



Chemical Engineering Division, American Society for Engineering Education

American Institute of Chemical Engineers



AIChE CENTENNIAL CELEBRATION

Creative Learning in a Microdevice Research-Inspired Elective Course for Undergraduate and Graduate Students (p. 189)

Minerick

Feature Articles . . .

- Ehrenfest's Lottery — Time and Entropy Maximization (p. 229) Ashbaugh
A Graphical Representation for the Fugacity of a Pure Substance (p. 208) Book, Sitton
Teaching Tip: Approaches to Academic Integrity: Confessions of a Reluctant Expert (inside front cover) Bullard
Polymerization Simulator for Introductory Polymer and Material Science Courses (p. 222) Chirdon
Using Aspen to Teach Chromatographic Bioprocessing: A Case Study in Weak Partitioning Chromatography for Biotechnology Applications (p. 198) Evans, Huang, Cramer
Random Thoughts: The Link Between Research and Teaching 2. How to Strengthen Each Without Weakening the Other (p. 213) Felder
YouTube Fridays: Engaging the Net Generation in 5 Minutes a Week (p. 215) Liberatore
Gas Pressure-Drop Experiment (p. 183) Luyben, Tuzla
Vapor-Liquid Equilibria Using the Gibbs Energy and the Common Tangent Plane Criterion (p. 236) Olaya, Reyes-Labarta, Serrano, Marcilla
Book Review: Heat Transfer by Gregory Nellis and Sanford Klein (inside back cover) Reviewed by Kemal Tuzla

and ChE at . . .

The University of North Dakota

This one-page column will present practical teaching tips in sufficient detail that ChE educators can adopt the tip. The focus should be on the teaching method, not content. With no tables or figures the column should be approximately 500 words. If graphics are included, the length needs to be reduced. Tips that are too long will be edited to fit on one page. Please submit a Word file to Phil Wankat <wankat@ecn.purdue.edu>, subject: CEE Teaching Tip.

## APPROACHES TO ACADEMIC INTEGRITY: Confessions of a Reluctant Expert

LISA G. BULLARD

*North Carolina State University*

In an increasingly competitive job market, students view high course grades as critical to achieving their post-graduation goals (a view that is often justified), and this attitude drives some to cheat. For faculty, the challenges are to create an environment that minimizes the likelihood of cheating, to detect cheating when it occurs, and to deal firmly but fairly with those who choose to cheat. This Teaching Tip suggests some specific tools to accomplish these goals:

- **Communication:** Clearly communicate your expectations regarding academic integrity to your students, both in the syllabus and on the first day of class. Students benefit from clear examples of acceptable and unacceptable behaviors. Adam Melvin and I developed a short skit of examples, which later became a series of short videos (<[http://www.che.ncsu.edu/bullard/Academic\\_integrity.htm](http://www.che.ncsu.edu/bullard/Academic_integrity.htm)>).
- **Collaboration:** Collaboration is desirable, as long as it remains within the boundaries established by the instructor. Encourage students to help each other within your boundaries. Grading on an absolute scale instead of a curve encourages students to help classmates legally, promoting a more collegial environment. Clearly and carefully define expectations for acceptable and unacceptable behavior regarding collaboration on individual assignments. Is it OK for students to consult homework or exams from a previous semester? To check each other's final answers? To work together closely as long as they submit their own work? Examples of specific syllabus language are shown at <[http://www.che.ncsu.edu/bullard/Academic\\_integrity.htm](http://www.che.ncsu.edu/bullard/Academic_integrity.htm)>.
- **Homework:** Some instructors weight homework as a small percentage of the class grade to minimize cheating on individual assignments; others allow students to work collaboratively as long as the contributing members' names are listed on the assignment. Choose a strategy based on students' maturity, course objectives, and the importance of completing the homework to learn the material.
- **Reflection:** Especially when teaching the first ChE course, assign the students to write a reflective essay on academic integrity early in the semester to reinforce your expecta-

tions and ensure that they have a clear understanding of acceptable and unacceptable behavior. An example of this type of assignment is shown at <[http://www.che.ncsu.edu/bullard/Academic\\_Integrity/Reflection.htm](http://www.che.ncsu.edu/bullard/Academic_Integrity/Reflection.htm)>. Doing this not only educates students about your expectations but begins to create and foster a departmental culture of integrity.

