of commercial acids and bases, and buffers. The aqueous solubility of various inorganics and organics are also given.

Chapters 9 and 10 are concerned with chemical hygiene and safety, and materials selection, respectively. Chapter 11 contains miscellaneous topics such as unit conversion tables, sieve sizes, etc., that might come in handy in daily pilot plant operations.

There are many books on process development, equipment and chemical data,^[2-6] but this book is unique. Capturing the experience of a seasoned pilot plant practitioner, it delivers what is wanted and needed in a compact package, particularly for pharmaceutical pilot plant projects. The topics selected are highly relevant, the extent of coverage is to the point, the data chosen are consistent with what a chemist and engineer might need, and the style of writing is direct and concise. There is also an extensive bibliography in case additional information is required on the various topics.

This beautiful book is highly recommended for pilot plant personnel as well as people engaging in chemical processing and research. Its contribution to the education of process development is still limited, however. My suggestion is to include pilot plant case studies to illustrate how the information and tools are used to complete a process development project, thereby taking it one step closer to a truly “Real Book.”

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Random Thoughts . . .

CHANGING TIMES AND PARADIGMS

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Colleagues at a large public university I recently visited are doing some excellent research on first-year engineering students—what attracted them to engineering, how they view engineering as a curriculum and career, how they feel about their first-year courses (it isn't pretty!), their confidence levels before and after those courses, and why the ones who drop out do so. I sat in on one of their weekly meetings, and one of them—an education professor—expressed bewilderment and dismay that with so much known about what makes teaching effective, engineering programs persist in using the same old ineffective methods. She wondered if there was any point in continuing research directed at improving a system that is this intransigent.

I've heard the same thing from others engaged in educational reform—it's definitely an uphill battle, and it's easy to get discouraged when your focus is restricted to a single campus. Taking a broader view, though, things don't look that bad. Engineering education went through a major sea change once before, and the signs are that it is doing so again. I tried to offer some words of encouragement at the meeting and thought I'd repeat them here for readers engaged in similar lonely battles.

First, a little history. From the late 19th century through the 1950s, engineering education was a combination of lecture and hands-on instruction closely tied to industrial practice, and the faculty consisted primarily of experienced engineers and consultants to industry. In the mid-1950s, America seemed to be falling behind Russia in the space program and calls were issued for an increased curricular emphasis on the mathematical and scientific foundations of engineering. In the years that followed, external funding opportunities for basic research skyrocketed, faculty started to be hired primarily for their potential as researchers, and most laboratory and field experiences disappeared from the engineering curriculum to be replaced by lectures on applied math and science. The para-

digm shift from practice to science was essentially complete in most engineering schools by the early 1970s.

In the 1990s, a rising chorus of complaints from industry about the inadequate preparation of new engineering graduates for industrial jobs started to be acknowledged inside the academy. In addition, evidence began to emerge from both cognitive science and empirical classroom research that the prevailing instructional model (“I show derivations of formulas in class, then you plug into the formulas and do similar derivations in assignments and on tests”) was ineffective for promoting learning and the acquisition of critical thinking and problem-solving skills. Teaching workshops began to be heavily subscribed at engineering conferences and on campuses around the country, and NSF-funded programs and individual campus initiatives—such as Project LE/ARN at Iowa State—began to involve hundreds of previously traditional engineering faculty in education reform. Another major step was ABET's adoption of new accreditation criteria that required engineering programs to address both technical and social outcomes in their curricula, all but forcing them to adopt nontraditional methods in their classroom instruction. (You clearly can't equip students with the ability to work efficiently in multidisciplinary design teams or give effective technical presentations by giving them a few lectures on those topics.)



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These developments have given rise to a national movement toward a more active, cooperative, problem-based instructional model for engineering education. While the new approach cannot yet be said to have become dominant and some universities seem determined to resist it (and ABET) to the bitter end, evidence of its eventual ascendancy is mounting. In the remainder of this article I want to share some of the evidence I've recently seen.

I've given teaching workshops on campuses around the country since the late 1980s in which I discuss active and cooperative learning, and I usually ask the participants to raise their hands if they use those methods in their classes. Ten years ago, two or three hands would typically be raised. Now, 25–50% of the participants indicate that they use active learning and lower but still significant percentages use cooperative learning. This trend was also indicated by a 1997 survey of over 500 engineering faculty at eight schools who were shown to be representative of their faculties in most important respects. Many of the respondents reported regularly using active learning, team-based assignments, and other student-centered methods.^[1]

I frequently see impressive instructional innovations on campuses I visit and learn about others in the literature and at conferences, the most dramatic of which involve project-based and problem-based learning. Extensive research has shown that students learn best when they perceive a clear need to know the material being taught. Project/problem-based learning (PBL) uses this principle by introducing course material on a just-in-time basis in the context of realistic engineering problems and projects. This instructional strategy has been used for many years at the Colorado School of Mines and McMaster University, and numerous published articles report its successful adoption at other universities around the world. An outstanding example is ChemEngine (www.chemengine.net), a student-owned and operated consulting firm at Virginia Commonwealth University that tackles engineering problems for industrial clients and has saved those clients millions of dollars in its few years of existence.

PBL has become the foundation of some course sequences and clusters and departmental curricula. Texas A&M and several other schools in the Foundation Coalition have transformed their freshman engineering programs, integrating the

basic science and math courses traditionally taught in isolation and emphasizing their interrelationships and applications to engineering problems. In the spiral curriculum in chemical engineering at Worcester Polytechnic Institute, traditional content is taught on a just-in-time basis in a sequence of project-based courses. In each year of the curricula of several engineering departments at the University of Queensland in Australia, one or two project courses are taught that anticipate and integrate the material taught in parallel traditional courses. Several entire universities have taken one form or another of PBL as the basis of *all* of their curricula, including the University of Aalborg in Denmark and Olin University in Massachusetts.

This is not to say that engineering education reform is a done deal. If you look into a random class at a random engineering school today, you are still likely to see a professor deriving equations on a board, or (worse) flashing PowerPoint slides of derivations to half-asleep students in a half-empty room, and administrators abound who still argue that this approach somehow promotes learning (research evidence to the contrary notwithstanding). It may indeed turn out that ten years from now the old teacher-centered approach will *still* dominate engineering education. I doubt it, though, considering (a) the active, cooperative, and problem-based courses and curricula springing up at universities everywhere, the concurrent growth of engineering-based programs that equip faculty and graduate students to implement those instructional strategies, and the new ABET criteria that (if seriously enforced) will compel their use, (b) the power of instructional technology to provide stimulating interactive

lessons and the growing occurrence and effectiveness of its use at both traditional and on-line institutions, and (c) an awareness among high school graduates that alternative methods exist and an increasing unwillingness on their part to put up with the old approach (a point that clearly came out in the study mentioned at the beginning of this column). Again, these things are never certain, but with all that going on it's clear to me that the new paradigm is the horse to bet on.

References

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Engineering education went through a major sea change once before, and the signs are that it is doing so again. . . . developments have given rise to a national movement toward a more active, cooperative, problem-based instructional model for engineering education.

All of the *Random Thoughts* columns are now available on the World Wide Web at http://www.ncsu.edu/effective_teaching and at <http://che.ufl.edu/~cee/>

NANOSTRUCTURED MATERIALS

Synthesis of Zeolites

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Zeolites are crystalline aluminosilicates whose principal constituents are aluminum, silicon, and oxygen.^[1] They were discovered by Baron Axel F. Cronstedt, who coined their name using the Greek words *zeo* (to boil) and *lithos* (stone) because they bubbled under heating.^[2-4] The fundamental building blocks of the zeolite framework are the tetrahedral units: $[\text{SiO}_4]$ and $[\text{AlO}_4]$. The silicate $[\text{SiO}_4]$ unit, shown in Figure 1a, consists of a silicon atom surrounded by four oxygen atoms; $[\text{AlO}_4]$, in which Al replaces silicon at the center of the tetrahedron, bears a negative charge. This charge is balanced by that of positive metal ions, mostly alkali cations, sitting in the gaps of the framework.

During zeolite synthesis, the tetrahedral units are joined together via a common oxygen atom to form rings or cage structures, referred to as secondary building units (SBU). The SBUs can be assembled in many ways to produce various types of zeolites. For example, the so-called 5-1 ring SBU (see Figure 1b) generates either ZSM-5 or ZSM-11. Figure 1c illustrates the construction of a continuous framework of ZSM-5 using 5-1 SBUs. This zeolite (Figure 1d) exhibits two intersecting channels: one straight and the other zig-zag.

The extensive research in zeolites was initiated after recognition of the similarity in the composition of zeolites and silica-alumina.^[5] The latter was used as a cracking catalyst in refineries in the 1950s. At present, zeolites, including ZSM-5, are used to process over 7 billion barrels of petroleum and other chemicals annually, producing tens of billions of dollars per year in revenues.^[6] ZSM-5, one of the most widely studied zeolites, has dominated the patent literature in applications of nanostructured materials. In addition, the well-defined pores or cavities in nanometer range give rise to unique molecular sieving capabilities and high internal surface areas suitable for a wide range of applications in fields other than industrial catalysis, *e.g.*, ceramics, electronic materials, drug release media, sorbents, and ion exchangers.

The syntheses of zeolites often require the use of small organic species such as quaternary ammonium ions (*e.g.*, R_4N^+) as templates or structure-directing agents. Detailed mechanistic studies of ZSM-5 synthesis suggest that the hydrophobic hydration sphere formed around TPA (*i.e.*, tetrapropyl ammonium ion) is replaced by inorganic species forming an organic-inorganic nanocomposite. Aggregation of these species results in nucleation and eventually crystal growth in a layer-by-layer fashion.^[7,8] In 1992, Kresge, *et al.*, had the clever idea of using supramolecular assemblies such as surfactants or polymer liquid crystals as templates, instead of the individual molecules or cations currently used as structure-directing agents for the synthesis of zeolites.^[5,9,10] The ordered materials were obtained and referred to as mesoporous molecular sieves (MMS). These materials are similar to zeolites, with the notable difference being that their pore sizes are much larger (*i.e.*, from 2 to over 30 nm).

The evolution from the concept of structure-directing to

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that of supramolecular assemblies has led to rapid development in the synthesis of nanostructured materials. These novel nanomaterials opened new opportunities in many areas, such as biosensing, drug delivery, bioseparation, and heterogeneous catalysis.^[11-20] The simplicity in the concepts of template synthesis, along with the complexity of interrelated factors in zeolite synthesis, make ZSM-5 synthesis an excellent project that allows students to integrate basic principles of nanomaterials synthesis into reaction engineering.

This paper describes an experiment on ZSM-5 synthesis that was performed in our juniors' chemical engineering laboratory at the University of Akron. The objective of this experiment is to provide hands-on experience for the students that includes formation of working teams, performing literature searches, grasping basic concepts of nanostructured material synthesis, experimental design, reactor operation, infrared spectroscopic analysis, troubleshooting, and learning assessment.

EXPERIMENTAL

Materials and Equipment • Sodium hydroxide (certified A.C.S. grade), tetrapropyl ammonium bromide (*i.e.*, TPA) (98+%), and sulfuric acid (0.1 M standardized solution) were obtained through Alfa Aesar; sodium aluminate (~8% H₂O, 99.9% Al) was purchased from Strem Chemicals; and Aerosil silica was generously donated by Cabot Corporation. All chemicals were used without further purification. The hy-

drothermal synthesis of zeolite was conducted in a 300 cm³ stainless steel autoclave (Pressure Products Inc). The samples were analyzed by X-ray diffraction (XRD) [Phillips APD3700 X-ray diffractometer (Cu-K_α radiation)] and infrared spectroscopy (IR) [Nicolet Magna 550 Series II infrared spectrometer equipped with a DTGS (deuterated tri-glycine sulfate) detector].

Synthesis • The key steps involved in the hydrothermal synthesis of ZSM-5 can be seen in Figure 2 (next page): preparation of solutions containing the Si and Al precursors along with the structure-directing agent, mixing, aging, hydrothermal treatment, filtration, drying, and calcination. Solution A, containing the Si precursor and the structure-directing agent (TPA), was prepared by dissolving 11.1 g of Aerosil silica in 32 ml of 1.25 M NaOH solution and then adding 81 ml of 3.2 wt% TPA aqueous solution. Solution B was obtained by dissolving 0.6 g of sodium aluminate (NaAlO₂) in 10 ml of H₂O.

Mixing Solutions A and B under vigorous stirring resulted in a homogeneous gel at pH 13. The pH of the gel was then adjusted to 11 by addition of 0.1 M H₂SO₄. The resulting gel was aged for 2 h prior to hydrothermal treatment. Aging is crucial to obtain the desired crystalline phase and to accelerate crystallization. The aged gel was finally loaded in a stainless steel autoclave and heated at 150°C for 4 h. The hydrothermal treatment is a thermally activated process. Increasing the temperature of the reactant solution above the boiling point facilitates the crystallization process, *i.e.*, supersatura-

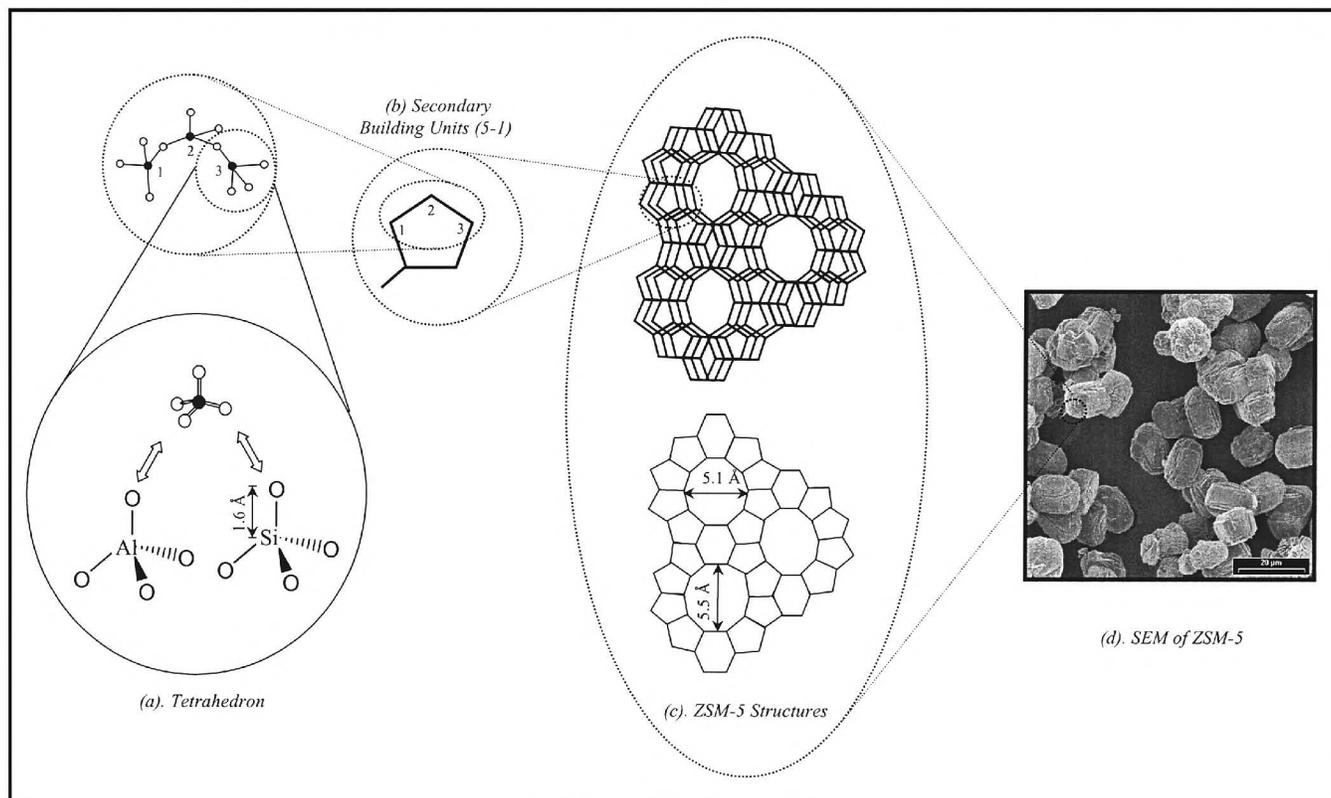


Figure 1. Structure of ZSM-5.

tion, nucleation, and crystal growth. To monitor the crystallization process, 8 ml of gel reactant/ZSM-5 product mixture was sampled via a sampling valve every 30 min for analysis. The samples were filtered, dried, and then pressed in the form of thin disks for XFD and IR analyses.

RESULTS AND ANALYSIS

The appearance and evolution of an XRD pattern characteristic of ZSM-5 zeolite is shown in Figure 3. The well-defined X-ray diffraction pattern manifests the crystalline microstructure of XSM-5.^[21] The IR spectra of ZSM-5 samples, which exhibit two key bands at 450 cm^{-1} and 548 cm^{-1} , are shown in Figure 4. The former is due to the Si-O stretching of the tetrahedral unit, whereas the latter is due to the double 5-1 ring (SBU) vibration.^[22] The peak intensity in the XRD pattern and the IR intensity of the 548 cm^{-1} band reflect the extent of the crystallization process.

The crystallinity of the samples was determined by comparing the XRD peak intensity and the intensity ratio of the 548 to 458 cm^{-1} IR bands with those of calibrated samples. Crystallinity calibration was carried out by measuring the intensity of a number of standard samples (*i.e.*, mixtures of pure ZSM-5 from Zeolyst and Aerosil silica) of known ZSM-5 concentrations. The crystallinity determined here corresponds to the zeolite yield, which is defined as the ratio of the amount of zeolite to the initial amount of SiO_2 and NaAlO_2 .

The experimental ZSM-5 crystallization curve, which plots the crystallinity of the zeolite versus the hydrothermal treatment time, is shown in Figure 5. The parallel between the crystallinity as measured by XRD and by IR indicates that the relative intensity of the 458 cm^{-1} band can serve as a reliable index of the ZSM-5 crystallinity and yield during its synthesis, allowing the use of a low-cost infrared spectrometer to determine the ZSM-5 structure. The zeolite crystallization curve usually exhibits an S-shaped profile with an inflection point, which separates the induction period and the autocatalytic growth period. ZSM-5 synthesis at 150°C can be completed in 5.5 h with a final crystallinity near 100%. The key parameters governing the zeolite crystallization include hydrogel molar concentration, alkalinity (*i.e.*, pH), temperature, template, pressure, and seeding. The complexity of the interactions of these factors makes zeolite synthesis an interesting laboratory project that allows each team of students to design their own experimental parameters and carry out the experiment at a specific set of conditions.

DISCUSSION

In a two-hour lecture, the instructor covered nanomaterial synthesis and applications, the basic principles of zeolite synthesis, and typical characterization techniques such as X-ray diffraction and infrared spectroscopy as well as safety issues. A graduate assistant demonstrated the operation procedure of the autoclave and the infrared spectrometer. A list of the tasks and time needed to complete them can be found in Table 1.

A typical experiment team consists of four students, and a typical synthesis procedure for ZSM-5, as shown in Figure 2, is given to them. The first homework assignment is to use SciFinder Scholar to search for a ZSM-5 synthesis recipe from journal articles or patents and to compare the literature recipe with the given one. Experience with literature searches allows students to gain a better understanding of the process of translating scien-

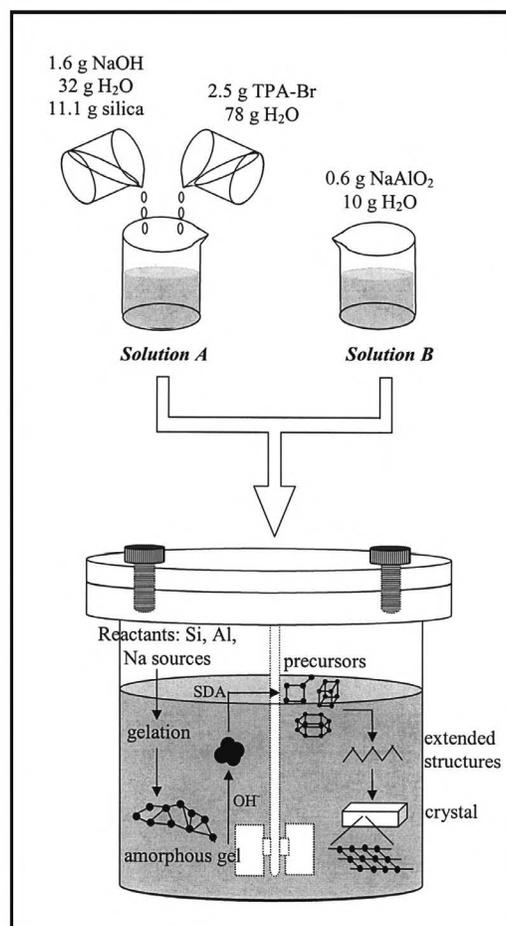


Figure 2. Hydrothermal synthesis of ZSM-5.

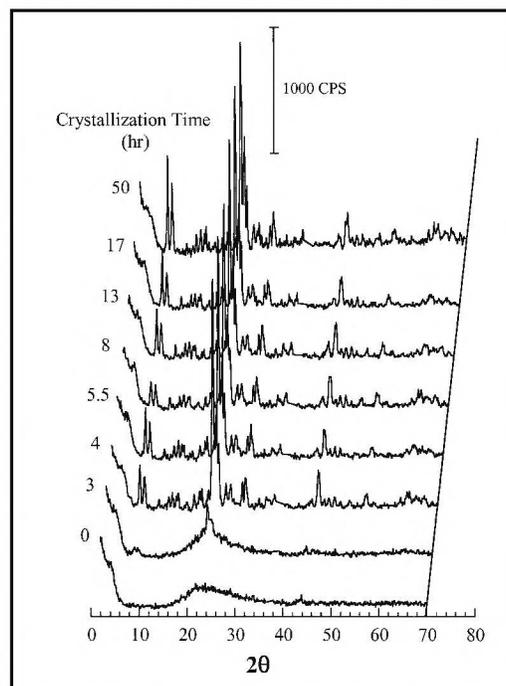


Figure 3. XRD pattern of as-synthesized XSM-5 samples vs. crystallization time at 150°C .

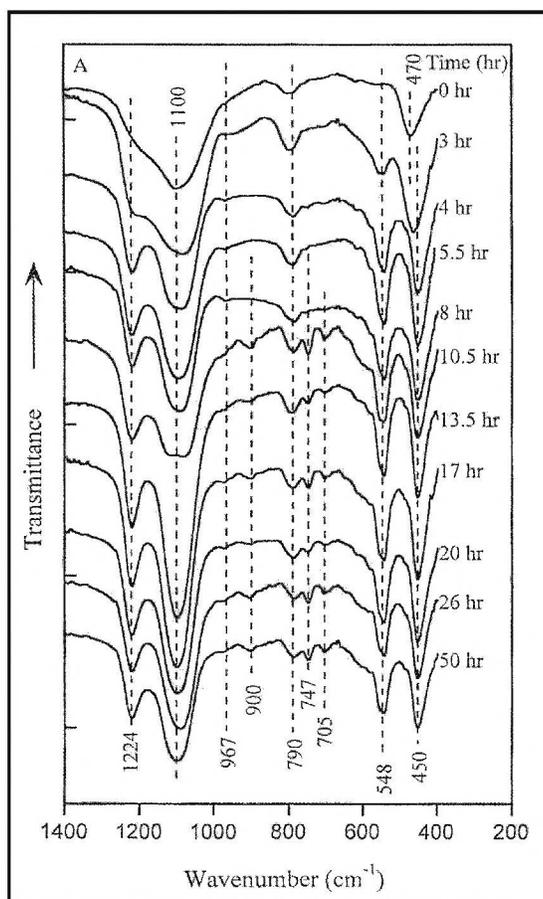


Figure 4. IR spectra of as-synthesized XSM-5 samples vs. crystallization time at 150°C.