- **Troublesome Websites:** There are websites (e.g. <<http://www.coursehero.com/>>) where students are either charged a fee to access course materials and solutions to textbook problems or asked to upload such content in order to access other students' content. Other websites post solutions that can be accessed for free. To address these issues, our faculty have responded by asking students in all of our classes to sign a form, "Restriction on sharing content of course material with third parties," <[http://www.che.ncsu.edu/bullard/Academic\\_Integrity/Content.pdf](http://www.che.ncsu.edu/bullard/Academic_Integrity/Content.pdf)> which emphasizes that uploading or downloading course materials without permission is illegal, and those who do it are subject to substantial penalties.

These strategies make a difference. In the three years since I've implemented them in a large class, cheating cases have dropped by an encouraging 28%. The video, the syllabus, and the reflection assignments containing concrete examples of appropriate and inappropriate behaviors have cleared up much of the previous ambiguity in academic misconduct policies.

Unfortunately, no precautions or strategies will ever totally eliminate cheating. Some students, even with heightened awareness, are willing to take the risk in order to get a better grade. The best we can do is to minimize the incidence of cheating and to impose meaningful consequences when it occurs, but it is critically important to do that. Our responsibility as faculty members is not just to teach course content but to prepare our students for their professional careers. Dealing with cheating effectively in college will make its occurrence less likely after graduation, when the potential consequences of integrity violations are much more severe.

**EDITORIAL AND BUSINESS ADDRESS:**

*Chemical Engineering Education*  
Department of Chemical Engineering  
University of Florida • Gainesville, FL 32611  
PHONE and FAX : 352-392-0861  
e-mail: [cee@che.ufl.edu](mailto:cee@che.ufl.edu)

**EDITOR**

*Tim Anderson*

**ASSOCIATE EDITOR**

*Phillip C. Wankat*

**MANAGING EDITOR**

*Lynn Heasley*

**PROBLEM EDITOR**

*Daina Briedis, Michigan State*

**LEARNING IN INDUSTRY EDITOR**

*William J. Koros, Georgia Institute of Technology*

**PUBLICATIONS BOARD****• CHAIRMAN •**

*John P. O'Connell*  
*University of Virginia*

**• VICE CHAIRMAN •**

*C. Stewart Slater*  
*Rowan University*

**• MEMBERS •**

*Lisa Bullard*

*North Carolina State*

*Jennifer Curtis*

*University of Florida*

*Rob Davis*

*University of Colorado*

*Pablo Debenedetti*

*Princeton University*

*Dianne Dorland*

*Rowan*

*Stephanie Farrell*

*Rowan University*

*Jim Henry*

*University of Tennessee, Chattanooga*

*Jason Keith*

*Michigan Technological University*

*Suzanne Kresta*

*University of Alberta*

*Steve LeBlanc*

*University of Toledo*

*Ron Miller*

*Colorado School of Mines*

*Lorenzo Saliceti*

*University of Puerto Rico*

*Stan Sandler*

*University of Delaware*

*Margot Vigeant*

*Bucknell University*

# Chemical Engineering Education

**Volume 44****Number 3****Summer 2010****► DEPARTMENT**

174 Chemical Engineering at the University of North Dakota

**► CLASSROOM**

183 Gas Pressure-Drop Experiment

*William L. Luyben, Kemal Tuzla*

208 A Graphical Representation for the Fugacity of a Pure Substance

*Neil L. Book and Oliver C. Sitton*

215 YouTube Fridays: Engaging the Net Generation in 5 Minutes a Week

*Matthew W. Liberatore*

222 Polymerization Simulator for Introductory Polymer and Material Science Courses

*William M. Chirdon*

**► RANDOM THOUGHTS**

213 The Link Between Research and Teaching 2. How to Strengthen Each Without Weakening the Other

*Richard Felder*

**► AIChE SPECIAL SECTION**

189 Creative Learning in a Microdevice Research-Inspired Elective Course for Undergraduate and Graduate Students

*Adrienne R. Minerick*

**► CURRICULUM**

229 Ehrenfest's Lottery — Time and Entropy Maximization

*Henry S. Ashbaugh*

198 Using Aspen to Teach Chromatographic Bioprocessing: A Case Study in Weak Partitioning Chromatography for Biotechnology Applications