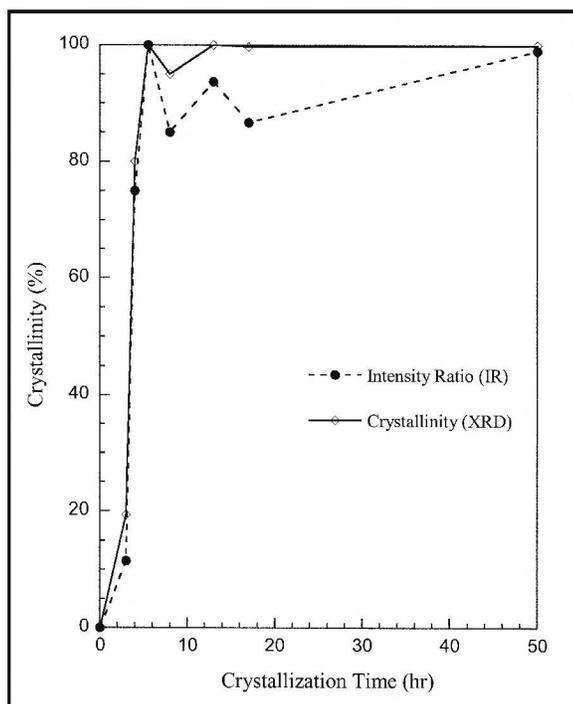


Figure 5. Crystallizations (%) vs. crystallinity time.

tific discovery to practical technology. Students are strongly encouraged to either modify the given recipe or use a literature or patented recipe to design and implement their experiment for zeolite synthesis. Extra bonus points are given to teams that use literature recipes. The team that chooses a literature recipe must submit its recipe to the instructor to ensure the safety and availability of required chemicals. Of the seven teams in the 2000 class, only two opted for a literature recipe.

Experimental planning involves selection of hydrothermal synthesis conditions and assignment of tasks to each student on the team. Each student is responsible for a specific task. Students who are not involved in a specific assignment are required to observe and understand their teammates' tasks. The total time needed for the experiments is 12.5 h.

To help students increase their understanding of the interrelationship between reaction engineering and nanomaterials synthesis, as well as to promote their ability to link experimental observations to fundamental concepts, we posed several questions, which can be found in Table 1. These questions provide a framework for students to prepare their reports and for the instructor to evaluate the students' understanding and creativity.

Our 1999 learning survey revealed that the typical problem encountered in zeolite synthesis was plugging of the sampling valve. Peer review and close supervision of the students' performances revealed that the majority (90%) of the students accomplished the assigned tasks. Peer review also pointed out the problems students encountered in coordinating the experimental work. The final grade of individual students was obtained by adjusting the team report grade based on each student's contribution

Continued on page 47.

TABLE 1
Experimental Tasks

- Formation of the team and distribution of tasks
- Literature search
- Selection of a synthesis process
- Designing and planning the experiment
- Implementation
 1. Preparation of precursor solution (0.5 hr)
 2. Hydrothermal treatment (7 h)
 3. Filtration and drying (3 h)
 4. Infrared analysis (2 h)
- Report preparation
 1. Kinetics of zeolite syntheses. Are you able to derive a meaningful rate expression and obtain reaction order and rate constant for zeolite synthesis?
 2. What are the factors governing the zeolite synthesis? Discuss the phase behavior as well as heat and mass transfer in the autoclave during zeolite synthesis.
 3. Compare the results obtained with those in the literature.
 4. Propose and design a novel nanostructured material based on the concept of templated synthesis and self-assembly.
- Peer review:
 1. Task distribution
 2. Time management
 3. Coordination
 4. Quality of work
 5. Objective accomplishment

THE FUEL CELL

An Ideal ChE Undergraduate Experiment

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There is much interest in developing fuel cells for commercial applications. This interest is driven by technical and environmental advantages offered by the fuel cell, including high performance characteristics, reliability, durability, and clean power. A fuel cell is similar to a battery—it uses an electrochemical process to directly convert chemical energy to electricity. Unlike a battery, however, a fuel cell does not run down as long as the fuel is provided. Fuel cells are characterized by their electrolytes since the electrolyte dictates key operating factors such as operating temperature. The main features of five types of fuel cells are summarized in Table 1.^[1]

The proton exchange membrane (PEM) fuel cell is particularly amenable for use as an undergraduate laboratory experiment due to safety and operational advantages, including use of a solid polymer electrolyte that reduces corrosion, a low operating temperature that allows quick startup, zero toxic emissions, and fairly good performance compared to other fuel cells. A cross-sectional diagram of a single-cell PEM fuel cell is shown in Figure 1. The proton exchange membrane (Nafion®) is in contact with the anode catalyst layer (shown on the left) and a cathode catalyst layer (shown on the right). Each catalyst layer is in contact with a gas diffusion layer. The membrane, catalyst layers, and the gas diffusion layers make up what is called the membrane-electrode-assembly (MEA).

Fuel (hydrogen in this figure) is fed into the anode side of the fuel cell. Oxidant (oxygen, either in air or as a pure gas) enters the fuel cell through the cathode side. Hydrogen and oxygen are fed through flow channels and diffuse through gas diffusion layers to the

TABLE 1
 Summary of Fuel Cell Technologies

<i>Fuel Cell</i>	<i>Electrolyte</i>	<i>Temperature (°C)</i>	<i>Applications</i>
Alkaline (AFC)	Potassium Hydroxide	90-100	Military Space Flight
Phosphoric Acid (PAFC)	Phosphoric Acid	175-200	Electric Utility Transportation
Molten Carbonate (MCFC)	Lithium, Sodium, and/or Potassium Carbonate	650	Electric Utility
Solid Oxide (SOFC)	Zirconium Oxide Doped by Yttrium	1000	Electric Utility
Proton Exchange Membrane (PEMFC)	Solid polymer (poly-perfluorosulfonic acid)	<100	Electric Utility Portable Power Transportation

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catalyst on their respective sides of the MEA. Activated by the catalyst in the anode, hydrogen is oxidized to form protons and electrons. The protons move through the proton exchange membrane and the electrons travel from the anode through an external circuit to the cathode. At the cathode catalyst, oxygen reacts with the protons that move through the membrane and the electrons that travel through the circuit to form water and heat.

Since the hydrogen and oxygen react to produce electricity directly rather than indirectly as in a combustion engine, the fuel cell is not limited by the Carnot efficiency. Although more efficient than combustion engines, the fuel cell does produce waste heat. The typical efficiency for a Nafion PEM fuel cell is approximately 50%.

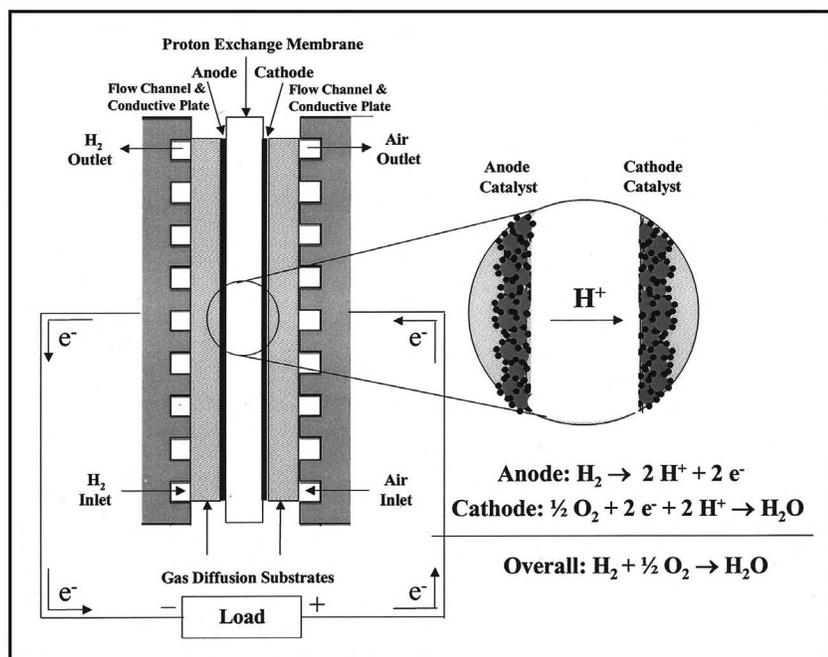


Figure 1. PEM fuel cell cross section.

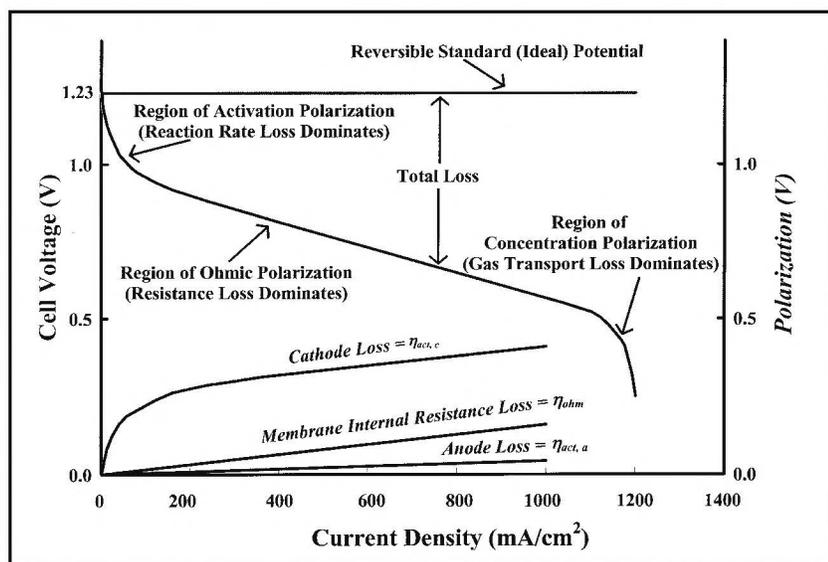


Figure 2. Representative fuel cell performance curve at 25 °C, 1 atm.

Fuel cells can be used to demonstrate a wide range of chemical engineering principles such as kinetics, thermodynamics, and transport phenomena. A general review of PEM fuel cell technology and basic electrochemical engineering principles can be found in the literature.^[1-8] Because of their increasing viability as environmentally friendly energy sources and high chemical engineering content, fuel cell experiments have been developed for the chemical engineering undergraduate laboratory as described in the remainder of this paper.

OBJECTIVES

The objectives of the fuel cell experiment are

- To familiarize students with the working principles and performance characteristics of the PEM fuel cell
- To demonstrate the effect of oxygen concentration and temperature on fuel cell performance
- To fit experimental data to a simple empirical model

Students will measure voltage and membrane internal resistance as a function of operating current at various oxygen concentrations and temperatures; generate current density vs. voltage performance curves; and calculate cell efficiency, reactant utilization, and power density. Current density is defined as the current produced by the cell divided by the active area of the MEA. By fitting current density vs. voltage data to a simple empirical model, students can estimate ohmic, activation (kinetic), and concentration (transport) polarization losses and compare them to experimental or theoretical values.

BACKGROUND

The performance of a fuel cell can be characterized by its

1. Current density versus voltage plot as shown in Figure 2
2. Efficiency
3. Reactant utilization (ratio of moles of fuel consumed to moles of fuel fed)
4. Power density (ratio of power produced by a single cell to the area of the cell (MEA))

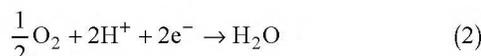
Current Density-Voltage Characteristics

Since a fuel cell is a device that facilitates the direct conversion of chemical energy to electricity, the ideal or best-attainable performance of a fuel cell is dictated only by the thermodynamics of the electrochemical reactions that occur (a function of the reactants and products). The electrochemical reactions in a hydrogen/oxygen fuel cell are shown in Eqs. (1) and (2).

Anode Reaction



Cathode Reaction



The reversible standard (*i.e.*, ideal) potential E° for the H_2/O_2 cell reaction is 1.23 volts per mole of hydrogen (at 25 °C, unit activity for the species, liquid water product) as determined by the change in Gibbs free energy. Reference 1 provides a derivation of this potential. The reversible standard potential for the hydrogen/oxygen cell is indicated on the current density-voltage diagram in Figure 2 as the horizontal line drawn at a voltage of 1.23. The Nernst equation can be used to calculate reversible potential at “non-standard” concentrations and a given temperature. Equation (3) is the Nernst equation specifically written for the H_2/O_2 cell based on the reactions as written.

$$E = E^\circ + \left(\frac{RT}{nF}\right) \ln \frac{(P_{\text{H}_2})(P_{\text{O}_2})^{1/2}}{(P_{\text{H}_2\text{O}})} \quad (3)$$

where

R gas constant (8.314 Joule/mol °K)

T temperature (°K)

F Faraday’s constant (96,485 coulombs/equiv)

n moles of electrons produced/mole of H_2 reacted (n=2 for this reaction)

E° reversible potential at standard concentrations and temperature T (volts)

E reversible potential at non-standard concentrations and temperature T (volts)

$P_{\text{H}_2}, P_{\text{O}_2}, P_{\text{H}_2\text{O}}$ partial pressures of H_2 , O_2 , and H_2O , respectively (atm)

Note: 1 volt = 1 joule/coulomb

The Nernst equation cannot be used to make both temperature and concentration corrections simultaneously. To do this, one must first apply Eq. (4) to “adjust” the standard potential E° for temperature and then apply the Nernst equation to adjust for concentration at the new temperature.^[6]

$$E_2^\circ - E_1^\circ = \frac{\Delta S}{nF} (T_2 - T_1) \quad (4)$$

Subscripts 1 and 2 on E° denote “at temperatures T_1 and T_2 ”

and ΔS is the entropy change of reaction (= - 163.2 J/°K for the H_2/O_2 reaction at 25 °C, unit activity for the species, liquid water product).

When a load (external resistance) is applied to the cell, non-equilibrium exists and a current flows. The total current passed or produced by the cell in a given amount of time is directly proportional to the amount of products formed (or reactants consumed) as expressed by Faraday’s law

$$I = \frac{mnF}{sMt} \quad (5)$$

where I (A) is the current, m (g) is the mass of product formed (or reactant consumed), n and F are defined above, s is the stoichiometric coefficient of either the product (a positive value) or reactant (a negative value) species, M (g/mol) is the atomic or molecular mass of the product (or reactant) species, and t (s) is the time elapsed. Equation (5) is valid for a constant current process. Faraday’s law can be written in the form of the kinetic rate expression for H_2/O_2 cell as

$$\frac{I}{2F} = \frac{d(\text{moles H}_2\text{O})}{dt} = \frac{-d(\text{moles H}_2)}{dt} = \frac{-2d(\text{moles O}_2)}{dt} \quad (6)$$

There is a trade-off between current and voltage at nonequilibrium (nonideal) conditions. The current density-voltage relationship for a given fuel cell (geometry, catalyst/electrode characteristics, and electrolyte/membrane properties) and operating conditions (concentration, flow rate, pressure, temperature, and relative humidity) is a function of kinetic, ohmic, and mass transfer resistances. The current density vs. voltage curve shown in Figure 2 is referred to as the polarization curve. Deviations between the reversible potential and the polarization curve provide a measure of fuel cell efficiency.

Kinetic Limitations • Performance loss (voltage loss) resulting from slow reaction kinetics at either/both the cathode and anode surfaces is called activation polarization ($\eta_{\text{act,c}}$ and $\eta_{\text{act,a}}$). Activation polarization is related to the activation energy barrier between reacting species and is primarily a function of temperature, pressure, concentration, and electrode properties. Competing reactions can also play a role in activation polarization.

Kinetic resistance dominates the low current density portion of the polarization curve, where deviations from equilibrium are small. At these conditions, reactants are plentiful (no mass transfer limitations) and the current density is so small that ohmic (= current density x resistance) losses are negligible. The Tafel equation describes the current density-voltage polarization curve in this region.

$$\eta_{\text{act}} = B \log|i| - A \quad (7)$$

where η_{act} is the voltage loss due to activation polarization (mV), i is current density (mA/cm²), and constants A and B are kinetic parameters (B is often called the Tafel slope).^[6]

As shown in Figure 2, the kinetic loss at the cathode, $\eta_{act,c}$ (the reduction of O_2 to form water) is much greater than kinetic loss at the anode, $\eta_{act,a}$, in the H_2/O_2 cell.

Ohmic Limitations • Performance loss due to resistance to the flow of current in the electrolyte and through the electrodes is called ohmic polarization (η_{ohm}). Ohmic polarization is described using Ohm's law ($V=iR$), where i is current density (mA/cm^2) and R is resistance ($\Omega\cdot cm^2$). These losses dominate the linear portion of the current density-voltage polarization curve as shown in Figure 2. Improving the ionic conductivity of the solid electrolyte separating the two electrodes can reduce ohmic losses.

Transport Limitations • Concentration polarization ($\eta_{conc,c}$ and $\eta_{conc,a}$) occurs when a reactant is consumed on the surface of the electrode forming a concentration gradient between the bulk gas and the surface. Transport mechanisms within the gas diffusion layer and electrode structure include the convection/diffusion and/or migration of reactants and products (H_2 , O_2 , H^+ ions, and water) into and out of catalyst sites in the anode and cathode. Transport of H^+ ions through the electrolyte is regarded as ohmic resistance mentioned above. Concentration polarization is affected primarily by concentration and flow rate of the reactants fed to their respective electrodes, the cell temperature, and the structure of the gas diffusion and catalyst layers.

The mass-transfer-limiting region of the current-voltage polarization curve is apparent at very high current density. Here, increasing current density results in a depletion of reactant immediately adjacent to the electrode. When the current is increased to a point where the concentration at the surface falls to zero, a further increase in current is impossible. The current density corresponding to zero surface concentration is called the limiting current density (i_{lim}), and is observed in Figure 2 at approximately 1200 mA/cm^2 as the polarization curve becomes vertical at high current density.

The actual cell voltage (V) at any given current density can be represented as the reversible potential minus the activation, ohmic, and concentration losses, as expressed in Eq. (8).

$$V = E - (\eta_{act,c} + \eta_{act,a}) - iR - (\eta_{conc,c} + \eta_{conc,a}) \quad (8)$$

Note that activation ($\eta_{act,c}$, $\eta_{act,a}$) and concentration ($\eta_{conc,c}$, $\eta_{conc,a}$) losses (all positive values in Eq. 8) occur at both electrodes, but anode losses are generally much smaller than cathode losses for the H_2/O_2 cell and are neglected. Ohmic losses (iR) occur mainly in the solid electrolyte membrane. An additional small loss will occur due to the reduction in oxygen pressure as the current density increases. Current fuel cell research is focused on reducing kinetic, ohmic, and transport polarization losses.

Cell Efficiency

Fuel cell efficiency can be defined several ways. In an energy-producing process such as a fuel cell, *current efficiency* is defined as

$$\epsilon_f = \frac{\text{theoretical amount of reactant required to produce a given current}}{\text{actual amount of reactant consumed}} \quad (9)$$

In typical fuel cell operation, current efficiency is 100% because there are no competing reactions or fuel loss. *Voltage efficiency* is

$$\epsilon_v = \frac{\text{actual cell voltage}}{\text{reversible potential}} = \frac{V}{E} \quad (10)$$

The actual cell voltage at any given current density is represented by Eq. (8) and reversible potential by Eq. (3). *Overall energy efficiency* is defined as

$$\epsilon_e = \epsilon_f * \epsilon_v \quad (11)$$

The H_2/O_2 fuel cell of Figure 2 operating at 0.8 V has a voltage efficiency of about 65% ($=0.8/1.23*100$). The overall efficiency at this voltage, assuming that the current efficiency is 100%, is also 65%. In other words, 65% of the maximum useful energy is being delivered as electricity and the remaining energy is released as heat (35%).

A fuel cell can be operated at any current density up to the limiting current density. Higher overall efficiency can be obtained by operating the cell at a low current density. Low current density operation requires a larger active cell area to obtain the requisite amount of power, however. In designing a fuel cell, capital costs and operating cost must be optimized based on knowledge of the fuel cell's performance and intended application.

Reactant Utilization

Reactant utilization and gas composition have major impact on fuel cell efficiency. Reactant utilization is defined as

$$U = \frac{\text{Molar flowrate}_{\text{reactant,in}} - \text{Molar flowrate}_{\text{reactant,out}}}{\text{Molar flowrate}_{\text{reactant,in}}} = \frac{\text{Mol } H_2 / \text{s consumed}}{\text{Mol } H_2 / \text{s fed}} \quad (12)$$

"Molar flow rate consumed" in this equation is directly proportional to the current produced by the cell and can be calculated from Eq. (6). In typical fuel cell operation, reactants are fed in excess of the amount required as calculated by Faraday's law (*i.e.*, reactant utilization < 1). Higher partial pressures of fuel and oxidant gases generate a higher reversible potential and affect kinetic and transport polarization losses.

Power Density

The power density delivered by a fuel cell is the product of the current density and the cell voltage at that current density. Because the size of the fuel cell is very important, other terms are also used to describe fuel cell performance. Specific power is defined as the ratio of the power generated by a cell (or stack) to the mass of that cell (or stack).

EQUIPMENT, PROCEDURE, AND IMPLEMENTATION

The experiments presented here are designed to give the experimenter a “feel” for fuel cell operation and to demonstrate temperature and concentration effects on fuel cell performance. The manipulated variables are cell temperature, concentration of oxygen fed to the cathode, and current. Flow rates are held constant and all experiments are performed at 1 atm pressure. The measured variables are voltage and resistance, from which polarization curves are generated and fuel cell performance is evaluated. A simple empirical model can be fit to the data, allowing students to separately estimate ohmic resistance, kinetic parameters, and limiting current density. Table 2 summarizes the conditions investigated in this study.

Many other experimental options are available with the system described in this paper, including an investigation of the effect of 1) catalyst poisoning, 2) relative humidity of the feed gases, or 3) flow rate on fuel cell performance.

Equipment

A schematic diagram of the experimental setup is shown in Figure 3. An equipment list for in-house-built systems, including approximate cost and the names of several suppliers, is provided in Table 3. Completely assembled systems can be purchased from Scribner Associates, Inc. (www.scribner.com), Lynntech Inc. (www.lynn-tech.com), ElectroChem Inc. (www.fuelcell.com), and TVN (www.tvnsystems.com).

Hydrogen, supplied from a pressurized cylinder, is sent through the heated anode humidifier before being fed through heated tubes to the anode side of the fuel cell. Similarly, oxidant with any desired composition (oxygen

TABLE 2
Experimental Conditions: All at P=1 atm

Anode Feed			Cathode Feed		
Temp (°C)	Flow rate (ml/min)	Dry basis Composition (Mole %)	Temp (°C)	Flow rate (ml/min)	Dry basis Composition (Mole %)
80	98	100% H ₂	80	376	100% O ₂
80	98	100% H ₂	80	376	Air-21% O ₂ in N ₂
80	98	100% H ₂	80	376	10.5% O ₂ in N ₂
80	98	100% H ₂	80	376	5.25% O ₂ in N ₂
18	98	100% H ₂	18	376	100% O ₂

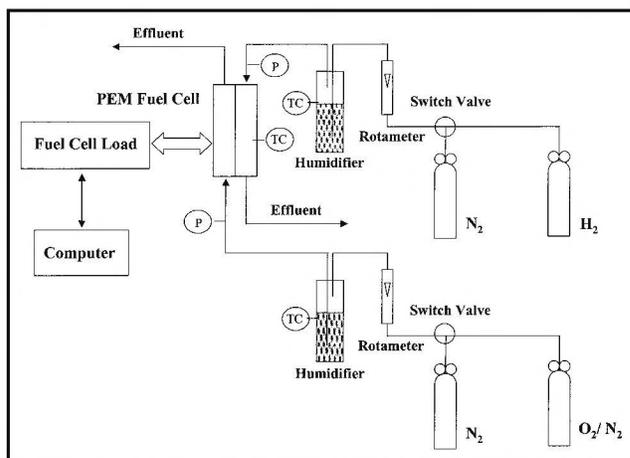


Figure 3. Schematic of experimental setup.

TABLE 3
Equipment List for In-House-Built Systems

Quant.	Equipment/Supplies	Approx. Cost	Vendor*
1	Fuel cell load (sink and power supply)	\$2,000	Scribner, Lynntech, Electrochem, TVN
1	Computer (optional)	\$1,000	Dell, IBM, Compaq
1	Data acquisition card (optional)	\$1,000	National Instruments
1	Single cell hardware w/heating element (5 cm ²)	\$1,500	Electrochem, Fuel Cell Technology
1	Membrane-electrode-assembly (5 cm ²)	\$200	Electrochem, Lynntech, Gore Associates
5	Temperature controller: 0-100°C	\$1,000	OMEGA
4	Heating element (heating tape)	\$400	OMEGA
5	Thermocouple	\$200	OMEGA
2	Humidifier (2" ID stainless pipes and caps)	\$200	McMaster-Carr
2	Rotameter (0-200 cc/min for H ₂ fuel; 0-400 cc/min for oxidant)	\$400	OMEGA
N/A	Valves and fittings (stainless steel)	\$1,500	Swagelok
20 ft	Tubing (1/4" stainless steel)	\$200	
4	Regulator	\$1,000	Airgas
N/A	Gas (H ₂ , N ₂ , Air, O ₂ /N ₂)	\$1,000	Airgas
1	Digital flow meter (for calibration of rotameter)	\$500	Humonics
	Other	\$1,000	
	TOTAL	~\$13,000	

*List is not exhaustive

in nitrogen) is supplied from a pressurized cylinder and sent to the heated cathode humidifier before being fed through heated tubes to the cathode side of the fuel cell. Constant volumetric flow rates for anode and cathode feeds are manually controlled by rotameters. Humidification of the feed streams is necessary to maintain conductivity of the electrolyte membrane. Heating of the humidifiers, the tubes leading to the fuel cell, and preheating of the fuel cell is accomplished using heating tape, and temperatures of the feed streams and fuel cell are maintained using temperature controllers. To avoid flooding the catalyst structure, the humidifier temperature is maintained at or slightly below the cell temperature. The relative humidity of a stream exiting a humidifier can be determined manually by flowing the stream across a temperature controlled, polished metal surface and measuring its dew point. Effluent from the fuel cell is vented to a hood for safety purposes.

The PEM fuel cell comprises an MEA with an active area of 5 cm² (prepared at the University of Connecticut) and is housed in single-cell hardware with a single-pass serpentine flow channel. Our fuel cell load and data acquisition electronics are integrated in a single unit manufactured by Scribner Associates. During a typical experimental run (constant flow rate, oxidant composition, and temperature), the current is manipulated/adjusted on the fuel cell load and the voltage and resistance are read from built-in meters in the load. The fuel cell load uses the "current-interrupt technique"^[3] to measure the total resistance between the two electrodes.

Procedure

A fuel cell with a prepared or commercial MEA is first connected to the fuel cell test system. Before feeding the hydrogen and oxidant into the fuel cell, humidified nitrogen is

introduced to purge the anode and cathode sides of the single cell. During the purge (at 50 cc/min), the cell and humidifiers are heated to their respective operating temperatures (*e.g.*, cell, 80 °C, humidifiers, 80 °C). When the cell and humidifiers reach the desired temperature, the humidified nitrogen is replaced by humidified hydrogen and oxidant for the anode and cathode, respectively. During experiments, fuel and oxidant are always fed in excess of the amount required to produce a current of 1 A as calculated by Faraday's law (Eq. 5). The hydrogen and oxidant flow rates used in these experiments are based on operating at 1 A/cm² with an approximate reactant utilization of 45% for the hydrogen and 30% for oxidant (based on air). A sample calculation is provided in Table 4.

After introducing the fuel and oxidant into the cell, the open circuit voltage (zero current) should be between 0.8 and 1 volt. Fuel cell performance curves are generated by recording steady state voltage at different currents. Approximately 5 minutes is required to reach steady state for changes in current at constant composition and temperature, but it might take 20 to 30 minutes to reach steady state for a change in either oxidant composition or temperature. The system should be purged with nitrogen during shutdown. Short-circuiting the fuel cell will destroy the MEA.

Implementation and Assessment

This experiment will be included as part of a three-credit senior-level chemical engineering undergraduate laboratory. The course consists of two 4-hour labs per week, during which groups of 3 to 4 students perform experiments on five different unit operations throughout the semester (*e.g.*, distillation, heat exchanger, gas absorption, batch reactor, etc.). Each unit is studied for either one or two weeks, depending on the complexity and scale of the equipment. Given only general goals for each experiment, students are required to define their own objectives, develop an experimental plan, prepare a pre-lab report (including a discussion of safety), perform the experiments, analyze the data, and prepare group or individual written and/or oral reports.

The fuel cell experiment described above can easily be completed in one week (two 4-hour lab periods). Additional experiments can be added to convert this lab into a two-week experiment. Due to their similar nature and focus (generation of performance/characteristic curves and analysis of efficiency at various operating conditions), the fuel cell experiment could be used in place of the existing centrifugal pump experiment.

Immediate assessment of the experiment will be based on student feedback and student performance on the pre-lab presentation, lab execution, and technical content of the written/oral reports. Existing assessment tools (End-of-Course Survey, Senior Exit Interview, Alumni Survey, Industrial Advi-

TABLE 4
Sample Flow-Rate Calculation

$$\text{Faraday's Law: } \frac{m}{Mt} = \frac{Is}{nF} \text{ mol / time}$$

Hydrogen consumption in fuel cell = $I/(2F)$ mol/time

Oxygen consumption in fuel cell = $I/(4F)$ mol/time

To produce a current of $I = 1$ Amp, H₂ consumption is:

$$= I/(2F) = 1/(2 \times 96485) = 5.18 \times 10^{-6} \text{ mol/s} \\ = 3.11 \times 10^{-4} \text{ mol/min}$$

According to gas law: $PV = NRT$

At 80°C and 1 atm, $V/N = RT/P = 0.082 \times (273.15 + 80)/1 = 29 \text{ L/mol}$

So H₂ consumption is: $V_{H_2} = 9.0 \text{ ml/min @ 1 Amp current}$

O₂ consumption is: $V_{O_2} = 4.5 \text{ ml/min @ 1 Amp current}$

Corresponding $V_{air} = 4.5/0.21 = 21.4 \text{ ml.min @ 1 Amp current}$

To convert the above numbers to vol flowrates at a desired current density (amp/cm²), divide ml/min by 1 cm² to get ml/min/cm².

For desired 45% H₂ utilization at 1 Amp/cm² current density

$U = \text{moles consumed}/\text{moles fed} = 0.45$

H₂ feed flow rate is: $V_{H_2} = 9.0/0.45 = 20 \text{ ml/min/cm}^2 \text{ @ 1 Amp/cm}^2$

$= 100 \text{ ml/min @ 1 A current with } 5 \text{ cm}^2 \text{ MEA}$

sory Board input, and annual faculty curriculum review) will be used to evaluate the overall impact of the experiment.

RESULTS AND DISCUSSION

Performance

Performance curves (voltage vs. current density) and membrane resistance vs. current density at 80 °C with different oxidant compositions (pure oxygen, air, 10.5% O₂ in N₂ and 5.25% O₂ in N₂) are shown in Figure 4. Measured open circuit voltage (V_{oc}) can be compared to reversible potential calculated via Eqs. (3) and (4). These values are presented in the legend of Figure 4. Students will observe that the actual open circuit voltage is slightly lower than the theoretical maximum potential of the reactions. Activation polarization (kinetic limitation) is observed at very low current density (0-150 mA/cm²). Kinetic losses increase with a decrease in oxygen concentration. At low current densities, membrane resistance (ohmic polarization) is nearly constant (about 0.14 Ω-cm²) and is independent of oxidant composition. Membrane resistance begins to increase slightly with increasing current density at 800 mA/cm² due to dry-out of the membrane on the anode side. Dry-out occurs at high current density because water molecules associated with migrating protons are carried from the anode side to the cathode at a higher rate than they can diffuse back to the anode. Mass transport limitations due to insufficient supply of oxygen to the surface of the catalyst at high current density is observed, especially for gases containing low concentrations of oxygen. Limiting currents are evident at about 340 mA/cm² and 680 mA/cm² for the 5.25% and 10.5% oxygen gases, respectively, but are not obvious for pure oxygen and air. Limiting current density can be shown to be directly proportional to oxygen content.

The effect of operating temperature (18°C vs. 80°C, both at 100% relative humidity) on cell performance and membrane resistance for a pure O₂/H₂ cell is shown in Figure 5. Measured open-circuit voltage and reversible potential at 80°C are slightly lower than the corresponding voltages at 18°C. This is due to higher concentrations of reactants when fed at lower temperatures and 100% relative humidity. Elevated temperatures favor faster kinetics on the catalyst surface and lower membrane resistance, however, resulting in better cell performance. Under fully hydrated environments (100% RH), membrane resistance decreases with increasing temperature due to increased mobility of the protons. Again, limiting current density for pure oxygen is not obvious in this plot.

A linear relationship between current density and reactant utilization (per Eq. 5) is clearly evident in Figure 6. Reactant utilization decreases with increasing inlet oxygen concentration (at constant flow rate) because of an increase in the moles reactant feed.

Power density (W/cm²) delivered by a fuel cell is defined by the product of current density drawn and voltage at that

current density. The effect of current density on power density for various oxidant compositions is shown in Figure 7. For a given feed composition, maximum power density is achieved approximately halfway between no-load and limiting current densities. The selection of “optimal” operating

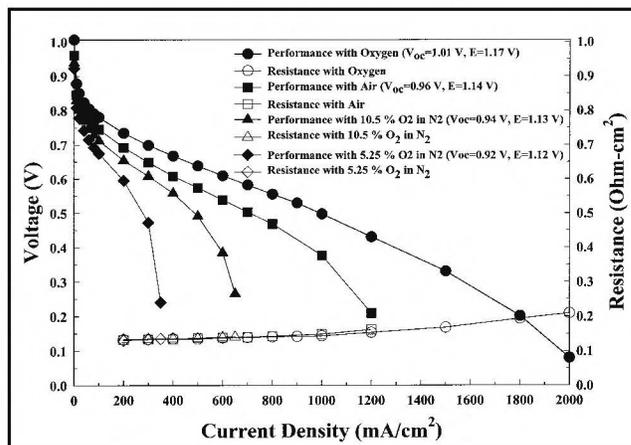


Figure 4. Effect of oxidant concentration on cell performance and membrane resistance at 80°C, 1 atm.

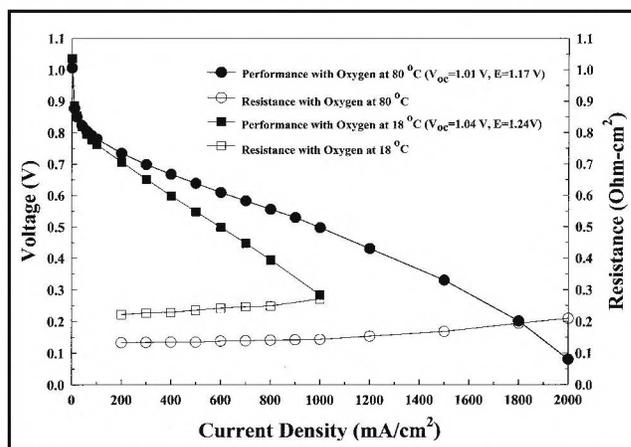


Figure 5. Effect of temperature on cell performance and membrane resistance at 1 atm, pure O₂.

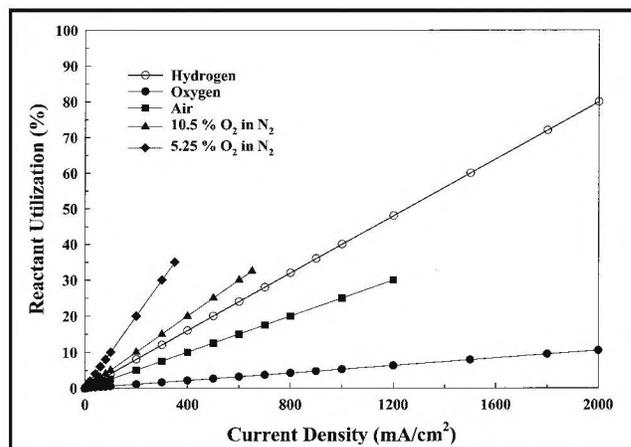


Figure 6. Effect of current density and oxidant composition on reactant utilization at 80°C, 1 atm.

conditions depends on how the fuel cell is to be used. For example, for vehicular applications, higher power density is required to minimize the weight of the car at the expense of efficiency. For residential (non-mobile) applications, a cell with higher efficiency would be preferred.

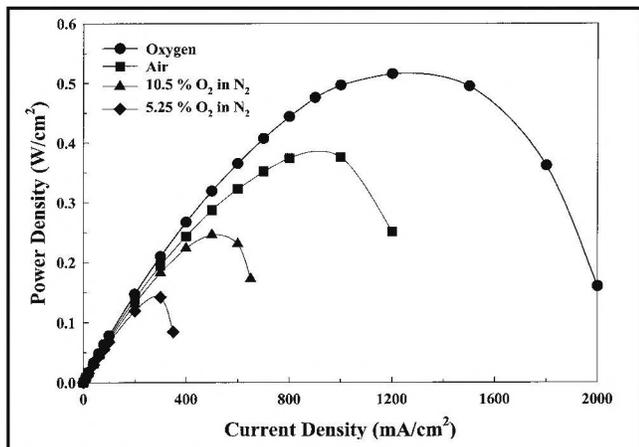


Figure 7. Effect of current density and oxidant composition on power density at 80°C, 1 atm.

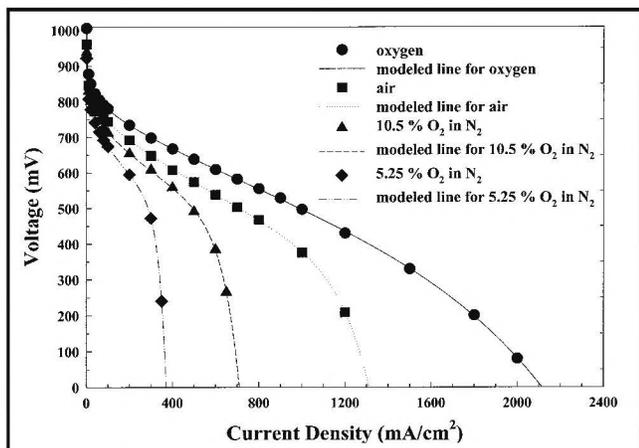


Figure 8. Nonlinear regression fit of experimental data at 80°C, 1 atm.

TABLE 5
Best-Fit Values for Kinetic Parameters, Ohmic Losses, and Transport Parameters Obtained Using Eq. (14) Compared to Values Calculated or Measured by Other Means

$$\text{Eq. (14): } V = E + A - (B \log(i)) - iR - w \exp(zi)$$

$$\text{Eq. (7): } \eta_{\text{act}} = B \log|i| - A$$

Oxidant Comp	Temp (°C)	E + A (mV)	B _{fit to Eq. 14} (mV/dec)	B _{fit to Eq. 7} (mV/dec)	R _{fit to Eq. 14} (Ω-cm²)	R _{measured} (Ω-cm²)	w (mV)	z (cm²/MA)	Correlation Coefficient (R ²)
Oxygen	80	963	79	85	0.20	0.14 - 0.16	4.202	0.0020	0.999
Air	80	927	77	84	0.29	0.14 - 0.16	0.018	0.0074	0.999
10.5% O ₂ in N ₂	80	921	87	94	0.33	0.14 - 0.16	0.035	0.0133	0.999
5.25% O ₂ in N ₂	80	902	88	95	0.51	0.14 - 0.16	0.008	0.0297	0.999

Empirical Model

Although comprehensive modeling of a fuel cell system is beyond the scope of an undergraduate lab, a simple model describing voltage-current characteristics of the fuel cell can be introduced to the students and tested for 1) its ability to fit the data, and 2) its usefulness as an analytical tool. The following empirical model describing the loss of cell voltage due to kinetic, ohmic, and transport limitations was proposed by Srinivasan, *et al.*:^[9]

$$V = E - (B \log(i) - A) - iR - w \exp(zi) \quad (13)$$

where E, B, A, R, w, and z are “fit” parameters. Lumping E and A together gives

$$V = E + A - (B \log(i)) - iR - w \exp(zi) \quad (14)$$

Equation (14) is modeled after Eq. (8) assuming the anode polarization terms in Eq. (8) are negligible, that the kinetic limitations of the cathode can be described by the Tafel Eq. (7), and that mass transport losses can be fit using the parameters w and z. The purely empirical term, w exp(zi), in Eq. (14) can be replaced with a more physically meaningful term

$$C \log \left(\frac{1}{1 - \frac{i}{i_{\text{lim}}}} \right) \quad (15)$$

where i_{lim} (mA/cm²) is the current density corresponding to a zero surface concentration, and C (mV/decade) is a parameter related to the Tafel slope. Due to space limitations, however, the physical meanings and the accurate estimation of C and i_{lim} will be explained in a forthcoming publication.^[10]

The model fit to experimental data using nonlinear regression software (Polymath) is shown in Figure 8. All curves generated using this model have correlation coefficients in excess of 0.999. The model therefore is excellent as a fitting function for fuel cell performance curves from which values can be interpolated or extrapolated. This is particularly handy

for estimating limiting current density in cases where the data is insufficient.

Values for the adjustable parameters [(E+A), B, R, w, z] calculated by the regression software are summarized in Table 5. The “regression generated” values for R can be compared to experimentally measured values (shown on the right-hand scale of Figures 4 and 5) and “regression generated” values for B can be compared to those predicted using theory. In this way the model can be tested for its “analytical” capability.

Contrary to experimental results, resistance calculated using Eq. (14) increases with decreasing oxygen concentration and is 40%-200% higher than measured membrane resistance (0.14 - 0.16 $\Omega\text{-cm}^2$ measured by the current-interrupt technique). This suggests that R from Eq. (14) includes voltage losses other than the ohmic resistance of the membrane and that the model is not reliable in predicting true physical behavior of individual contributions to the polarization curve. For instance, "model R" is assumed to be constant over the entire range of current densities, but in actual fuel cell operation, R is a function of current density at high current density.

Theoretical Tafel slope, B, is equal to $2.303 RT/\alpha_a F$ where R is the ideal gas constant, T is absolute temperature, F is Faraday's constant, and α_a is a lumped kinetic parameter equal to 1 for the oxygen reduction reaction occurring on the cathode.⁶¹ According to this theory, the Tafel slope should be about 70 mV/decade at 80°C. Table 5 shows the regression generated B is 20-36% higher than the value of 70 mV/decade. Again, one might suggest some physical reasons for this discrepancy, such as the existence of diffusion or resistive losses in the cathode catalyst layer of the electrode. We may argue, however, that the model is too "flexible" to assign any physical significance to the values of the "fit" parameters (*i.e.*, a huge range of values for each parameter will yield a good fit).

Tafel slopes are more accurately obtained from raw data using the Tafel equation, Eq. (7). In this case, B can be found by plotting iR -free voltage ($V + iR$) vs. $\log i$ (see Figure 9) and measuring the slope of the line in the kinetically controlled portion of the plot (at low values of $\log i$). Values for B found by using this technique have been included in Table 5. While those values found from Eq. (7) are more accurate than those from Eq. (14), they still differ from the theoretical value of 70.

The Tafel slope should not be a function of the oxygen concentration at low current density, so the lines in Figure 9 should all be parallel. It is clear that mass transport does not interfere with the calculation for the oxygen performance (straight line over the full decade of 10 to 100 mA/cm²). The 5.25% oxygen curve, however, is linear only for two points, 10 and 20 mA/cm², as mass transport resistances occur at lower current densities.

The parameters w and z are intended to describe mass transport limitations, but actually have no physical basis. One might expect these parameters to be dependent on flow characteristics in the cell that were not investigated in this study. Therefore, the predictive or analytical usefulness of w and z cannot be evaluated.

CONCLUSIONS

Fuel-cell based experiments embody principles in electrochemistry, thermodynamics, kinetics, and transport, and are

well suited for the chemical engineering curricula. Students are given an opportunity to familiarize themselves with fuel cell operation and performance characteristics by obtaining voltage-versus-current-density data for the unit at varying oxidant compositions and temperatures.

A simple model can be used as a fitting function for interpolation and extrapolation purposes. Model sensitivity analysis can be performed to evaluate its usefulness as an analytical tool. The lab can be completed easily in two 4-hour lab periods. The experiment is also suitable for use as a demonstration in a typical lecture course or as a hands-on project for high school students and teachers. The experimental system is described, including cost and vendor information.

NOMENCLATURE

- A kinetic parameter used in Eqs. (7), (13), and (14) (mV)
- B Tafel slope (mV/decade)
- C parameter related to the Tafel slope (mV/decade)
- E reversible potential at nonstandard concentration at temperature T (V or mV)
- E⁰ reversible potential at standard concentration at temperature T (V or mV)
- F Faraday's constant = 96,485 (coulombs/equivalent)
- I current (A)
- i current density (mA/cm²)
- i_{lim} limiting current density (mA/cm²)
- M molecular weight (g/mol)
- m mass of product formed or reactant consumed (g)
- n moles of electrons participating in the reaction per mole of reactant (equiv/mol)
- N moles
- P_{H₂}, P_{O₂}, P_{H₂O} partial pressures (atm)
- R electrical resistance ($\Omega\text{-cm}^2$)

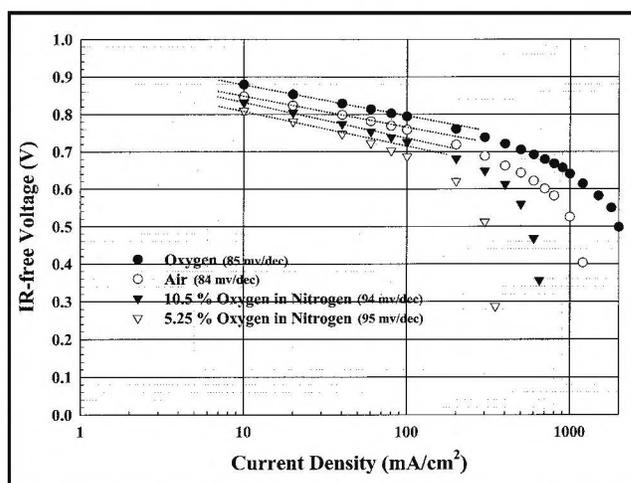


Figure 9. Tafel slope estimation using iR -free voltage plot of experimental data at 80°C, 1 atm.

R	universal gas constant = 8.31 (J/mol-K)
s	Stoichiometric coefficient of the product (positive value) or reactant (negative value) species
ΔS	entropy change of reaction (J/K)
T	temperature (K)
t	time (s)
U	reactant utilization (moles consumed/moles fed)
V	voltage (V or mV)
w	mass transport parameter used in Eqs. (13) and (14) (mV)
z	mass transport parameter used in Eqs. (13) and (14) (cm ² /mA)
α_a	a lumped kinetic parameter equal to 1 for the oxygen reduction reaction
ϵ_e	overall energy efficiency = current efficiency * voltage efficiency
ϵ_f	current efficiency = theoretical reactant required/ amount of reactant consumed (g/g)
ϵ_v	voltage efficiency = actual cell voltage/reversible potential (V/V)
$\eta_{act,a}, \eta_{act,c}$	activation polarization at the anode and cathode, respectively (mV)
$\eta_{conc,a}, \eta_{conc,c}$	concentration polarization at the anode and cathode, respectively (mV)

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Nanostructured Materials

Continued from page 37.

and results of peer evaluation.

CONCLUSION

ZSM-5 synthesis serves as an excellent example to introduce students to the basic concepts of templated synthesis and self-assembly that govern nanomaterials synthesis. This experiment brings together a number of subjects that students have learned from their previous courses: infrared spectroscopy (from organic chemistry), kinetic analysis and reactor operation (from reaction engineering), heat transfer (from transport phenomena), and phase behavior (from thermodynamics). The project also requires students to demonstrate their creativity and innovation through the experimental design and implementation of a nanostructured material synthesis.

ACKNOWLEDGMENTS

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The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

Incorporating **GREEN ENGINEERING** *Into a Material and Energy Balance Course*

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Through the support of the US Environmental Protection Agency (EPA), a Green Engineering Project has fostered efforts to incorporate green engineering into the chemical engineering curriculum. Green engineering is defined as the design, commercialization, and use of processes and products that are feasible and economical while minimizing generation of pollution at the source and risk to human health and the environment.

The Green Engineering Project has supported several initiatives, including development of a textbook, *Green Engineering: Environmentally Conscious Design of Chemical Processes*,^[1] and dissemination through regional and national workshops.^[2] The latest phase of this project supports the development of curriculum modules for various chemical engineering courses.^[3] This paper describes how the green engineering topics are “mapped” into a material and energy balances course and presents a sample of the types of problems that were developed for instructor use.

Green engineering principles should be familiar to and used by all engineers, and the need to introduce the concepts to undergraduates has become increasingly important.^[4-6] The most common method of incorporating it into the curriculum has been through a senior/graduate elective course on environmental engineering or pollution prevention.^[7-9] Integrating green engineering principles into various chemical engineering courses has been more challenging;^[10] it is most of-

ten integrated into the design sequence.^[11] Incorporating environmental issues into a material balance course has been reported by Rochefort^[12] by using a material balance module developed by the Multimedia Engineering Laboratory at the University of Michigan.^[13] The uniqueness of the problem module described in this paper is that it can be easily integrated into a material and energy balances course and that it maps many of the green engineering principles and underlying concepts to topics covered at this level, thus providing the basis for further integration of green engineering in subsequent courses.

The introductory material and energy balances course is a logical place to put basic terminology and concepts of green engineering. The initial goal of this module was to “map” some topics from the *Green Engineering* text to those taught

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in the material and energy balances course, which predominately uses the text *Elementary Principles of Chemical Processes*.^[14] The curriculum module developed^[15] has 25 problems (with solutions) that can be used by an instructor for in-class examples, cooperative learning, homework problems, etc.

Two to four problems have been developed for each main topic in material and energy balances and the majority of them have multiple parts. Most require a quantitative solution, while others combine both a chemical principle calculation with a subjective or qualitative inquiry. The problems take a topic from a particular subtopic/topic (section/chapter) and then find a green engineering analog. Some cover specific terminology, principle, or calculation covered in both texts, such as in the calculation of vapor pressures of volatile organic compounds (VOCs), while others introduce concepts only covered in a green engineering text.

Presenting a topic found only in the green engineering text is the most challenging integration of course material. For example, the concept of occupational exposure is introduced by having students perform a unit conversion with a dermal exposure equation. In a similar way, workplace exposure limits are introduced in the context of calculating concentration

using mole and mass fractions. This helps optimize time usage and course flow, since as prior papers on various subjects have pointed out, “to put in X, you need to take out Y.” By taking basic material and energy concepts and designing a problem to introduce a green engineering concept, a unique integration of concepts occurs.

Some problems have additional questions that require students to investigate the literature, go to a web site, or perform a more qualitative analysis of the problem. For example, in the dermal exposure problem, the student must go to an EPA or related web site to determine threshold limiting values and permissible exposure limits for other chemicals. The level of green engineering material is quite elementary since the objective is to give students some familiarity with concepts that would form the basis for more substantial green engineering problems in subsequent courses such as transport, thermodynamics, reactor design, separations, plant design, etc.

An overall conceptual view of green engineering topics mapped to those in a material and energy balances course is presented in Table 1. The mapping is done in a very generic way so that an instructor can see the general outline of the topics taught in a material and energy balances course and

some of the general areas of green engineering concepts. Not all of the concepts covered in a material and energy balances course have a green engineering analog and *vice versa*. That is why the EPA-supported Green Engineering Project has multiple modules developed for other courses in the chemical engineering curriculum. The material in this module was developed to be used at the first-semester sophomore level and therefore integrates green engineering concepts in a way that a student starting a chemical engineering program can readily understand. Several problems from the module have been presented below, following the order of in-

TABLE 1
Conceptual Mapping of Green Engineering Topics
in a Material and Energy Balances Course

<i>Green Engineering Topic</i>	<i>Material and Energy Balances Topic*</i>
• How green engineering is used by chemical engineers in the profession	Chap. 1: What Some ChEs do for a Living
• Unit conversions typically used in green engineering process calculations	Chap. 2: Intro. to Engineering Calculations
• Various defining equations used in green engineering	
• Typical method of representing concentrations of pollutants in a process (% , fractions, ppm, etc)	Chap. 3: Process and Process Variables
• Overall “closing the balance” of a chemical manufacturing process	Chap 4: Fundamentals of Material Balances
• Balances on recycle operations in green engineered processes	
• Green chemistry in stoichiometry	
• Combustion processes and environmental impact	
• Use of various equations of state in green engineering design calculations for gas systems	Chap. 5: Single Phase Systems
• Pollutant concentrations in gaseous form	
• Representation and calculation of pollutant volatility using vapor pressure	Chap. 6: Multiphase Systems
• Condensation calculations (gas-liquid equilibrium) for vapor recovery systems	
• Liquid-liquid extraction balances for pollutant recovery systems	
• Representation of various forms of energy in a green engineering process	Chap. 7: Energy and Energy Balances
• Recovery of energy in a process-energy integration	Chap. 8: Balances on Nonreactive Processes
• Use of heat capacity and phase change calculations	
• Mixing and solutions issues in green engineering	
• Energy use in green chemistry reactions, combustion processes	Chap. 9: Balances on Reactive Processes
• Overall integration of mass and energy balances in green engineering on an overall plant design basis	
• Use of various simulation tools and specifically designed software for green engineering design	Chap. 10: Computer-Aided Calculations
• Representation of mass and energy flows for transient processes with green engineering significance	Chap. 11: Balances on Transient Processes
• Industrial case studies of green engineered manufacturing processes	Chap. 12-14: Case Studies
• From Felder & Rousseau ¹⁴	

corporation in the course. A full set of solved problems is available at <http://www.rowan.edu/greenengineering>.

PROBLEM 1

Occupational Dermal Chemical Exposure Equation

Problem Statement

Undesired occupational exposure to chemicals contacting the skin during sampling, splashing, weighing, transfer of chemicals, process maintenance, etc., can be estimated as the sum of the products of the exposed skin areas (cm²) and the amount of chemical contacting the exposed area of the skin (mg/cm²/event). The dermal exposure equation given below can be used to estimate the exposure to a chemical absorbed through the skin.

$$DA = (S)(Q)(N)(WF)(ABS) \quad (1)$$

where

- DA dermal (skin) absorbed dose rate of the chemical (mass/time)
- S surface area of the skin contacted by the chemical (length²)
- Q quantity deposited on the skin per event (mass/length²/event)
- N number of exposure events per day (event/time)
- WF mass fraction of chemical of concern in the mixture (dimensionless)
- ABS fraction of the applied dose absorbed during the event (dimensionless)

Roberta Reactor, a process technician, is sampling a reactor containing acrylonitrile. Unfortunately, she is not following proper safety procedures for personal protection and is not wearing the required gloves. As plant safety officer, you are asked to estimate her dermal absorption rate (mg/workday) for this unwanted exposure. Data from US EPA indicates that batch process sampling yields between 0.7 and 2.1 mg/cm² for the quantity Q in the dermal exposure equation.

- a) Show that this equation is dimensionally homogeneous using the following units for the parameters: DA (g/min); S (cm²); Q (mg/cm²/event); N (event/day).
- b) Using the following data, determine DA in the units of mg/workday for this exposure using the upper limit of Q. During the workday, which is an 8-hour shift, Roberta samples the reactor every hour and exposes one of her hands. The mass fraction of acrylonitrile in the reactor is 0.10 and the fraction of the applied dose absorbed during the sampling is 1.0 (representing that all of the acrylonitrile contacting the skin is absorbed).
- c) What personal protective equipment must Roberta wear?

(Problem can be used in Sections 2.2 and 2.6 of Felder and Rousseau.)

Problem Solution

This problem introduces students to the concept of workplace exposure to chemicals and methods for presenting the associated risk. The parameters needed to solve the problem are either given in the statement, found in the literature, or must be measured. The surface area of the hand can be found in texts—or for more fun, have the students trace their hands on engineering paper and estimate the area, model the hand as a trapezoid (palm) with cylinders (fingers), or use a planimeter. This part of the problem gives the “hands-on” characteristic to the learning experience.

To prove the equation is dimensionally correct, the student inputs the units from the problem to show that they cancel on the left-hand and right-hand sides of the equation. To solve for the dermal absorption, the values are put into the equation and units are converted. A value of 325 cm² for a student’s hand surface area is measured (literature value^[1] is 408.5 cm² for median size of one adult woman’s hand).

$$DA = \frac{325 \text{ cm}^2}{\text{cm}^2 \langle \text{event} \rangle} \left| \frac{2.1 \text{ mg}}{\text{day}} \right| \left| \frac{8 \text{ event}}{\text{day}} \right| \left| \frac{0.1}{1.00} \right| = 546 \frac{\text{mg}}{\text{day}} \quad (2)$$

Information on the hazards associated with contact with this chemical can be obtained by going to <http://hazard.com/msds> and viewing a representative material safety data sheet (MSDS) on acrylonitrile. Students will see that exposure to it causes skin irritation, is harmful if absorbed through the skin, may cause skin sensitization (an allergic reaction), that prolonged and/or repeated contact may cause defatting of the skin and dermatitis, and that it is toxic in contact with skin. They will also note from the web site that proper personal protective equipment (gloves, safety goggles, and respirator) must be used.

Students may also suggest that a method other than manual sampling could be used to reduce risks to the technician and avoid discharges into the workplace. This is a good practical exercise and would help any student in a hazards and operability study (HAZOP) performed in subsequent laboratory or project-based courses.

PROBLEM 2

Concentration Determination Using Threshold Limit Value and Permissible Exposure Limits

Problem Statement

Two parameters that are used to establish workplace limits for concentrations of chemicals are the Threshold Limit Value (TLV) and Permissible Exposure Limits (PEL). TLV is the level at which no adverse effect would be expected over a

worker's lifetime. It is a guideline set by a nongovernmental body, but the PEL is set by the U.S. Occupational Safety and Health Administration (OSHA) and is considered the legal limit in manufacturing facilities.

The solvent n-heptane is used in the manufacture of metal components for washing the parts to remove oils used in the cutting step. Several meters are used to monitor airborne concentration values in the plant. Your job as a process engineer is to convert the data provided for TLV and PEL values for n-heptane into the units used by the concentration meters shown below.

- Meter A: ppb
- Meter B: mole fraction
- Meter C: mass fraction
- What are the consequences of an unwanted release of n-heptane?
- Suggest a more environmentally benign solvent for the washing operation.

(This problem can be used in Section 3.3 of Felder and Rousseau.)

Problem Solution

This problem involves the concept of concentration and incorporates the green engineering principle relating that concentration to workplace exposure limits of TLV and PEL. The solution will involve the student first going to one of the EPA-suggested websites and looking up the TLV and PEL for n-heptane. By going to <<http://hazard.com/msds>> and using the Mallinckrodt Baker MSDS for n-heptane, the values of TLV = 400 ppm and PEL = 500 ppm are obtained. This problem can also involve students in learning how to read an MSDS (which is shown later when they examine the consequences of unwanted exposure). Next, students convert to the desired units using conversions from ppm to ppb, mole fraction, and mass fraction.

PEL Meter A

$$\frac{500 \text{ ppm}}{10^3 \text{ ppm}} \left| \frac{10^3 \text{ ppb}}{\text{ppm}} \right| = 5.00 \times 10^5 \text{ ppb} \quad (3)$$

PEL Meter B

$$\frac{500 \text{ ppm}}{10^6 \text{ ppm}} \left| \frac{y_i}{10^6 \text{ ppm}} \right| = 5.00 \times 10^{-4} \text{ mol C}_7\text{H}_{16} / \text{mol} \quad (4)$$

PEL Meter C

Choosing a basis of 100 moles and starting with the mole fraction for meter B

$$\frac{5.00 \times 10^{-4} \text{ mol C}_7\text{H}_{16}}{\text{mol}} \left| \frac{100 \text{ mol}}{\text{mol}} \right| \left| \frac{100.2 \text{ g}}{\text{mol}} \right| + \frac{5.00 \times 10^{-4} \text{ mol C}_7\text{H}_{16}}{\text{mol}} \left| \frac{100 \text{ mol}}{\text{mol}} \right| \left| \frac{100.2 \text{ g}}{\text{mol}} \right| + \frac{(1 - 5.00 \times 10^{-4}) \text{ mol Air}}{\text{mol}} \left| \frac{100 \text{ mol}}{\text{mol}} \right| \left| \frac{29 \text{ g}}{\text{mol}} \right| = 1.73 \times 10^{-3} \text{ g C}_7\text{H}_{16} / \text{g} \quad (5)$$

To determine the risk associated with undesired release of n-heptane in the plant workplace, students examine the MSDS and see a health rating of 2, and for the section on hazards/potential health effects they see the following for inhalation: inhalation of vapors irritates the respiratory tract; it may produce light-headedness, dizziness, muscle incoordination, loss of appetite, and nausea; and higher concentrations can produce central nervous system depression, narcosis, and unconsciousness.

In the last part of the problem, students investigate whether an alternate solvent is more environmentally benign. Thinking of what solvents they might be using in a chemistry lab, they might choose acetone, for which the same website would give an overall health rating of 1, or slight, and PEL = 750 ppm and TLV = 750 ppm. So the solvent acetone is slightly better environmentally than n-heptane to use. A listing of solvents and their physical properties can be found using EPA's free green chemistry expert system software.^[16]

PROBLEM 3

Mass Balance on Reverse Osmosis Process for Electroplating Waste Reuse and Recovery

Problem Statement

Reverse osmosis is a separation process used for pollution prevention in many industries. It is an environmentally effective separation process since it can be used for material recovery and recycle while it eliminates unwanted discharges from a chemical manufacturing operation. In reverse osmosis, a liquid feed stream under pressure passes across a semi-permeable membrane filter that allows the passage of water, but rejects organic and inorganic contaminants. In this operation, the purified water stream produced is called the "permeate," and the stream of concentrated impurities is called the "retentate."

You have been hired as a process development engineer for Shiny Electroplaters, and your first assignment is to look at the reduction of chromium discharge from its operation, as shown in Figure 1. Considering the process to be a steady-state continuous operation, determine

- The permeate quantity (kg/hr) and chromium concentration (mass fraction) being produced.
- The potential uses for the permeate and retentate streams in a "green" process design.
- The advantages this process has over other pollution

prevention techniques.

(This problem can be used in Section 4.3 of Felder and Rousseau.)

Problem Solution

This problem gives an example of a green manufacturing process that uses a modern separation system such as reverse osmosis for pollution prevention. It makes students think about how the separation is used to make the manufacturing operation “green.” The problem is solved using a material balance working on a continuous process at steady state. The student performs a total mass balance and balance on chromium over the process, yielding the following two relationships:

$$\begin{aligned} \dot{m}_1 &= \dot{m}_2 + \dot{m}_3 & x_1 \dot{m}_1 &= x_2 \dot{m}_2 + x_3 \dot{m}_3 \\ 210 \text{ kg/hr} &= 50 \text{ kg/hr} + \dot{m}_3 & (0.10)(210 \text{ kg/hr}) &= \\ & & (0.40)(50 \text{ kg/hr}) + x_3(160 \text{ kg/hr}) & \\ \dot{m}_3 &= 160 \text{ kg/hr} & x_3 &= 0.00625 \end{aligned}$$

Students can brainstorm the potential uses of the permeate and retentate to make this a “green” process by recycle and reuse (see Table 2) and can then redraw the overall process to show mass integration (Figure 2). Students speculate on the advantages of this process from a green engineering standpoint and find that it simultaneously produces a purified water stream and concentrate with no phase change required—energy savings: no by-products produced, no additional chemicals required, operates at ambient temperature.

PROBLEM 4

Heating Value of Renewable Fuels

Problem Statement

Energy use, conservation, and the environmental impacts of the production and use of fuels are important green engineering topics. Currently available oil and coal reserves are nonrenewable and have air-quality issues associated with their use. Although there is no perfect fuel from an economic and environmental perspective, there are alternatives that should be considered.

Ethanol is considered a “green fuel” since it can be made from renewable and sustainable resources and burns cleaner than fossil fuels. The process to produce ethanol can use a renewable resource such as domestically grown crops and

thereby lessens the need for importation of crude oil. Since ethanol contains none of the carcinogenic compounds that are found in fossil fuels, worker exposure risk is reduced. In addition, when it is burned, ethanol generates fewer undesired by-products than gasoline.

- Investigate and draw a process flow diagram for the production of ethanol from corn. Suggest methods of mass and energy integration in this process to make it more environmentally efficient
- Calculate the higher heating value (HHV) and lower heating value (LHV) of ethanol (kJ/mol).
- How does this compare to the HHV of fuel oil gasoline at 44 kJ/g? What are other comparisons of fuel oil/gasoline combustion and ethanol combustion?
- The use of hydrogen as a potential fuel of the future

<u>Permeate Uses</u>	<u>Retentate Uses</u>
Process water	Recovery of Chromium; send concentrate to an electrolytic cell
Wash water/rinse water	Recycle to plating bath for make-up of chromium losses
Water for dilution	
Heat exchanging (energy integration)	

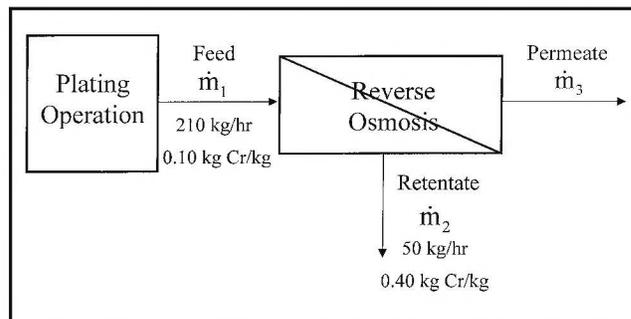


Figure 1. Process flow diagram of reverse osmosis for the reduction of chromium discharge from electroplating operation.

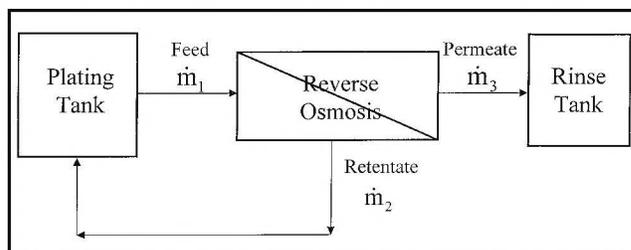


Figure 2. Process flow diagram showing the integration of permeate and retentate streams.

has received much recent attention. What is its HHV (kJ/mol) and what are the environmental issues and challenges related to its use?

(Problem can be used in Sections 9.4, 9.6, and Chapters 12-14 of Felder and Rousseau.)

Problem Solution

This problem requires that students investigate the production and use of ethanol fuel from a renewable and sustainable resource. To find a suitable flow diagram for the production of ethanol from biomass, students should be required to go to the library and report the literature source used, such as a biochemical engineering text or a technical encyclopedia.^[17,18] Students typically find the corn-to-ethanol process uses fermentation followed by various separations (including distillation, membranes) that also show overall process integration of mass and energy.

Students next determine the heating values of ethanol yielding HHV = 1366.9 kJ/mol and LHV = 1234.9 kJ/mol. A comparison of the heating values to gasoline is made and students are asked to investigate other comparisons. From a green engineering perspective, students are asked to investigate the combustion products of gasoline and other fuel oils. They will find that a 10% blend of ethanol reduces CO, CO₂, VOCs from evaporation, SO₂, particulate matter, and aromatics compared to burning gasoline.^[19]

Finally, students are asked to examine hydrogen and determine heating values and other combustion issues. Here they find that on a mole basis the HHV is 285.8 kJ/mol, but on a mass basis, HHV is 141.5 kJ/g, which is higher than gasoline or ethanol. They also see that H₂ burns much more environmentally efficiently since only water is produced as a combustion product. A major issue in the use of hydrogen is its source, which is typically a hydrocarbon.

Upon investigation, students will also see that it currently costs more to produce hydrogen. Technology needs to be developed to use it in the next generation of vehicles, and the infrastructure to transport and dispense hydrogen fuels needs to be developed.

CONCLUSIONS

Green engineering concepts can be integrated into a material and energy balances course by using uniquely developed examples and problems. These problems introduce terminology and basic concepts that lay the groundwork for more extensive incorporation of green engineering in subsequent courses. Problems were developed within the framework of a material and energy balances course and teach students about topics such as workplace exposure routes/limits, recycle and recovery processes, green chemistry, combustion, and mass and energy integration. By using in-class examples or home problems with a cooperative learning approach, students can

learn the concepts needed in both a material and energy balances course and green engineering.

ACKNOWLEDGMENTS

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TOP TEN WAYS TO IMPROVE TECHNICAL WRITING

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While engineers often claim that they spend more time writing than they do on any other single task, providing constructive criticism of students' reports is the most difficult and thankless task a faculty member may face. Most schools do not have the luxury of having a writing specialist who can help engineering students with their reports, and even if students take a writing course, they need feedback on their technical reports.

What rules of grammar, usage, and writing style should students and faculty focus on? English usage changes with time, and experts do not always agree, but in spite of numerous excellent (and voluminous) style guides,^[1-6] editing for correct usage need not be a daunting task. There is a relatively small list of topics that are particularly troublesome, even for well-educated chemical engineering students.

In this paper, ten general suggestions are offered to help improve one's technical writing style. They have been gleaned during the past six years from several hundred drafts of industry reports submitted by over a hundred students at the David H. Koch School of Chemical Engineering Practice at MIT. Practice School students are candidates for the Masters degree, and all have been well educated in some of the best chemical engineering programs, both here and abroad. Reports are submitted by two or three students working as a group on real industrial projects at a company site. All reports are written with an impending deadline, with two reports expected during the typical one-month project duration.

The engineering education literature contains many examples of technical writing as part of the curriculum^[7-12] and of writing pedagogy.^[13,14] In contrast, this top-ten list is intended to supplement standard usage and style manuals that have more depth. Strunk and White^[15] remains a classic for its brevity and good advice, and the ACS *Manual of Style*^[16]

is a comprehensive book that is useful to chemical engineers. There are two useful manuals written by chemical engineers.^[17-19] No writer should suffer from a lack of reference material. Spell- and grammar-check software should be used as a minimum level of guidance, and style guides are available on the World Wide Web.^[20,21]

This paper is intended to focus attention of both instructors and students on the most prevalent writing problems. With apologies to David Letterman, I will present and discuss the top-ten list in reverse order. Each will be illustrated with actual examples of sentences from report drafts.

- 10 -

Select Words with Care

Misuse or overuse of some words occurs frequently enough in technical writing to deserve special mention and ranks tenth on my list of admonitions. There is such a diverse range of examples that it almost defies categorization, but several of the more common ones will be used to illustrate the problem.

It is well known that a spell or grammar checker cannot be relied on as the sole source of misused words. Writing must be proofread with care to make sure you have said what you think you said. Sometimes an inadvertent slip seems so ap-



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appropriate that it cannot be distinguished from a deliberate put-on, as in

Original: This would lead to extra liquor sipping cost, which is given in row 4.

Better: This would lead to extra liquor shipping cost, which is given in row 4.

Chemical engineering students frequently use the words *setup/set up*, *scaleup/scale up*, and *shutdown/shut down* in their reports and misuse is not uncommon. The following example shows that *set up* should be used when a verb phrase is needed:

Original: The apparatus is setup so that any overflow would be collected in the trap.

Better: The apparatus is set up so that any overflow would be collected in the trap.

If the objective of a technical report is to get across a message to the reader, pretentious words have no place.^[22] Perhaps no word gets overused as much as *utilize*. It has a well-deserved reputation of pretentiousness and should probably never be used, since *use* is a simpler synonym. Beware of trendy big words (such as *-ize* verbs made from nouns, or nouns made from verbs) that sounds like bureaucratese (another example!) at its worst. Do not try to make your prose impressive—make it understandable.

For the most part, students have a good sense of the proper use of words. Occasional lapses occur, however, on common word pairs. Look out for *there/their*, *fewer/less*, *between/among*, *it's/its*, *continuously/continually*, *varying/various*, and *altogether/all together*. It is easy to slip up and use the wrong one.

Finally, technical writing is necessarily replete with acronyms. Some are so common (such as CSTR), that they may not need definition, but it is best to be cautious and consider the reader. If a chance exists that your report will be read by someone without your same perspective (and that includes virtually everyone), define your acronyms the first time they are used, and even more frequently if necessary. Never use so many different acronyms that your reader is forced to divert attention away from what you are saying to mentally decode the terminology.

- 9 -

Use Parallel Construction

Writing is more effective when parallel ideas are presented in parallel fashion. The reader's burden is lessened when the

wording or words follow a pattern. This pattern can be in verbs, nouns, adjectives, phrases, clauses, and sentences. It can be extended to the organization of paragraphs, or even to sections of a report. It improves the style and can make the reader better understand that the ideas are parallel.

Two obvious situations that call for parallel construction are in enumerated lists and compound expressions joined by correlative conjunctions. Each one of the enumerated section headings of this paper is an imperative admonition starting with a verb and followed by its object. Parallel construction may not always be possible to maintain, but deviations from it can be unnecessarily jarring to the reader. On the other hand, correlative constructions using the conjunction pairs *both...and*, *either...or*, *neither...nor*, and *not only...but also* can be misleading or even incorrect if the words following the correlative conjunctions are not parallel to each other. Consider the example below. In the original form, a verb form follows *either*, but a noun phrase follows *or*. The natural correction would be to move *either* so that *based on* applies to either noun phrase. Both noun phrases following the correlative conjunctions are parallel, and it is clear that the values will be assigned in either case.

Original: Values that are either based on engineering terms or financial terms will be assigned to each piece of equipment.

Better: Values that are based on either engineering terms or financial terms will be assigned to each piece of equipment.

- 8 -

Avoid Passive Voice and First Person

Good prose is direct and forceful. This is no less true in technical writing. It is better to say that the subject *did* something than to say that something *was done* by the subject. Technical writing tends to overuse the passive voice, sometimes with good reason. It is not wrong to use the passive voice, but it should be avoided when possible.

Most technical writing also tends to avoid using the first person. The message conveyed should focus on the technical content without putting undue focus on the authors. Unfortunately, the choice is often between using the first person (or its close equivalent "the author") and using the passive voice. It is not wrong to use the first person, but it should be avoided when possible.

In the following example, the active voice makes the sentence simpler and more direct. In this case, the Microsoft Word

... editing for correct usage need not be a daunting task. There is a relatively small list of topics that are particularly troublesome, even for well-educated chemical engineering students.

Most important, always consider those who will be reading what you have written and try to make it easier for them to grasp your message.

grammar checker not only identified the passive sentence but also suggested an improvement. Consider whether rewriting each passive sentence would improve the flow of the sentence and still convey the same information. If your sentence is too complicated for the grammar checker to offer an improvement, maybe the sentence should be simplified.

Original: Two methods are being examined by the company for possible implementation.

Better: The company is examining two methods for possible implementation.

Technical writing should usually emphasize your accomplishments, not you yourself. This is the reason for avoiding the first person, as illustrated in the example below. Using other words, such as *the authors*, *the group*, and *the project team*, may avoid the first person, but they do not avoid placing the emphasis in the wrong place. Use them advisedly, even if it means using the passive voice.

Original: We followed established protocols to carry out the measurements.

Better: Measurements were made following established protocols.

- 7 -

Use Proper Punctuation

The wide variety of possible punctuation problems justifies its ranking of seventh on the top-ten list of things to watch for. Most writers have a good sense of how to punctuate properly, so a comprehensive summary of the rules seems unnecessary. Only two of the more common rules will be mentioned here.

Technical writing too often uses long and complicated sentence structures. If this is really necessary, good writing practice guides your reader through long sentences by using a comma whenever it is appropriate to pause slightly. The following is a good example of where a comma prevents the words from running together:

Original: The tin-catalyzed racemization rate also decreases resulting in higher quality product.

Better: The tin-catalyzed racemization rate also decreases, resulting in higher quality product.

The single comma should never be used to separate the subject from the predicate of the sentence or the verb from its predicate complement, however. The reader should proceed directly from one to the other with no pause.

A related situation with the use of a colon arises frequently in technical writing. The colon has only one proper use in sentences: it separates a definition, a list, or other explanatory material from the rest of a complete sentence. It should never be used to separate a verb from the rest of the predicate or any other part of speech from its required complement. The original version of the example below uses the list as the direct object of the preposition *into*. The colon should *not* be used there. If you want to use the colon, add *the following* or some other object before the colon. The same rules apply if the explanatory material is set off on the following line, as in an enumerated list or an equation.

Original: These mechanisms can be classified into: solid-solid interactions, liquid necking, adhesive and cohesive forces, and chemical reactions.

Better: These mechanisms can be classified into solid-solid interactions, liquid necking, adhesive and cohesive forces, and chemical reactions.

Or: These mechanisms can be classified into the following: solid-solid interactions, liquid necking, adhesive and cohesive forces, and chemical reaction.

- 6 -

Ensure Agreement in Number

Subjects and verbs must agree in both number and person. Similarly, pronouns must agree with their noun antecedents. Since most technical writing is done in the third person, person agreement is not usually a problem. Number agreement, however, can sometimes be a problem, especially in two common instances: recognizing the number of certain nouns and recalling the true subject of a more complicated sentence. The latter problem appears frequently enough in student reports to justify this admonition as sixth most important.

A common mistake is to give the verb the number of the closest noun rather than the true subject of the sentence. The subject in the example below is *measurements*, not *extraction*, and the verb should thus be plural. Intervening phrases or clauses, especially when they end with a noun, can draw the writer's attention away from the true subject.

Original: The temperature measurements for the lab-scale extraction was compared with the simulation described above for validation.

Better: The temperature measurements for the lab-scale extraction were compared with the simulation described above for validation.

It is well known that words such as *kinetics*, *economics*, and *physics* are singular in spite of the final *s*. *Data* can be more troublesome. Classically plural, as the counterpart of the currently unused *datum*, data has acquired a collective use as well, requiring a singular verb. A good key to the difference is whether *data points are* or *data set is* can be substituted. If you can substitute either one, your sentence is prob-

ably too vague to be useful. My suggestion is to be as helpful to the reader as possible and avoid ambiguity. Think first that the word *data* is plural and use *data set* if you really want it used in the collective sense.

- 5 -

Place Modifiers with Care

Modifiers should always be placed as close to what they modify as possible. No ambiguity about what word the modifier belongs to should exist. The classic examples of inadvertent absurdities introduced by misplaced modifiers are easy to catch, and the more subtle ones are fodder for technical editors. Technical writing spawns more modifying words and phrases than is consistent with clarity. The more modifiers introduced into a sentence, the more likely that some ambiguity will arise. Grammar-check software can be used to alert you to too many modifiers in your sentences. If the sentence cannot be recast to avoid some of them, at least check to make sure they are modifying what you wanted them to modify so the reader will face no ambiguity.

The next example illustrates that the simple placement of a modifier can drastically alter the sense of a sentence. In the original wording, one might picture Erickson submerged in a caustic solution making the diffusion measurement, instead of the reaction occurring in the caustic tank. Place the modifying phrase after the word *reaction* rather than as an introductory phrase.

Original: In the caustic retention tank, Erickson (1995) has already confirmed that the neutralization reaction is diffusion controlled.

Better: Erickson (1995) has already confirmed that the neutralization reaction in the caustic retention tank is diffusion controlled.

When a phrase has no word that it can logically modify, it is called “dangling.” The following is a good example. The opening participial phrase should modify the person doing the comparison. Placement of the phrase suggests that the subject of the sentence would be the agent, but neither *it* nor the *cooking system* could possibly be what the phrase modifies. By the time the long modifying phrase was completed, the writer had forgotten that the agent should be the subject of the sentence.

Original: Comparing the characteristics of the steam tunnel and those of the RotaTherm, as claimed by Gold Peg and its distributors, it appears that the RotaTherm steam fusion continuous cooking system would be more advantageous.

Better: Comparing the characteristics of the steam tunnel and those of the RotaTherm, as claimed by Gold Peg and its distributors, we concluded that the RotaTherm steam fusion continuous cooking system would be more advantageous.

- 4 -

Use a Hyphen Only When Needed

Technical writing is plagued with jargon, and authors need to learn how to use it consistently. Too often words are coined ad hoc, using standard prefixes in combination with technical words to form a new word with a precise meaning understood by the reader. When to hyphenate such a prefix is clearly not well defined, if one is to judge by the number of times that *non-linear* appears in respected publications. A good dictionary should always be the accepted arbiter, but even the best ones will not cover all the technical terms clever students choose to use. This problem frequently puzzles students.

The general rule is that particles such as *bi*, *by*, *co*, *de*, *non*, *pre*, *re*, *un*, etc., that are not words by themselves should not be hyphenated when added as a prefix to a word. (Modern usage is different from that in older literature when new compound words were hyphenated until they became accepted in the vocabulary.) Also, no hyphen is called for when a number of longer prefixes are used, and the *ACS Manual of Style* gives a long list of them, including *anti*, *poly*, *post*, *counter*, *super*, *over*, *under*, *infra*, *pseudo*, etc. Consider the following example.

Original: Agitate the device for a pre-determined period.

Better: Agitate the device for a predetermined period.

Two exceptions to the above rule should be noted. First, use a hyphen when omitting it might cause confusion to the reader. Any time ambiguity in meaning or pronunciation might result, a hyphen should be used. Think, for example, of the interpretation of “post-aging” if a hyphen is not used. Also, always use a hyphen when the modified word requires a capital letter (for example, *non-Newtonian*). Second, consider using a hyphen whenever the prefix introduces a double vowel into the word. A hyphen is not needed in well-known words, such as *cooperative*, however. For example, I would consider *preexponential* a common enough term in chemical engineering to permit dropping the hyphen, but others would still require it.

Compound modifiers (words used together to modify a noun) should be hyphenated. Application of this rule is straightforward in many cases, but in others it is not. In the example below, *small-scale* is a modifier of *batch vessel*. Note, however, that *batch* is also a modifier of *vessel*. It is not hyphenated with *small-scale*. In this case, *batch vessel* seems more natural as the noun expression being modified.

Original: Experiments were performed in a small scale batch vessel, with samples taken periodically for rheology measurements.

Better: Experiments were performed in a small-scale batch vessel, with samples taken periodically for rheology measurements.

Common technical terms that have a meaning together

should not be hyphenated, however, even when used as a modifier or descriptor. The hyphen tends to take away from the common meaning of the expression *mass transfer* in the example that follows.

Original: The capping experiments so far have been useful for obtaining estimates of mass-transfer parameters.

Better: The capping experiments so far have been useful for obtaining estimates of mass transfer parameters.

- 3 -

Go “Which” Hunting

This is a classic admonition from Strunk and White^[15] that White apparently added to the original version.^[23] How often it is ignored is perhaps surprising and is what makes it the third most frequent writing problem I’ve encountered. Too frequently it appears that the rules of usage are not known rather than being consciously subverted.

That is a relative pronoun used to introduce a restrictive clause, one that is necessary for the definition of the antecedent that it should immediately follow. If the clause is removed, the sentence will not convey its full meaning or the same meaning. Such a restrictive clause should not be set off from the antecedent by commas.

Which is a pronoun used to introduce a nonrestrictive clause, one that is incidental to the definition of the antecedent that it should immediately follow. Such a nonrestrictive clause can be omitted without destroying the sense of the rest of the sentence, and it should be set off from the rest of the sentence by commas. In the example that follows, the sentence ending at “parameters” would be incomplete—the following clause is restrictive to the nature of parameters being described. The clause should be introduced by *that* rather than *which*. The grammar check in Microsoft Word will catch the incorrect use in the original sentence.

Original: a_1 and b_1 are parameters which can be determined by flux measurement.

Better: a_1 and b_1 are parameters that can be determined by flux measurement.

Unfortunately, some good writers will use *which* in place of *that* to introduce a restrictive clause. It has had an accepted literary use for effect,^[24] although the advantage is more often than not difficult to see. Whether such use was purposeful or inadvertent is impossible to determine. For modern technical writing, it is probably best to avoid such use and to go *which* hunting as White advises.

Which clauses may also be used to modify the sense of the entire main clause of the sentence. This use is hardly necessary, however, and a simple rewording can avoid it. The reader is spared the possible ambiguity of trying to discover the noun that the *which* clause modifies. In technical writing this use should probably also be avoided. The following example,

although not incorrect as originally written, shows that changing the *which* clause to a participial phrase avoids possible confusion about whether the *which* clause actually modified the natural antecedent *solution*.

Original: CO₂ was observed bubbling out of solution, which would result in a higher pH.

Better: CO₂ was observed bubbling out of solution, resulting in a higher pH.

- 2 -

Use Direct and Concise Statements

The second most common problem with writing styles is verbosity. Writing concisely is an art that needs to be practiced. If there is a direct way to say something, use it. If there is a shorter way to say something, use it. Of the many ways verbosity appears in student reports, two have been selected here for illustration.

An introductory phrase or clause can be useful in making a transition from, or connection to, previous sentences and to orient the reader to the main clause that follows. A common writing problem is the use of such a phrase to indirectly say what the sentence is about when a more direct and concise approach would suffice. Consider the following example in which the introductory prepositional phrase was meant to help the reader know what was being compared. The shorter sentence is more direct and less awkward, however, and conveys the sense just as well.

Original: Between water content and temperature, the latter had the stronger effect on the viscosity.

Better: The temperature had a stronger effect on the viscosity than water did.

A common example of verbosity is to use a phrase in place of a single word. Many phrases have become clichés and should not be used at all. Others should be used with discretion. In the following example, *due to the fact that* is used when a simple *because* would be appropriate. Other phrases you should look out for include *the reason is because*, *it is because*, *considered to be*, *by means of*, *in order to*, and *for the case where*. Other phrases, such as *in terms of*, *as is understood*, *result of*, *is that of*, *kind of*, *the fact that*, and *type of* might best be eliminated entirely.

Original: This was due to the fact that more water condensation from the vapor was required to vaporize the additional hexane.

Better: This occurred because more water condensation from the vapor was required to vaporize the additional hexane.

- 1 -

Use Specific and Precise Language

By far the most common weakness I have found is a fail-

ure to be specific enough. This may arise because of uncertain knowledge of new material or because of the material's relevance, but it shows in a number of ways. In many cases, specific information is easy to include; in others it may not be, but the wording should not be vague or imprecise.

Of the many different types of nonspecific writing, three have been singled out for illustration here. The first type is related to weak words that include *such as*, *like*, *including*, *for example*, *various*, *diverse*, *certain*, and *some*. They do have a definite place in writing, but too frequently they appear to weaken the strength of an otherwise specific statement. In the next example, no other property was of interest in the study, and the use of *such as* added an element of vagueness that was totally unnecessary. Look for examples in your own writing and ask yourself if the specific cases would not serve your purpose better. Reserve the use of *such as* for places where you truly need to give illustrative examples from a much larger set.

Original: A fundamental study was conducted to obtain fundamental data such as isosteric heat of adsorption.

Better: A fundamental study was conducted to obtain the isosteric heat of adsorption.

The second type of shortcoming is a failure to use specific numbers when possible. When conveying technical results in a report, specific numerical values should be used whenever possible. The next example shows that amounts with nonspecific adjectives of degree should be replaced by specific values when possible. Although the original statement may not be wrong, the more specific the reporting, the better the result usually is. Watch out for similar modifiers, such as *majority*, *most*, *high*, *low*, *large*, *small*, and even *some*, and other expressions such as *around about*, *approximately*, and *the order of magnitude*, to see if they can be removed by using specific numerical values. Reserve the use of such words for situations in which the numerical values are not precise, but in which you want to convey some sense of magnitude.

Original: A representative crude oil composition containing high amounts of tocopherol was used as the feed for these processes.

Better: A representative crude oil composition containing 2% tocopherol was used as the feed for these processes.

The third type of nonspecific writing deals with the presentation of results. Too frequently, students feel that it is sufficient to present their results in a table or graph without explanation. Although this is sometimes enough, more often it is not. Only in rare cases will the readers be able to pick out the gist of the results and draw the same conclusion that the author did. It is the responsibility of the writer to point out what the results showed and how conclusions were drawn from them. Do not force the readers to interrupt their train of thought in the report to study the details of the results. Chances

are, their focus will be different from your own.

CONCLUSION

Writing technical reports or assessing someone else's writing should not be an overwhelming task. The top ten suggestions made here can be used to good advantage in focusing on the most common problems in technical writing. Practice in recognizing when and how writing can be improved will go a long way toward making you a better technical writer. Most important, always consider those who will be reading what you have written and try to make it easier for them to grasp your message.

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This column provides examples of cases in which students have gained knowledge, insight, and experience in the practice of chemical engineering while in an industrial setting. Summer internships and co-op assignments typify such experiences; however, reports of more unusual cases are also welcome. Description of the analytical tools used and the skills developed during the project should be emphasized. These examples should stimulate innovative approaches to bring real-world tools and experiences back to campus for integration into the curriculum. Please submit manuscripts to Professor W. J. Koros, Chemical Engineering Department, Georgia Institute of Technology, Atlanta, GA 30332-0100

UOP-CHULALONGKORN UNIVERSITY INDUSTRIAL-UNIVERSITY JOINT PROGRAM

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Since recovery of natural gas began in the Gulf of Thailand in the late 1970s, the need for petrochemical technology in that area has continually increased due to the rapid development of value-added processes for natural gas and LPG. Examples of such processes are dehydrogenation of ethane to ethylene and of propane to propylene. In addition to natural gas conversion, other areas of petroleum and petrochemical processing for converting petroleum to higher value-added products are of increasing interest in Thailand. One example is the conversion of naphtha to aromatics, followed by the separation of individual aromatics from each other. The individual pure aromatics can then be converted to even higher value products. For example, para-xylene can be converted to terephthalic acid, and subsequently to polyester.

Because of the high demand for petrochemical technology in Thailand, an international graduate program in "Petrochemical Technology and Polymer Science" was inaugurated in 1992 at Chulalongkorn University, one of Thailand's prominent universities. Through this international graduate program, select students who are enrolled in the Petroleum and Petrochemical College (PPC) at Chulalongkorn University have an opportunity to perform research for their thesis at one of three participating universities located in the United States. The participating U.S. universities and departments include the Department of Macromolecular Science and En-

gineering at Case Western Reserve University, the Department of Chemical Engineering at the University of Michigan, and the School of Chemical Engineering and Materials Science at the University of Oklahoma. When the Petroleum Technology Program was launched in 2002, the international graduate program was also extended to include an institute located in France, the Institut Francais du Petrole.

Through these international graduate programs, U.S. and French faculty members teach at PPC each year, and in addi-

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tion to teaching, some of the U.S. faculty members work with a Thai counterpart in supervising graduate students. Because they are jointly supervised by U.S. and Thai faculty members, some of the Thai students at Chulalongkorn University are given the opportunity to carry out part of their thesis work at one of the three U.S. universities.

After initial implementation of the international program, PPC recognized the importance of exposing its graduate students to practical experience. Thus, the international graduate program subsequently expanded its collaboration to an industrial setting. The UOP-PPC program is a first endeavor at providing Thai students with an opportunity to carry out research in an international industrial environment.

INDUSTRIAL INVOLVEMENT

The program was begun with the purpose of producing graduates of high international standards and developing world-class research and development (R&D) in the petroleum and petrochemical fields. As part of the program, industrial scientists are invited to give lectures and to supervise graduate students in their research at PPC.

In conjunction with this purpose, in 1997 Dr. Santi Kulprathipanja of UOP LLC, a graduate of Chulalongkorn University with over 25 years of industrial experience, was invited to give special experience- and industrial-application based lectures. In addition to his technical expertise, Dr. Kulprathipanja's knowledge of both the Thai and American cultures functions as a useful bridge by providing insight as to how to most effectively assist the students in adapting to their new environment.

UOP is a company known for process innovation, technology delivery, and catalyst/adsorbent supply to the petroleum refining, petrochemical, and gas processing industries. In 1998, Dr. Kulprathipanja supervised his first graduate student at PPC, and she later presented her research at a Canadian chemical engineering conference.

Observing that the program would be beneficial to Thai students, Dr. Kulprathipanja agreed to supervise two of them in 1999, allowing one to perform research at UOP for two weeks. From this beginning, future students supervised by Dr. Kulprathipanja were permitted to conduct basic research at UOP. Prior to returning to Thailand to complete their graduate work, the students are given an opportunity to present their research at a meeting of the American Institute of Chemical Engineers (AIChE), the American Chemical Society (ACS), or the North American Membrane Society (NAMS).

INVOLVEMENT/CONTRIBUTIONS OF UOP

The industrial aspect of the Petrochemical Technology and

Polymer Science Program is currently supported by UOP. Housing expenses, along with a limited stipend for living expenses while the students are conducting experiments at UOP, are also provided by UOP each year. Travel expenses from Thailand to the United States are paid by the students while expenses incurred by attendance at the technical conference are provided by the university. UOP's

Exposure to industrial practices provides the students with a more comprehensive background than a solely academic-based education. The experience gained then acts as a model for scientists and engineers in the refining and petrochemical fields.

participation caters to the mutual interests of the company and the students.

Through the program, UOP has an opportunity to help contribute to the establishment of petroleum and petrochemical R&D in Thailand by educating the students. The students learn industrial techniques while obtaining valuable research experience. With the guidance of other knowledgeable research scientists and technicians at UOP, the Thai students are exposed to proper experimentation procedures and safety guidelines, which are more stringent in the U.S. In return, through the students' research, UOP gains useful data and basic analytical information that it might otherwise not have the time or resources to explore.

CASE STUDIES

While at UOP, the students focused on four major research areas: adsorption, mixed matrix membranes, reactive separation, and catalysis. The following case studies will demonstrate the students' capabilities as they researched areas of adsorption and mixed matrix membranes at UOP LLC.

■ **Case 1 – Adsorption:** The Parex™ process, which uses UOP's well-known Sorbex™ "simulated moving bed" adsorptive separation technology to separate p-xylene from other C-8 aromatics, generates more than half of the p-xylene in the world. Because of UOP's expertise in C-8 aromatics adsorptive separation, three students were encouraged to carry out adsorption research in September and October of the years 2000 through 2002. The purpose of the adsorption study was to understand the interaction mechanism between the adsorbents and adsorbates. The adsorbents were zeolites X and Y exchanged with Li, Na, K, Rb, Mg, Ca, Sr, and Ba. The adsorbates were C-8 aromatics: p-xylene, m-xylene, o-xylene, and ethylbenzene. The adsorbents were characterized

using x-ray, TGA, ammonia-TPD, and chemical analysis. The students were initially trained to prepare adsorbents and C-8 aromatic feed stock. They subsequently studied the interaction using a myriad of techniques, including: the multicomponent dynamic pulse test to determine adsorbent selectivity to each C-8 aromatic, the multicomponent dynamic breakthrough to measure adsorbent selectivity, mass transfer rate and capacity for each C-8 aromatic, and single and multicomponent equilibrium adsorption isotherm to measure adsorbent selectivity and capacity for each C-8 aromatic. The results were then analyzed by a model simulation. In brief, the study indicated that the interaction mechanism between the adsorbents and C-8 aromatics is influenced by various factors, including: the acid-base interaction between zeolite and C-8 aromatics, exchanged cation size, C-8 aromatics feed composition, and zeolite Si/Al ratio. The results were used to fulfill the students' MS theses^[1-3] and were presented at the AIChE meetings. UOP benefited from the results by gaining a basic understanding that will assist in further C-8 aromatics separation improvement development.

■ **Case 2 - Mixed Matrix Membranes:** There were two types of mixed matrix membranes (MMM) developed at UOP LLC in the early 1980s. The first MMM has zeolite embedded in the cellulose acetate (CA) polymer phase.^[4,5] The second MMM is produced by casting an emulsion of polyethylene glycol (PEG) and silicone rubber (SIL) on a porous polysulfone (PS) support.^[6-9] It was found that both types of MMMs offered many interesting features in enhancing selectivity and permeability if the MMM was composed of a comparable pair of polymer and zeolite or PEG. Based on this finding, four students were invited to the UOP Research Center during September and October of 1999 to 2002 to study/explore/discover new MMMs for interesting applications. Their objectives were to develop new types of MMMs for olefin/paraffin separation and carbon dioxide separation from natural gas. During the program, the students were trained to formulate MMMs, carry out permeation studies, and analyze data. Many encouraging MMMs were developed by the students for olefin/paraffin separation.^[10-11] For example, the students found that ethylene/ethane and propylene/propane selectivity were enhanced by PEG/SIL/PS MMM.^[10] Their selectivity was reversed with NaX/CA and AgX/CA MMMs, however.^[11] In the case of carbon dioxide separation, a novel type of MMM was developed to enhance both CO₂/N₂ selectivity and CO₂ permeability. The MMM was composed of PEG, activated carbon, and silicone rubber on polysulfone.^[12,13] Through this novel MMM, it was found that activated carbon can stabilize PEG and further enhance CO₂ permeability and selectivity. In addition to the basic understanding that UOP obtained from the students' work on activated carbon and PEG, UOP also filed a patent application due to the novel nature of the silicone rubber on polysulfone composite MMM. The data and analyses obtained

from the research were used to fulfill the students' MS theses^[10-13] and were presented at the AIChE meetings.

CONCLUSION

The Petrochemical Technology and Polymer Science Program stresses the reality that most graduate students will eventually work in industry. Exposure to industrial practices provides the students with a more comprehensive background than a solely academic-based education. The experience gained then acts as a model for scientists and engineers in the refining and petrochemical fields. In addition to the experience obtained by the students, UOP also benefited from the students' work. UOP has gained basic research information and has continued to use the information to further commercial process development. Overall, with the collaboration of UOP management, scientists, technicians, and others, the students in the program gained practical experience, presentation experience, and a more established reputation. The participating universities also benefited by gaining recognition on an international level.

The primary accomplishment of the program is to offer the opportunity for students in developing countries to obtain a solid foundation of knowledge by learning about other cultures and working in a professional environment. The following paragraphs demonstrate the impact the program has had on former participants.

TESTIMONIALS

By Ms. Warangkana Sukapintha and Mr. Thera Ngamkitidachkul' (1999) • Learning under real working conditions has broadened my vision and has enabled me to prepare for practical work. For two weeks, UOP allowed me to train in the R&D department, tour a UOP pilot plant, and visit the engineering and patent departments. These opportunities gave me the invaluable experience of seeing real work in a real company. I learned that one of the most important factors of doing work efficiently is being able to work well as part of a team. Additionally, as an unknown graduate student, it is almost impossible to be invited to an international meeting. Therefore, the opportunity to present a paper and attend the AIChE 2000 Spring National Meeting was one of the greatest experiences of my life. Now, in addition to the fundamental knowledge that I gained from my studies at PPC, I have also expanded my vision through industrial training. Overall, the opportunities to work under Dr. Kulprathipanja, to visit UOP, and to attend an AIChE meeting helped potential employers realize my capabilities.

By Mr. Varoon Varayanond, Ms. Worrarat Rattanawong, and Ms. Passawadee Vijitjunya (2000) • We obtained benefits from our stay at UOP that could not be obtained solely*

*Thera Ngamkitidachkul, Passawadee Vijitjunya, Prueng Mahasaowapakkul, Kathavut Visedchaisri did not intern at UOP. They carried out their research work at PPC.

from the University. The strongest advantage of working in a company was the availability of technical knowledge. Under the guidance of an expert, we acquired wider and deeper points-of-views. The state-of-the-art equipment and facilities also enabled us to effectively work on our research. We felt that anything was possible. The picture of how to apply the knowledge that we obtained from the classroom became clear. One of the most important educational tools we gained was the safety indoctrination provided by UOP. We also had the honor of presenting our work at an international conference where we developed communication skills and a result-focused style of thinking. These skills are some of our strongest points in getting a job. We believe the program will certainly give students a chance to develop themselves, as well as profit industry. Last, but not least, we would like to express our gratitude to Dr. Kulprathipanja, who worked so hard to give us this precious opportunity.

By Ms. Rattiya Suntornpun, Ms. Jutima Charoenphol, Mr. Visava Lertrudjanapanya, and Mr. Prueng Mahasaowapakul' (2001) • For two months we were able to carry out our research at UOP under the close supervision of Dr. Kulprathipanja. This was a great opportunity for us to learn from a person with a strong industrial background. Meeting people from different backgrounds allowed us to learn more than just technical know-how. For example, they stimulated diverse ideas, increasing the likelihood that we would find the best solution to any problem. Moreover, we became more open-minded to other people's thoughts. We also learned that there were no exceptions when it came to safety matters. A large advantage of researching at UOP was the access to information. While we sometimes have to wait for a publication to be sent from abroad at PPC, this was never a problem at the UOP library. At the end of the program, our research was presented to an international audience at the AIChE 2001 Annual Meeting. We were able to practice our oral presentation skills and learn from the questions people asked about our research. Overall, this experience gave us more confidence in ourselves, making us more attractive to employers.

By Ms. Raweewan Klaewkla, Ms. Saowalak Kalapanulak, Ms. Parichart Santiworawut, Ms. Suwanna Limsamutchai, and Mr. Kathavut Visedchaisri' (2002) • We received a great opportunity from UOP to perform some of our research at UOP. We learned various techniques such as: preparing catalysts, casting membranes, setting up adsorption experimental lines, and using modern analysis instruments. An important observation that we made regarding UOP's working style was that while they directed most of their attention to their work, they were also prompt to provide each other with assistance. This general rule-of-practice influenced us to effectively work on our research. We were able to obtain both high quality and high quantity work in a limited amount of time. Before we left the United States, we also

had a chance to present our research at the 2002 AIChE Annual Meeting. This trip opened our minds to the international world that we would not have been able to experience if we stayed only in our country and our college. Moreover, we learned a lot from the different cultures, languages, foods, living styles, and beautiful places. These impressive things could not have happened without Dr. Kulprathipanja and the UOP LLC staff. We would like to express our thanks and let them know that we are all very appreciative.

ACKNOWLEDGEMENTS

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USE OF CONCEPTTESTS AND INSTANT FEEDBACK IN THERMODYNAMICS

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Many studies have emphasized the fact that cooperative learning can improve engineering education.^[1,2] One form of cooperative learning in physics and chemistry departments is in-class ConcepTests^[3,4]—multiple-choice conceptual questions posed to the class. After all the students respond with an answer, they are asked to discuss the answers among themselves (peer instruction) and are given the opportunity to change their answer.

Mazur^[3] showed a lack of correlation between students' conceptual understanding of physics and their ability to do quantitative problems. They could do quantitative problems better than conceptual problems that used the same concept. He found that students memorized algorithms for solving the problems without understanding the concept, and thus had difficulty when a problem they had to solve was different from ones they have previously solved. He reported a gain in student performance with the use of ConcepTests. The students' conceptual understanding increased because they were better able to explain concepts to one another than their teachers could. The percentage of students with the correct answer always increased after they discussed the question with their peers.

This effectiveness of ConcepTests can be further improved if students are graded on their answers because it increases

both their participation and their motivation. The grading is done with IR transmitters and receivers, as described below. My experience in a thermodynamics course showed the following advantages:

- *Students liked using ConcepTests and getting instant feedback on how well they understood material as it was presented to them.*
- *The instructor obtained instant feedback on how well the class understood a concept.*
- *Students were more motivated to be prepared and thus learned more in class.*
- *Attendance in class was higher than in previous semesters when ConcepTests were not used. (Although statistics were not obtained for the previous semesters, attendance was over 90% when ConcepTests were used and graded.)*
- *Everyone participated in class.*
- *The discussions among students were quite lively. Students interacted, teaching and learning from their fellow students. This creates a more engaged class and students hear more than one explanation. This increases learning.*

Although ConcepTests were a small part of the course grade, grading them motivated the students. For the thermodynamics course, the lowest five days of grades were dropped to allow for sickness, outside activities, etc. The ConcepTest grades then counted either 5% or 10% of the final course grade. The higher of the two grading methods was used for each student. Since the average on the ConcepTests was 88%, almost all students counted the ConcepTests as 10% of their grade. An important aspect was the use of an absolute grading scale for the course. This encouraged students to cooperate; they were also required to do homework in groups.

This brief article describes ConcepTests and the relatively



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inexpensive technology available that significantly improves their application. Both the technology and ConcepTests have been in use for some time in physics and chemistry departments. The purpose of this article is to indicate that they are also effective in chemical engineering courses, particularly those courses that require significant conceptual understanding, and that inexpensive technology exists for implementing the test and getting instant feedback.

Examples used during the Fall 2002 semester for a junior-level chemical engineering thermodynamics course will be presented here. Grading and instant feedback were accomplished by installing IR detectors in the classroom and requiring students to purchase IR transmitters (clickers) manufactured by H-ITT.^[5] There were fifty students in the class.

EXPLANATION OF CONCEPTTESTS

The ConcepTests with transmitters (clickers) works as follows:

1. The instructor poses a conceptual question and presents possible answers (multiple choice).
2. Each student picks an answer by selecting A,B,C,D, or E on a clicker.
3. The instructor displays a histogram of answers for the class to see. If most answers are correct, a short explanation is given and the next topic is started.
4. If many of the answers are incorrect, students are told to discuss the question with their neighbors. This peer instruction is a critical aspect of ConcepTests and learning. It fosters student involvement and engagement.
5. Students are allowed to change their answers after the discussion. As a result, most of the students end up with the correct answer and a better understanding.
6. If most students have the correct answer, a brief explanation is given. If not, the question is discussed further, and the instructor provides additional ideas to help the students learn the concept.

Three receivers were mounted high on the walls in the room for a class of fifty students. The receivers are small (3.5 x 2.5 x 1.5 cm) and are daisy-chained together by cables. The cost of 3 receivers and cables was around \$600. The receivers collect the signals and send them to a PC running acquisition software, which can be downloaded free from the H-ITT web site.^[5]

Each student has their own hand-held transmitter (clicker), purchased from the bookstore for \$30. The H-ITT hand-held IR transmitter, similar to a TV remote control, has a unique ID number. It is slightly larger than a pen and is battery operated. Each student responds to the multiple-choice questions by aiming the clicker at a wall-mounted receiver and pressing A, B, C, D, or E. The H-ITT acquisition program display

is also projected onto a screen for the entire class to see. The ID number (or the student initials) of each clicker is displayed, indicating that the student response has been successfully collected, but it does not show the student answer. The H-ITT acquisition program summarizes the data and displays the class responses in histogram form.

After class, a separate program associates student names with the remote ID numbers and grades the responses instantly. It allows the instructor to assign point values to each answer for each question (*e.g.*, 3 points for a correct answer and 1 point for an incorrect answer). The software also allows a list of the student names and point totals to be quickly exported into a spreadsheet.

EXAMPLES FROM THERMODYNAMICS

Several examples from the thermodynamics course are presented here. Many students initially had problems answering these types of questions since some of them require higher levels of Bloom's taxonomy. The examples are presented to give the reader an idea of how ConcepTests are applied in class. Similar problems were then used on the course exams, but without the multiple-choice options and with the requirement that the students explain the reason for their answers.

1. Components (A and B) are in vapor-liquid equilibrium. One mole of liquid ($x_A = 0.4$) and 0.1 mol of vapor ($y_A = 0.7$) are present (see Figure 1). When 0.5 mol of A is added and the system goes to equilibrium at the same T and P, what happens?
 - A. The amount of liquid increases.
 - B. The amount of liquid decreases.
 - C. The concentration of A in the gas phase increases.
 - D. The concentration of A in the liquid phase increases.
2. Is the fugacity of water at 150°C and 100 atm closer to
 - A. 1 atm
 - B. 5 atm

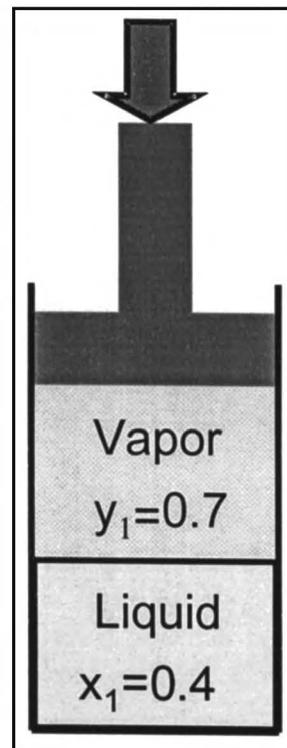


Figure 1. Two-component vapor-liquid phase equilibrium in a piston/cylinder at constant pressure equilibrium.

- C. 50 atm
D. 100 atm

3. For the $H-x_A$ diagram at 80 °C in Figure 2, what is the maximum value of the partial molar enthalpy in cal/mol of component A?

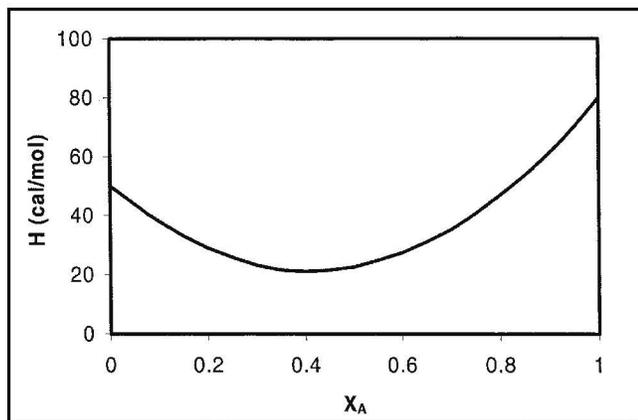
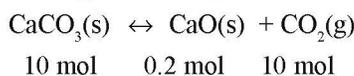


Figure 2. Enthalpy of a binary mixture versus mole fraction of component A.

- A. 50
B. 22
C. 85
D. 100
E. 0
4. Two identical flasks at 45 °C are connected by a tube. One flask (A) contains water and the other (B) contains the same amount of a 95/5 mixture of water and salt. After five hours
- A. Beaker A has more water.
B. Beaker B has more water.
C. The amounts of water do not change since they are at the same temperature.
D. All the salt moves to beaker A.
5. Consider the reversible reaction and the indicated number of moles present at equilibrium:



If we push down on the piston (see Figure 3) to decrease the volume to half and keep the temperature constant, what happens at equilibrium?

- A. The CO_2 pressure almost doubles.
B. CaO and CO_2 react, so the CO_2 pressure does not change.
C. The system is at equilibrium, so nothing changes.
D. All the CO_2 reacts.

6. 6 mol A and 4 mol B are in equilibrium at 100 °C and 3.0 atm. A and B are completely immiscible in the liquid phase. Their vapor pressures at 100 °C are

$$P_A^{\text{sat}} = 2.0 \text{ atm}$$

$$P_B^{\text{sat}} = 0.5 \text{ atm.}$$

What phases are present?

- A. Liquid B and vapor of A + B
B. Two liquids
C. Two liquids in equilibrium with vapor
D. All vapor
E. Liquid A and vapor of A + B

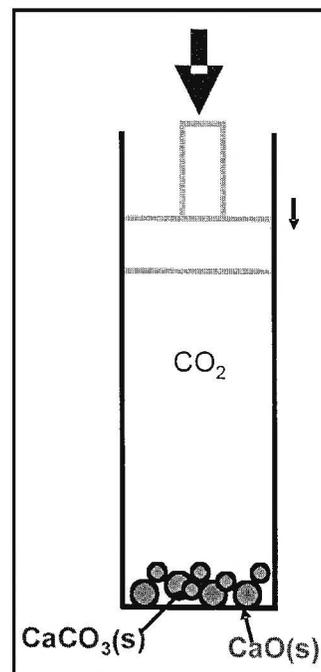


Figure 3. Gas-solid chemical equilibrium in a piston/cylinder.

7. Water alone is present and is in VLE at 1.2 atm in a piston/cylinder. You inject 5 cm³ of air into the system, but keep P and T constant. What happens?
- A. All the water vaporized.
B. All the water condenses.
C. Some water vaporizes.
D. Some water condenses.

FEEDBACK FROM THE FALL 2002 THERMODYNAMICS CLASS

At the end of the Fall semester, students turned in an anonymous typed course evaluation to the TA. These evaluations were given to the instructor after course grades were posted. One area that the students were asked to address was the use of clickers and ConcepTests. Partial comments from fifteen of those evaluations follow. Almost everyone in the class liked the clickers and ConcepTests.

- The greatest part about it was that you made thermodynamics a fun class to attend. The IR transmitters did not follow a straight lecture and I found they are a good idea, and I found them to be quite useful in understanding the ConcepTests.
- There was one thing in particular that I really enjoyed, and that was the clicker questions.
- As for the instant response clicker system, it was generally a big help. I think it is essential to

teaching such technically difficult material as we study in thermodynamics. Being able to immediately apply what we were learning to a problem and receive instantaneous feedback on our understanding, as a class, was fantastic.

- Although I was a bit skeptical of the transmitters at first, I found that I actually liked them a lot. It kept the class interesting to be able to participate every day.
- The transmitters were very effective in adding to the class as a learning experience. They gave support to myself in times when I felt unwilling to ask a question for fear I was the only one who didn't understand.
- The ConcepTests were extremely helpful in getting a grasp on what is happening. I also liked the use of the transmitters.
- I thought the clickers worked well in class. These questions were very useful at helping me grasp the conceptual part of the course.
- I thought the overhead ConcepTests were a great idea, and a good usage of the clickers.
- I felt the use of the transmitters greatly enhanced my understanding of the topics we discussed.
- The IR transmitters receive two thumbs up. I was skeptical of them at first, but they really help in making sure that not only I but the majority of the class understands what is being taught.
- I also liked the concept questions.... I thought the IR transmitters worked very well and were used well. The IR transmitter is good because there is no peer pressure factor when you're answering the question for the first time, and you can get a good idea of the class understanding of the concept.
- My favorite parts to this course were the supplements in the notes and the IR transmitter...I felt the IR transmitter and the ConcepTests were a valuable tool to this class.
- I thought the best aspects of the course were the transmitters, the reviews, and the homework help sessions. The transmitters were definitely a good way to get people to participate.
- I felt the IR transmitter and ConcepTests were a valuable tool in this class.
- Ultimately I found that the clicker really helped my learning. It also keeps you involved with the lecture, rather than just mindlessly copying down notes.

The concerns expressed by the students were small. The biggest concern was that they had to spend \$30 to purchase a

The purpose of this article is to indicate that [ConcepTests] are also effective in chemical engineering courses, particularly those courses that require significant conceptual understanding . . .

transmitter they could use only in one course. Since they should be able to sell their transmitters to students in next year's class, that should become less of a problem. Some students were concerned that the grading in every class forced them to come to class more often. Two students did not like the transmitters or the ConcepTests.

SUMMARY

Even though students could work numerical problems, many did not have a good grasp of the thermodynamic concept involved. For example, they could calculate the vapor pressure at a given temperature with Antoine's equation, but a large fraction of them did not understand the concept of vapor pressure well enough to answer questions such as #7 above.

For many of the ConcepTests used, more than half the class initially answered incorrectly, but the percentage of correct answers increased, usually dramatically, after discussions with other students.

The H-ITT software was easy to use in class, and the students could readily see their clicker ID number on the projected display. Since their ID number always appeared in the same location on the screen, it was easy to find. We have since installed the detectors in a second room in the engineering building, and two other faculty members have indicated they will use the clickers in their classes in the future.

ACKNOWLEDGMENTS

I could not have incorporated this method into my class without the help and advice of Dr. Michael A. Dubson in the Physics Department at the University of Colorado. I would also like to acknowledge the funds from the President's Teaching Scholar program and from the Dean's Office to purchase the equipment.

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RUBRIC DEVELOPMENT FOR ASSESSMENT OF UNDERGRADUATE RESEARCH

Evaluating Multidisciplinary Team Projects

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Experts agree on the importance of involving undergraduates in research-based learning^[1-3] and teamwork.^[4-6] The Boyer Commission suggested that research-based learning should become the standard for undergraduate education.^[7] Many universities are responding to this challenge by introducing multidisciplinary laboratory or design courses.^[8,9] At Rowan University, we developed a method of addressing these diverse challenges while also implementing valuable pedagogical hands-on learning experiences^[10,11] and technical communications.^[12-14]

At Rowan University, all engineering students participate in an eight-semester course sequence known as the engineering clinics.^[15] In the junior and senior years, these clinic courses involve multidisciplinary student teams working on semester-long or year-long research projects led by an engineering professor. Most of the projects have been sponsored by regional industries. Student teams under the supervision of chemical engineering faculty have worked on emerging topics that included enhancing the compressive properties of Kevlar, examining the performance of polymer fiber-wrapped concrete systems, advanced vegetable processing technology, metals purification, combustion, membrane separation processes, and many other areas of interest. Every engineering student participates in these projects and benefits from hands-on learning, exposure to emerging technologies, industrial contact, teamwork experience, and technical communications.

Difficulties arise in trying to assess student learning and performance in project-based team settings, however. Angelo and Cross^[16] provided significant suggestions for assessing the attitude of students toward group work, but provided little insight into distinguishing individual and team performances.

One difficulty is that evaluating the semester-long performance of teams working on projects involves a substantial number of variables. Clearly, successful completion of the project's technical aspects is an essential component for demonstrating student understanding, but Seat and Lord^[17] observed that while industry seldom complains about the technical skills of engineering graduates, industrial employers and educators are concerned with performance skills (*i.e.*, interpersonal, communication, and teaming). Lewis, *et al.*,^[18] correctly observed that if students are to develop effective teaming skills, teaming must be an explicit focus of the project.

It is unreasonable to expect students to achieve specific learning objectives from a series of courses when the faculty members themselves are unclear about what the learning objectives are and how to measure them. Young, *et al.*,^[19] dis-

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cussed development of a criterion-based grading system to clarify expectations to students and to reduce inter-rater variability in grading, based on the ideas developed by Walvoord and Anderson.^[20] This effort represented a significant step forward in course assessment; however, for graded assignments to capture the programmatic objectives, a daunting set of conditions would have to be met. Specifically,

- *Proper course objectives that arise exclusively from the educational objectives and fully encompass all of these objectives must be set*
- *Tests and other graded assignments must completely capture these objectives*
- *Student performance on exams or assignments must be a direct reflection of their abilities and not be influenced by test anxiety, poor test-taking skills, etc.*

There should be a direct correlation between student performance in courses and the overall learning of the students only if all of these conditions are met every time. Moreover, much of the pedagogical research warns of numerous pitfalls associated with using evaluative instruments (*e.g.*, grades on exams, papers, etc.) within courses as the primary basis for program assessment.^[21]

Obviously, a more comprehensive assessment method for a team-oriented, research-project based course must be developed. Woods^[22] listed the following five fundamental principles for assessment of teams:

1. *Assessment is based on performance*

Part of the purpose of this pilot program was to clarify for the students the expectations in junior/senior clinic by providing specific information about their learning goals.

2. *Assessment is a judgment based on evidence rather than on feelings*
3. *Assessment must have a purpose and have clearly defined performance goals*
4. *Assessment is done in the context of published goals and measurable criteria*
5. *Assessment should be based on multidimensional evidence*

Rowan's Chemical Engineering Department is implementing the following strategy for improved assessment of student team projects: decide on the desired learning outcomes for the clinic, develop indicators that demonstrate whether or not the teams (and each member of the team) have achieved each of the outcomes, develop rubrics to evaluate student performance in each of the areas, and present all of this information to the students at the start of the project.

PILOT PROGRAM

In the junior/senior engineering clinic, each student team submits a final written report and gives an oral presentation, which allows the communication aspects of the project to be evaluated directly, but the remaining elements of a successful project experience had to be identified and measured. As a first effort to address the assessment of team performance in project-based research experiences, the faculty developed the following list of four learning objectives of primary importance that were common to all projects:

- *Technical performance*
- *Project planning and logistics*
- *Laboratory operation*
- *Teaming*

Once these objectives were identified, specific indicators were developed for each so the students would have clearly defined behaviors. Table 1 summarizes these indicators.

With the specific indicators determined, the next step involved developing descriptive phrases that would assist both students and faculty members in evaluating student performance. It became clear that specific descriptions of the level of performance in each area would be

TABLE 1
Summary of Specific Indicators for Areas of Importance

<i>Area of Importance</i>	<i>Specific Indicators</i>
<i>Technical</i>	<ul style="list-style-type: none"> • Defined objectives • Demonstrated technical awareness • Obtained and interpreted appropriate results • Formulated supportable conclusions • Properly considered error • Provided recommendations for future work
<i>Logistical</i>	<ul style="list-style-type: none"> • Organized project • Met deadlines • Executed project plan • Kept detailed records
<i>Laboratory Operation</i>	<ul style="list-style-type: none"> • Maintained safe practices • Developed hazardous operations (HAZOP) report • Dressed appropriately • Proper use/maintenance of equipment • Performed end-of-semester shut down
<i>Teaming</i>	<ul style="list-style-type: none"> • Division of labor • Professional conduct • Learning experiences for all team members

required. The goal of our rubrics was to map student work directly to the individual learning outcomes. As Banta^[23] stated, “The challenge for assessment specialists, faculty, and administrators is not collecting data but connecting them.” The assessment rubric also followed the format developed by Olds and Miller^[24] for evaluating unit operations laboratory reports at the Colorado School of Mines.

The decision to frame the rubrics based on only three levels was significant and requires explanation. At one time, many of the other program-assessment instruments used by

Rowan’s Chemical Engineering Department used a 5-point Likert scale with qualitative labels (5=excellent, 4=very good, 3=good, 2=marginal, 1=poor), but the qualitative natures of the descriptive labels led to confusion in scoring. Some professors have different distinctions between “excellent” and “very good” and tended to use them more than the descriptive phrases that define the difference between levels for each indicator. More important, if the rubrics are well designed, the descriptive phrases should stand alone, without the need for subjective clarifiers such as “excellent” and “good.” Ulti-

TABLE 2
Behaviors Corresponding to Technical Performance

<i>Indicator</i>	<i>An “A” Team</i>	<i>A “B” Team</i>	<i>A “C”-or-Lower Team</i>
Defined objectives	Is actively involved in defining aggressive and achievable objectives that thoroughly address fundamental project needs.	Aids in defining objectives. Some may be too simplistic or unrealistic.	Takes little initiative in defining the project.
Demonstrated technical awareness	Clearly demonstrates awareness of the work of others and establishes a context for their project. Shows an understanding of information from multiple literature sources.	Shows understanding of the work in the field, but has limited depth and breadth. Knowledge is limited to faculty-provided materials.	Fails to demonstrate an awareness of the work of others and the significance of their project.
Obtained appropriate results	Obtained meaningful results with minimal wasted effort.	Produced some results but not enough (or too many).	Generated few meaningful results.
Interpreted data appropriately	Provided thorough and correct analysis of data.	Provided analysis but partially incorrect or insufficiently thorough.	Little meaningful analysis of data or blatantly incorrect.
Formulated supportable conclusions	Formulated and adequately supported meaningful conclusions.	Needed significant help in formulating meaningful conclusions or lacked sufficient support for their conclusions.	Conclusions are absent, wrong, trivial, or unsubstantiated.
Properly considered error	Used appropriate mathematical and technical skills to quantitatively express limitations of the data.	Error analysis is largely qualitative or incomplete.	Sources of error and reproducibility issues are ignored or misinterpreted.
Provided recommendations for future work	Makes insightful recommendations about future work.	Makes broad or obvious suggestions for future work.	Makes no plausible suggestions for future work.

TABLE 3
Behaviors Corresponding to Project Planning and Logistics

<i>Indicator</i>	<i>An “A” Team</i>	<i>A “B” Team</i>	<i>A “C”-or-Lower Team</i>
Organized project	Effectively organizes project tasks to minimize wasted time and effort.	Identifies relevant tasks but may struggle with setting priorities and planning.	Has difficulty converting broad objectives to specific tasks.
Met deadlines	Consistently meets deadlines.	Misses some deadlines despite reasonable effort.	Routinely ignores deadlines.
Executed project plan	Effectively and safely executes the project plan. Makes significant progress. Modifies the plan as necessary.	Executes the project plan but has difficulty overcoming setbacks.	Works haphazardly with little chance of achieving project objectives.
Kept detailed records	Keeps detailed records easily followed by others. These records include a laboratory notebook, computer files, purchase records, and others.	Keeps a lab notebook but records lack organization or contain omissions.	Keeps poor, sketchy, or no records.

mately, we decided to eliminate such descriptors and divide rubric elements by listing behaviors that demonstrated the level (1, 2, or 3) at which the student had obtained the desired learning outcomes.^[25]

These previously developed rubrics, however, were programmatic assessment tools that were seen and used only by the faculty. Part of the purpose of this pilot program was to clarify for the students the expectations in junior/senior clinic by providing specific information about their learning goals. Students tend to be more focused on grades than on learning outcomes, so characterizations such as “level 1 vs. level 2” would be meaningless to them, and subjective phrases such as “excellent” and “good” would be subject to the same shortcomings described above. Further, if grading truly represents

the measure of achievement of learning outcomes, it is not unreasonable to present the behaviors that demonstrate successful attainment of a learning outcome in terms of grades. Consequently, the rubrics were written for presentation to the students in terms of behaviors that an A-Team would demonstrate, a B-Team would demonstrate, etc., Tables 2 through 5 provide the rubrics.

Both the chemical engineering faculty at Rowan and the reviewers of this paper questioned if the “C-or-Lower” range was too broad. Some items were barely acceptable, while others could be dangerous. There was even a question about whether or not laboratory safety could be scaled at all. We decided to stay with three levels for several reasons. First, we did not want students bargaining about the lower-level

TABLE 4
Behaviors Corresponding to Laboratory Operations

<i>Indicator</i>	<i>An “A” Team</i>	<i>A “B” Team</i>	<i>A “C”-or-Lower Team</i>
Maintained safe practices	Develops and follows procedures that account for safety and clean-up. Lab is clean and neat.	Develops and follows procedures consistent with safe practices but sometimes misses minor safety issues or fails to clean up.	Fails to develop and follow safe procedures and/or clean up.
Developed Hazardous Operations (HAZOP) report	Conducts a thorough Haz-Op.	Performs a Haz-Op but focuses on obvious issues without depth (e.g., does not check MSDS sheets).	Fails to perform a Haz-Op or performs one inadequately.
Proper use/maintenance of equipment	Treats equipment with care and performs necessary maintenance.	Usually handles equipment properly but has an occasional lapse.	Uses equipment carelessly or fails to maintain it.
Performed end-of-semester shut down	Lab area is neat and clean. Lab notebook and electronic copies of all data and reports are provided to the faculty member. Samples and materials are labeled appropriately and are either stored or disposed of properly.	Must be pushed by the faculty member for the behaviors described previously.	Fails to accomplish some of the listed items.

TABLE 5
Behaviors Associated with Teaming

<i>Indicator</i>	<i>An “A” Team</i>	<i>A “B” Team</i>	<i>A “C”-or-Lower Team</i>
Division of labor	Has all members making significant contributions to a project that progresses satisfactorily.	Progresses satisfactorily but some members feel that workload distribution was disproportionate.	Internal conflicts result in team failing to achieve project goals.
Professional conduct	Consistently behaves in a professional manner (shows up for meetings prepared and on time; treats vendors, technicians, team members and staff with courtesy and respect; external communications are formal and businesslike). Always dresses appropriately (long pants and safety glasses in labs; business attire for industrial meetings and presentations, etc.).	Usually behaves in a professional manner (shows up for meetings prepared and on time; treats vendors, technicians, team members, and staff with courtesy and respect; external communications are formal and businesslike). Usually dresses appropriately (long pants and safety glasses in labs; business attire for industrial meetings and presentations, etc.). Does not repeat errors.	Frequently fails to behave in a professional manner (shows up for meetings prepared and on time; treats vendors, technicians, team members and staff with courtesy and respect; external communications are formal and businesslike). Frequently fails to dress appropriately (long pants and safety glasses in labs, business attire for industrial meetings and presentations, etc.).
Learning experiences for all team members	Has all team members demonstrate a thorough understanding of the technical issues of the project.	Has all technical issues understood by someone on the team, but is segmented. Some members do not have the whole picture.	Has team members with significant gaps in their understanding of technical issues.

Faculty distributed the tables to the students at the beginning of the semester, referred to them throughout the semester in giving feedback on student performance, and used them to aid in assigning and justifying a final grade.

behaviors (e.g., “I can be late for three meetings and still get a ‘C,’ but the fourth one gets me a ‘D.’”). The lowest-level behaviors were to be avoided entirely, so we chose not to put a distinction between “bad” and “really bad.” The other important point to keep in mind is that the rubric items do not represent individual grades, but rather a holistic approach to evaluating all of the factors on a team. If the team has mostly A-level performances but also has some “C-or-Lowers,” it would likely lower their project grade to a “B.”

TABLE 6
Faculty Assessment of Grading Rubrics
(1=strongly disagree...4=strongly agree)

<u>Statement</u>	<u>Mean Response</u>
• The grading rubrics helped me explain the expectations of my project.	3.80
• The grading rubrics helped me determine how my team would be graded.	3.70
• The grading rubrics helped me consider project issues that I otherwise might not have considered.	3.30
• I referred to the grading rubrics during the semester.	3.40
• I think that clinic is more fair using grading rubrics.	3.70
• I would like to use the rubrics again next semester.	3.80

Faculty members were asked to assess the effectiveness of the rubrics. Table 6 indicates that the faculty clearly felt the rubrics were useful in improving fairness and linking the grading to the learning objective. In our annual assessment review, however, the faculty decided that it would be more valuable to have the students do a mid-semester assessment of progress based on the rubrics. Ideally, this should help both the team and the professor identify areas that need improvement while there is still time to adjust. Specific faculty comments about the rubrics

included, “I felt much more confident that my grade meant something,” and “I was able to use items from the rubrics to drive my teams and help keep them on track.”

Student comments about the rubrics were more mixed. They were discussed with a focus group of seniors who had participated in the clinic the previous year without the rubrics. Their consensus was that the rubrics were useful and probably the correct way to do things, but one student asked, “Couldn’t you have waited until I graduated to implement these?” The students also expressed concern that the rubrics could be used as a basis for artificially lowering grades.

Ironically, part of the impetus for developing the rubrics was a concern that grading that seemed arbitrary might lead to grade inflation. In fact, more “A”s were given using the rubrics than had been given the previous year when no rubrics were used. The faculty attributed the change to improvement by the students. When we told the students what we expected them to do, more of them did it.

FUTURE WORK

Although development of the above rubrics represents a significant step forward, the results presented here describe a pilot study. Substantial work remains to be addressed. Meaningful assessment instruments must be developed to gauge student and faculty perceptions of these criteria. Are the critical learning objectives addressed in these rubrics and are the

RESULTS AND DISCUSSION

The rubrics have two uses, each of which was piloted within the Chemical Engineering Department during the 2002-03 academic year. The first is that it will facilitate grading that is uniform, fair, and clearly understood by the students. Faculty distributed the tables to the students at the beginning of the semester, referred to them throughout the semester in giving feedback on student performance, and used them to aid in assigning and justifying a final grade.

The second use of the rubrics is assessment of the junior/senior clinic program as a whole. As mentioned above, simply using course grades as a primary assessment tool (even when the grades are fair and based on well-constructed criteria) has pitfalls. In the junior/senior clinic, for example, there is a danger that students will perform well overall but have widespread deficiencies in one or two areas. In such a case, the fact that most teams earned A’s and B’s for the semester would imply that students in the junior/senior clinic are meeting the desired learning outcomes, when in reality there is a need for specific improvement. As part of the pilot assessment program, faculty went through the eighteen indicators, one by one, and examined the level of performance demonstrated by each team with respect to each indicator. Through this process, specific problem areas were uncovered even when the overall student performance was objectively very good.

measurements accurate? Appropriate and meaningful weightings must be developed for each of the behaviors. While appropriate dress has been listed as an important part of the project, one would be unlikely to argue that it is as significant a learning objective as “drew meaningful and supportable conclusions.”

Once the rubrics have been optimized, the next major task to be addressed is differentiating the performance of individuals from the performance of the team. It is possible that a team could have one (or more) member who fully attains the desired learning outcomes, but whose teammates fall substantially short of achieving those outcomes. Currently, the Chemical Engineering Department at Rowan University uses a peer-assessment technique modeled after a process described by Felder.^[26]

Although this is a useful tool, it is somewhat over-reliant on student evaluation of peers. Our experience indicates that reasonably successful teams generally recommend an equal distribution of points, while the recommendation of less successful teams often are clouded with personal issues and resentments. Because students tend to focus on grades rather than on learning outcomes, their responses tend to be holistic (person X should get 50% of the points) and more about evaluation and grading, but less about achieving specified learning outcomes.

A major thrust of this effort is to develop evidence-based tools to complement the Felder survey, such that students could more meaningfully assess the performance of their teammates without defaulting to meaningless (e.g., “everyone contributed equally”), hierarchical (e.g., “person X was terrible,” but no reasons provided), or personal assessments. Moreover, the students will be required to cite specific evidence linking their evaluations to the specific desired learning outcomes. Ideally, in addition to aiding the faculty member in attempting to discern individual achievement from a group experience, forcing an evidence-based approach may help the students recognize the importance of the learning outcomes.

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TEACHING ENGINEERING COURSES WITH WORKBOOKS

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Society expects that a modern college education will turn out students who are analytical, intellectually curious, culturally aware, employable, and capable of leadership.^[1] Some important skills needed for all degree programs are problem solving, communication (written and oral), team or group work, learning, and information processing and technology. Instructors feel rewarded and satisfied when they sense that they have made a difference in the life of a student.^[1]

All institutions of higher education emphasize that teaching is important and give high priority to developing learning and teaching strategies that focus on promoting students' subject-specific skills, knowledge, understanding, critical perspective, and intellectual curiosity.^[2-14] Some of the strategies are active and cooperative learning,^[3,11] problem- or case-based learning,^[12,13] and teaching through inquiry.^[14] Active and cooperative learning is one of the most frequently used teaching methodologies.^[15-17] Development of new learning and teaching methodologies should not be interpreted as an obstacle to the research activity of a faculty member and should be fully consistent with the university's research strategy.^[18]

As Kennedy^[1] suggests, new faculty members soon discover that effective lectures are hard to develop and deliver and take much longer to prepare than they anticipated. Effective teaching incorporates forms of creativity that are not usually thought of as research but which actually analyze, synthesize, and present knowledge in new and effective ways.^[1,17]

Traditional methods of learning and teaching embrace lectures, seminars, workshops, and classes, as well as various assignments that require the use of books, handouts, handbooks, and periodicals. As the student advances, incorporation of computers and information technology such as "BLACKBOARD" are developed. Currently, laptop computers are becoming com-

pulsory, and some courses are delivered entirely through the use of computers and information technology with supporting assignments. Some believe that the Internet has the potential of replacing face-to-face teaching, but most courses still use the chalkboard and verbal communication, and teaching and learning methods remain the responsibility of instructor and students.

It is widely recognized that students don't learn as much as we try to teach them. Their native ability, their background, and the match between their learning styles and the instructors' teaching styles determines the level of learning.^[17] To maximize the level of their learning, we have to improve the effectiveness of our teaching since, as instructors, we cannot do much about their ability or background.^[17,19-21]

Ineffective teaching can cause some students to drop courses, lose self-confidence after getting bad grades, change majors, or in the worst case, change to another institution or give up college altogether. Negative feedback of this nature can also negatively impact future enrollment in engineering degree programs.

To address this problem, two trial workbook projects have been introduced in two sophomore engineering courses at Virginia Tech: 1) introduction to chemical engineering thermodynamics, and 2) chemical engineering simulations. This study presents a first-hand experience with the preparation, use, and assessment of workbook projects that are integrated

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with class group work and the Internet teaching/learning platform BLACKBOARD.

LEARNING AND TEACHING STYLES

In addition to theory, equations, and words, engineering students are encouraged to work with course material that includes real-world applications, pictures, diagrams, and demonstrations.^[19] An effective teaching technique should engage students actively, stimulate a sense of enquiry, and encourage them to teach one another.^[6-8,14] For example, group work, which is widely used in science and engineering education,^[11,17,20,21] promotes problem-based learning and active participation, which can lead to a deep learning that is more likely to be retained. In group-work activity, two or three students can apply a newly learned concept to solve a short problem or to prepare a short essay.

Learning styles involve verbal or visual input modality, sensing or intuitive perception, active or reflective processing, and sequential or global understanding of course material.^[17] On the other hand, *teaching* styles involve an instructor's emphasis on factual or theoretical information, visual or verbal presentation, active or reflective student participation, and sequential or global perspective. Learning and teaching styles^[17,22,23] are summarized in Table 1. Felder and Silverman^[22] emphasize, however, that these dimensions of learning and teaching styles are neither unique nor comprehensive. Balances in various learning styles vary among stu-

A properly prepared workbook makes the content of a textbook more visible, extractable, and relevant for an application or process. The instructor prepares the workbook with all the essential verbal and visual learning elements by using the designated textbook, reference books, and the publishers' web sites.

dents and depend on the field or their background. For example, a student may be equally sensing and intuitive or one of these learning styles may be dominant.

A student will learn more when teaching is done in his or her preferred style.^[17,24,25] For example, if teaching targets both the visual and verbal learners, there is a good possibility that learning is enhanced for the whole group. Felder and Brent^[17] have suggested that there is a mismatch between learning and teaching styles since most students are visual and sensing learners but 90-95% of the content for most courses is verbal and most instructors are intuitive learners. Such a mismatch must be addressed for teaching to be effective.^[17,22-25]

PREPARING AND WORKING WITH WORKBOOKS

A properly prepared workbook makes the content of a textbook more visible, extractable, and relevant for an application or process. The instructor prepares the workbook with all the essential verbal and visual learning elements by using the designated textbook, reference books, and the publishers' web sites. The verbal elements include all theory and analysis, definitions, synthesis, and related applications. Figure 1 (next page) shows a typical page from a workbook prepared for the thermodynamics course. The visual elements have most of the related graphs, diagrams, schemes, configurations, symbols for process flow diagrams and streams, algorithms, flowcharts, tables, pictures, figures, schematics, plots, analogies, and data. All the predetermined homework assignments come from the textbook and appear with small spaces allocated to each question. The example problems, homework problems, and group work are prepared to relate the verbal and visual elements to each other in an effective way. Most verbal elements are presented with bullets and in categorized boxes. Some of the visual and verbal elements are deliberately left incomplete or missing so the instructor and students can

TABLE 1
Learning and Teaching Styles^[17,22,23]

<i>Learning Styles</i>		<i>Teaching Styles</i>	
Input Modality	<ul style="list-style-type: none"> • <i>Visual learners:</i> Prefer to see graphs, diagrams, flow charts, plots, schematics • <i>Verbal Learners:</i> Prefer explanations (oral or written) 	Presentation	<ul style="list-style-type: none"> • <i>Visual:</i> Graphs, Diagrams • <i>Verbal:</i> Lecture, reading, discussion
Perception	<ul style="list-style-type: none"> • <i>Sensing Learners:</i> Focus on sensory input, practical, observant • <i>Intuitive Learners:</i> Focus on imaginative and conceptual work, theory, and models 	Content	<ul style="list-style-type: none"> • <i>Concrete:</i> Factual • <i>Abstract:</i> Conceptual, theoretical
Processing	<ul style="list-style-type: none"> • <i>Active Learners:</i> Process actively think out loud, and like working in groups • <i>Reflective Learners:</i> Process introspectively, work quietly, like thinking and working alone or in pairs 	Student Participation	<ul style="list-style-type: none"> • <i>Active:</i> Students talk and discuss • <i>Passive:</i> Students watch and listen
Understanding	<ul style="list-style-type: none"> • <i>Sequential Learners:</i> Function in continual steps and steady progress, like analysis • <i>Global Learners:</i> Need whole picture to function, initially slow, like synthesis 	Perspective	<ul style="list-style-type: none"> • <i>Sequential:</i> Step-by-step progression • <i>Global:</i> Context and and relevance

complete them together in the classroom. The quality of a workbook depends on the instructor's experience, the textbook's organization, the level of the course, and feedback from the students.

The instructor delivers the lecture with an overhead projector and transparencies of the workbook pages, joining the verbal and visual elements of teaching. Students are exposed to the workbook pages on the screen while they work on them. Problem solving practices are performed in the blank spaces allocated within the workbook. Before assigning homework questions, they are briefly discussed (see Figure 3).

In the presentation, all the related verbal and visual elements support each other and hence stimulate active student participation, easy understanding, and relating the concepts to applications. Lecturing with the workbook incorporates group work on a newly introduced topic by solving a short problem or preparing short essays. This stimulates teamwork and results in the students teaching one another.^[20,21] In addition to the group work, the BLACKBOARD multi-user education platform is used with the workbook to provide supplemental course material, assignments, useful sites, text objectives, test solutions, announcements, and communications.

THE WORKBOOK TRIALS

Two workbooks were prepared and distributed to the ChE students at Virginia Tech during the first lecture meeting of two fundamental engineering courses. Although it was not applied in this trial, the Felder index of learning styles^[26] or any similar assessment study would be helpful for assessing learning styles of students and for preparing small study groups. Most of the students were sophomores, with small numbers of juniors and seniors in both the courses. The first workbook had 97 pages and was prepared for the textbook *Introduction to Chemical Engineering Thermodynamics*^[27] for the thermodynamics course. Some typical pages completed in the classroom from this workbook can be seen in Figures 2 to 4.

In Figure 2, the names of four thermodynamic potentials are given in separate boxes. In an attached box, the system is also defined as a closed system. All the primary properties of pressure P, volume V, temperature T, internal energy U, and entropy S are related to each other in the boxes. After completion, the boxes serve as visual elements containing the related expressions for a well-defined system. In the textbook, this same information is spread out and may necessitate more time and effort for the students to

Figure 2. A typical thermodynamic-workbook page with completed boxes for explaining the relations for thermodynamic properties and derivations of the Maxwell relations.

Thermodynamic properties of fluids

- Property relations

System	Properties			
	Internal energy	Enthalpy	Helmholtz energy	Gibbs energy
Homogeneous fluid with constant composition (closed system)				

- Maxwell relations

Exact differential equation of a function $F(x,y)$: $dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$

$dU = TdS - PdV$	$dH = TdS + VdP$	$dA = -PdV - SdT$	$dG = VdP - SdT$
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- Enthalpy and entropy as functions of T and P

$H = H(T,P)$ Enthalpy	
$S = S(T,P)$ Entropy	

Figure 1. A typical workbook page for the thermodynamics course.

Thermodynamic properties of fluids

H | A | G

- Property relations

System	Primary Properties P, V, T, U, S			
	Internal energy, U	Enthalpy, H	Helmholtz energy, A	Gibbs energy, G
Homogeneous fluid with constant composition (closed system)	$dU = dQ + dW$ $dU = TdS - PdV$	$dH = TdS + VdP$ $H = U + PV$	$dA = -PdV - SdT$ $A = U - TS$	$dG = VdP - SdT$ $G = H - TS$

- Maxwell relations

Exact differential equation of a function $F(x,y)$: $dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$ Total differential Criterion

Cross relations $\rightarrow \left(\frac{\partial H}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$dU = TdS - PdV$	$dH = TdS + VdP$	$dA = -PdV - SdT$	$dG = VdP - SdT$
$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_U$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_H$	$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_A$	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_G$

- Enthalpy and entropy as functions of T and P: $C_p dT + (1 - \beta T) V dP$

$H = H(T,P)$ Enthalpy	$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$
$S = S(T,P)$ Entropy	$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$

$\left(\frac{\partial H}{\partial T}\right)_P = T \frac{\partial S}{\partial T} + 0 ; \quad = C_p \frac{dT}{T} - \beta V dP$

fully understand it. On the same workbook page, one of the applications from the property relations has been demonstrated through derivations of the Maxwell relations. This associates a new concept with an application. The property relations for enthalpy and entropy are further demonstrated in a categorized way in the boxes.

The first part of Figure 3 relates the key expressions on generalized correlations for liquids to the figure for reduced density taken from the textbook. A short period of time for group work follows this introduction so the students can find the molar volume of ammonia at 310 K. The workbook contains the selected homework problems from the textbook. Before assigning them, they are briefly discussed, with emphasis on the critical points in the allocated boxes for each question. This enables students to start their homework assignments with little or no outside help. Also, they will be able to access the problems in the right location in the workbook when they wish to review the course material and the related problems.

Figure 4 starts with background information on vapor-liquid equilibrium calculations. In the following box, three col-

umns identify the type of calculations, the variables to calculate, and the variables specified for bubble point calculations using the gamma-phi method. The box is related to the block diagram underneath, which indicates how to start, proceed with, and finish the calculations by using Equations 14.8 and 14.10 from the textbook, supplied in the box above. The block diagram and equations are taken from the textbook and provide the necessary connections between the text and the diagram. Therefore students will not be distracted by searching for these equations when learning the block diagram.

The other workbook has 84 pages and was prepared for the textbook *Numerical Methods for Engineers*,^[28] used in the simulation course. Figures 5 and 6 (next page) show some typical pages completed in the classroom from this workbook. In Figure 5, matrix operations are introduced with an emphasis on multiplication of matrices. This concept is explained with a figure using the indices of coefficients matrix and the two vectors for unknowns and constants related to each other with the arrows. Next to that box, the computer code for multiplication is supplied.

Generalized correlation for liquids

- Rackett equation for estimating the molar volumes of saturated liquids

$$V_{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

In terms of the reduced properties $\rho_r = \frac{\rho}{\rho_c} = \frac{V_c}{V}$; $V_2 = V_1 \frac{\rho_1}{\rho_2}$

group work
Find V^L for NH_3 at 310 K

Figure 3.17: Generalized density correlation for liquids.

HW#3: 3.8; 3.32; 3.35; 3.45; 3.53

3.8	Ideal gas: $W = 0$ $T_2 = T_1 \frac{P_2}{P_1}$	
3.32	Calculate Z: vapor-like root $V = 2 \left(\frac{RT}{P} \right)$	
3.35	Use steam tables $V = 124.9 \text{ cm}^3/\text{g}$; $V = 2252 \text{ cm}^3/\text{mol}$	
3.45	mass = $\left(\frac{V_{vap}}{V_t} \right) / MW$ mass = 98.2 kg. MW: 58.123 $\frac{PV}{RT} = 1 + (B' + WB')$	$\frac{P_r}{T_c}$
3.53	Use Fig 3.17 (above); $P_1 = 0.63 \frac{\text{g}}{\text{cm}^3}$ $(P_{r,i}, T_{r,i}) \Rightarrow P_{r,i}$ $P_2 = 0.532 \frac{\text{g}}{\text{cm}^3}$	

Figure 3. A workbook page containing a figure and homework problems to be assigned from the textbook for the thermodynamics course.

VLE calculations $f_i^V = f_i^L \Rightarrow y_i \hat{\phi}_i P = x_i \gamma_i f_i$

- The gamma/phi formulation of VLE calculations

$$y_i \Phi_i P = x_i \gamma_i P_i^{sat} \quad f_i = \phi_i^S P_i^S \exp \left[\frac{V_i^L (P - P_i^S)}{RT} \right]$$

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp \left[-\frac{V_i^L (P - P_i^{sat})}{RT} \right] \approx \frac{\hat{\phi}_i}{\phi_i^S} = \frac{\exp \left[\frac{P}{RT} (B_{ii} + \frac{1}{2} \sum_k y_k (2\delta_{jk} - \delta_{jk})) \right]}{\exp \left(\frac{B_{ii} P_i^S}{RT} \right)}$$

Calculations	Calculate	Given
BUBL P $\sum y_i = 1$	$y_i = \frac{x_i \gamma_i P_i^{sat}}{\Phi_i P}$ (14.8) $P = \sum_i \frac{x_i \gamma_i P_i^{sat}}{\Phi_i}$ (14.10)	x T

```

graph TD
    Start([Read T, xi, constants.  
Set all phi_i = 1.0.  
Evaluate (P_i^sat), (gamma_i).  
Calc. P by Eq. (14.10).]) --> CalcPhi[Calc. (y_i) by Eq. (14.8).  
Evaluate (Phi_i).]
    CalcPhi --> CalcP[Calc. P by Eq. (14.10).]
    CalcP --> Decision{Is delta P < epsilon?}
    Decision -- No --> CalcPhi
    Decision -- Yes --> Print([Print P, (y_i).])
  
```

Figure 14.1: Block diagram for the calculation BUBL P.

- Study Example 14.2

$$\Phi_1 = \exp \left[\frac{B_{11} (P - P_1^S) + P y_2^2 \delta_{12}}{RT} \right]; \quad B_{ii} = \frac{RT_c}{P_c} (B^0 + \omega B^1)$$

$$\Phi_2 = \exp \left[\frac{B_{22} (P - P_2^S) + P y_1^2 \delta_{12}}{RT} \right]; \quad \delta_{12} = 2 B_{12} - B_{11} - B_{22}$$

$$\delta_{ij} = \delta_{ji}; \quad \delta_{ii} = \delta_{jj} = 0$$

$$\Phi_i = \left[B_{ii} (P_i - P_i^S) + \left(\frac{1}{2} \right) P \sum_k y_k (2\delta_{ki} - \delta_{jk}) \right] / RT$$

Figure 4. A typical thermodynamic workbook page on vapor-liquid phase equilibrium calculations completed in the classroom. From the flow chart shown above, the steps of the algorithm of bubble point calculations are discussed in the classroom.

For applying the rule of multiplication, a short group work is carried out first and then linear algebraic equations are represented in matrix form. This form is constructed in a set of two linear algebraic equations, and a 2-by-2 coefficients matrix is created. Following this, the concept of inverse matrix is introduced.

Figure 6 demonstrates the introduction of optimization. Here, the concept of extremum is related to minimum and maximums of a continuous function with some visual elements of figures immediately following. Later, the golden-section search is explained with the dimensions from an old Greek temple.

Some of the anticipated benefits of the workbooks are

- A detailed syllabus is an integrated part of the workbook and helps the students jointly and effectively use the textbook and workbook.
- It provides students with objective and vision statements, main definitions, graphs, diagrams, and data in a more apparent and categorized way than the textbook (see Figures 2 and 3). It presents the course material as a package of verbal and visual elements and helps reach the students with various learning

styles. This leads to effective use of the textbook.

- It makes note-taking easy and provides more time for the students' critical thinking and interactions with the instructor. This enhances deep understanding of the course material.
- It reduces the mismatches among the teaching/ learning styles of the instructor, textbook, and students and increases the visual elements, hence stimulating effective teaching and learning.
- Working on the workbook with the instructor stimulates the students' interest as the instructor and students unfold the missing visual and verbal elements in the right location and moment.
- It provides easy access to definitions, analyses, applications, synthesis, graphs, diagrams, figures, tables, data, and worked and tested examples leading to an effective learning and review of the course material.
- It provides the homework assignments with brief descriptions in boxes to relate them to the concepts of the chapter.

Matrix operating rules

- Addition of two matrices
 $c_{ij} = a_{ij} + b_{ij}$; $d_{ij} = c_{ij} - f_{ij}$
- Multiplication of matrices
 $[0] = g[A] = g a_{ij}$
 $c_{ij} = \sum_{k=1}^m a_{ik} b_{kj}$

Group work
 $\begin{bmatrix} 2 & 1 \\ 0 & 1 \\ 2 & 0 \end{bmatrix} \begin{bmatrix} 3 & 1 \\ 2 & 2 \end{bmatrix} =$

```

SUBROUTINE Mmult (a, b, c, m, n, l)
DO i = 1, n
DO j = 1, l
sum = 0
DO k = 1, m
sum = sum + a(i,k) * b(k,j)
END DO
c(i,j) = sum
END DO
END DO
  
```

$[A]_{n \times m} [B]_{m \times l} = [C]_{n \times l}$

Interior dimensions are equal; multiplication is possible
 Exterior dimensions define the dimensions of the result

Fig. PT3.4 pseudocode to multiply an n by m matrix [A], by and m by l matrix [B]

Group work
 $\begin{bmatrix} 2 & 1 \\ 4 & 2 \end{bmatrix} \begin{bmatrix} 5 & 2 \\ 3 & 3 \end{bmatrix} = \begin{bmatrix} 2 \cdot 5 + 1 \cdot 3 & 2 \cdot 2 + 1 \cdot 3 \\ 4 \cdot 5 + 2 \cdot 3 & 4 \cdot 2 + 2 \cdot 3 \end{bmatrix} = \begin{bmatrix} 13 & 7 \\ 26 & 14 \end{bmatrix}$

- We can represent LAE in matrix form: $[A]\{X\} = \{B\}$ consisting
- Matrix of coefficients $\{X\} = [A]^{-1}\{B\}$
- Vector of constants $[A]^{-1}$: inverse of matrix [A]
- Vector of unknowns

$a_{11}x_1 + a_{12}x_2 = b_1$
 $a_{21}x_1 + a_{22}x_2 = b_2$

$x_2 = -\left(\frac{a_{11}}{a_{12}}\right)x_1 + \frac{b_1}{a_{12}}$
 $x_2 = -\left(\frac{a_{21}}{a_{22}}\right)x_1 + \frac{b_2}{a_{22}}$
 $x_2 = (\text{slope})x_1 + \text{intercept}$

$[A]^{-1} = \frac{\begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix}}{D}$

Figure 5. A completed page on the matrix operations from the workbook for the simulation course.

Optimization (One-dimensional unconstrained optimization)

- Optimization involves finding a value of x that yields an extremum, either a maximum or minimum of a function f(x)

$f'(x) = 0$
 $f''(x) < 0$ max
 $f''(x) > 0$ min

Global maximum, Local maximum, Global minimum, Local minimum

- Golden-section search: general-purpose, single variable optimization technique

Conditions: $l_0 = l_1 + l_2$
 $\frac{l_1}{l_0} = \frac{l_2}{l_1}$
 Combination of these
 $\frac{l_1}{l_1 + l_2} = \frac{l_2}{l_1}$
 or $1 + R = \frac{1}{R}$; $R = \frac{l_2}{l_1}$
 or $R^2 + R - 1 = 0$
 $R = \frac{-1 + \sqrt{5}}{2} = 0.61803$
 This is "golden ratio"
 It allows optima to be found efficiently
 Fibonacci number
 0, 1, 1, 2, 3, 5, 8, 13, 21, 34

Old Greek temple

Figure 6. A completed page for optimization in the workbook for the simulation course.

ASSESSMENT OF THE WORKBOOKS

Proper assessment of the workbooks is essential for measuring their true level of effectiveness and developing the best procedure for a particular course. Therefore, a workbook will gain a level of maturity only after it is tried with an assessment study. It is the author's intention to seek, through a research proposal, a true assessment study from professional organizations such as the Center for Excellence in Undergraduate Teaching and the Center for Survey Research at Virginia Tech. Only after such an assessment study will the true effectiveness of workbook methodology be known.

Table 2 displays a preliminary questionnaire prepared by the author, along with responses in percentages for the thermodynamic and simulations courses carried out after twelve weeks with the workbooks. All the questions are treated with the same weight. For the thermodynamics course, 47 students

responded and for the simulations course, 31 students responded.

The following responses deserve reviewing:

- Around 94% of students agree or tend to agree that the workbook enhances problem-based learning, subject-specific skills, and deep understanding
- Around 90% of them agree or tend to agree that the workbook reduces mismatches between learning and teaching styles and offers a balanced teaching for various learning styles
- Around 85% of the students agree or tend to agree that the workbook stimulates active learning and group work
- Around 95% of the students agree or tend to agree that overall, the workbook is beneficial in effective learning

Only 36% from the thermodynamics and 20% from the simulation class disagree or tend to disagree that the workbook does not replace the textbook.

Some examples of written comments on the questionnaire are:

• I do not have any suggestions but I think the workbook is an excellent idea. It helps a great deal in truncating and stating all the information in each chapter.

• One way I think the workbook may be improved is to carry examples not included in the book. This would provide examples in addition to other problems given in the book. Many times I have already done book examples by the time we get to them in class.

• Sometimes space becomes too small or notes become a little confusing; attendance still seems the student responsibility. Overall, I believe the workbook is a great learning tool!

• I do not have suggestions because I highly approve of the use of workbook. It gives the students time to reflect on what is going on in the class instead of just blindly copying down notes. I encourage all teachers to adopt the workbook, which causes positive interactions between student and teacher.

• Workbook allows instructor to go over topics very quickly because notes are already in front of you. I think it would be more useful to go over each concept in detail and make sure every-

TABLE 2
Preliminary Questionnaire for Assessment of the Workbooks (WB)
1-disagree; 2-tend to disagree; 3-tend to agree; 4-agree; 5-not applicable

	Thermodynamics %					Simulations %				
	1	2	3	4	5	1	2	3	4	5
1 You have used WB in previous courses	75	10	2	0	13	58	13	3	10	16
2 WB contains a detailed syllabus	0	0	17	81	2	0	3	20	74	3
3 WB contains subject schedule from the textbook	0	4	13	77	6	0	6	23	71	0
4 WB provides objective, mission, and vision statements	0	0	23	73	4	0	6	19	75	0
5 WB provides related chapter and section readings	0	13	36	49	2	0	13	39	48	0
6 WB provides subject-related examples and homework problems	0	2	0	96	2	0	0	6	94	0
7 WB provides concepts, definitions, and working equations	0	2	19	79	0	0	0	23	77	0
8 WB enhances problem-based learning	0	4	23	71	2	0	3	45	52	0
9 WB enhances subject-specific skills and deep understanding	0	4	43	51	2	0	6	52	42	0
10 WB enhances problem-solving skills	0	17	36	45	2	0	6	35	59	0
11 WB makes it easy to locate subjects, definitions, and applications	0	4	30	64	2	0	0	42	58	0
12 WB relates a subject to data, tables, diagrams and figures	0	0	13	85	2	0	0	19	81	0
13 WB facilitates easy course note-taking	0	2	11	85	2	0	6	9	85	0
14 WB facilitates effective review of subjects and related problems	0	0	30	68	2	0	0	34	66	0
15 WB reduces mismatches between learning and teaching styles	2	4	51	39	4	0	13	26	61	0
16 WB reduces mismatches between textbook and instructor styles	0	2	47	49	2	0	6	32	62	0
17 WB offers a balanced teaching for various learning styles	0	6	45	45	4	0	6	32	62	0
18 WB encourages regular attendance	6	9	36	45	4	3	3	32	62	0
19 WB stimulates active learning	4	6	45	43	2	3	13	42	42	0
20 WB stimulates group work	0	9	42	49	0	0	9	35	56	0
21 WB facilitates higher grades from the tests	0	13	34	49	4	0	3	49	42	6
22 WB facilitates higher grades from the assignments	0	0	19	77	4	0	0	35	65	0
23 WB does not replace the textbook	4	32	19	45	0	0	20	33	47	0
24 WB stimulates effective use of the textbook	4	11	40	43	2	0	6	35	59	0
25 With group work and blackboard, WB becomes more effective	2	11	47	36	4	0	3	32	65	0
26 Overall, WB is beneficial in effective learning	2	0	26	68	4	0	3	16	81	0

one understands. The workbook also closely mirrors the book. If you don't understand the book, you probably will not understand the workbook.

- I really like the workbook. It makes the information a lot more clear and cuts out all the messy derivations and extraneous information, so we can understand the concepts then go back to look at it.

- The workbook is a good idea and an excellent study tool.

- The workbook is amazing! It condenses textbook into more meaningful and useful notes; makes more difficult concepts easier to understand. You can tell instructor cares about the student learning and appreciation of the subject matter. Needs no improvements, love the workbook!

- I really like the workbook. It helps me greatly in the course and I wish more teachers would use it. I understand more and have learned a lot.

- Workbook helps keep me organized, and allows me to pay attention in class and actively interact with what is going on. It motivates learning, reviewing and comprehension. I wish workbook would be used in all of my classes.

CONCLUSIONS

Preparation of the workbook, using it along with the group-work activity and BLACKBOARD, and a preliminary assessment study have been presented here. The assessment study indicates that the workbook methodology may be an effective strategy in learning and teaching. Most of the engineering students who took the courses in thermodynamics and simulation have found the workbooks beneficial in undergraduate engineering teaching. This is mainly because the workbooks, integrated with group work and BLACKBOARD, may help reduce the mismatches in teaching and learning styles, and may increase interactions between students and faculty, hence stimulating active and collaborative learning and effective teaching. The workbook trials need a true and coordinated assessment study, however, in order to measure their level of effectiveness in reducing the mismatches between learning and teaching styles.

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Note: Electronic sample copies of workbooks for the courses on thermodynamics and simulations are available in PDF format upon request to the author at ydemirel@vt.edu.

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