*Steven T. Evans, Xinqun Huang, and Steven M. Cramer*

236 Vapor-Liquid Equilibria Using the Gibbs Energy and the Common Tangent Plane Criterion

*María del Mar Olaya, Juan A. Reyes-Labarta, María Dolores Serrano, Antonio Marcilla*

**► TEACHING TIP**

inside front cover Approaches to Academic Integrity: Confessions of a Reluctant Expert

*Lisa G. Bullard*

**► BOOK REVIEW**

inside back cover *Heat Transfer* by Gregory Nellis and Sanford Klein

*Reviewed by Kemal Tuzla*

CHEMICAL ENGINEERING EDUCATION (ISSN 0009-2479) is published quarterly by the Chemical Engineering Division, American Society for Engineering Education, and is edited at the University of Florida. Correspondence regarding editorial matter, circulation, and changes of address should be sent to CEE, Chemical Engineering Department, University of Florida, Gainesville, FL 32611-6005. Copyright © 2010 by the Chemical Engineering Division, American Society for Engineering Education. The statements and opinions expressed in this periodical are those of the writers and not necessarily those of the ChE Division, ASEE, which body assumes no responsibility for them. Defective copies replaced if notified within 120 days of publication. Write for information on subscription costs and for back copy costs and availability. POSTMASTER: Send address changes to Chemical Engineering Education, Chemical Engineering Department, University of Florida, Gainesville, FL 32611-6005. Periodicals Postage Paid at Gainesville, Florida, and additional post offices (USPS 101900).

## Chemical Engineering at . . .

# The University of North Dakota

Founded by the Dakota Territorial Assembly in 1883—six years before statehood—the University of North Dakota (UND) has remained a university with a strong liberal arts foundation surrounded by a variety of professional and specialized programs. UND is one of only 47 public universities in the nation with accredited graduate schools of both law and medicine, and is regarded as a national leader in rural and family health issues, aerospace, energy and environmental research, and educational programs for American Indians. Recognized for its extensive programming for native peoples, UND has more than 30 academic programs for American Indians. For example, 20% of American Indian doctors in the country were trained at UND through the Indians Into Medicine program (INMED).

The university's 292 tenured and 207 tenure-track faculty mentor more than 13,000 on-campus students and 21,000 distance-education and continuing-enrollment students in 193 fields of study from baccalaureate through doctoral and professional degrees. Fifty-one percent come from North Dakota; the rest represent all other states, seven Canadian provinces, and more than 50 other countries. UND is located in Grand Forks, a college town of 50,000 on the Red River of the North separating North Dakota and Minnesota. The campus includes 223 buildings (5.33 million square feet under roof) on 549 acres.

### THE COLLEGE

Engineering programs began at UND in 1889 and the School of Engineering and Mines (SEM) was formed in 1916. SEM faculty instruct more than 1,000 students through programs administered by the departments of Chemical Engineering, Civil Engineering, Electrical Engineering, Geology



*Harrington Hall is home to the ChE department's offices and laboratories.*

and Geological Engineering, and Mechanical Engineering. Bachelor's and master's degrees are offered in chemical, civil, electrical, geological, and mechanical engineering, as well as in geology. Additional graduate degrees include master's degrees in environmental engineering and sustainable energy engineering plus doctorates in engineering (with specialty tracks), chemical engineering, and geology. SEM further provides its ABET-accredited engineering programs via distance education to industry and individuals through a Distance Engineering Degree Program (DEDP).

### THE DEPARTMENT'S HISTORY

The Department of Chemical Engineering was established in 1926 and the first degree, an M.S.ChE, was awarded in 1928. The department has a five-year average undergraduate enrollment of 92 resident and 21 distance undergraduates per year with a Fall 2009 enrollment count of 122 and 35 resident and distance undergraduates, respectively. The graduate-student population grew substantially in the mid-2000s

to a current stable size of around 35 per year. See Table 1 for historical highlights.

Transfer students are a significant portion of our students—around 10%. We encourage this source of students by providing customized programs of study for transfer students that are shared with guidance counselors and chemistry professors at the community and four-year colleges in our region. We have also assisted regional two-year colleges in establishing pre-ChE programs. The key is our willingness to provide access to our introductory freshman course (ChE 102) and our sophomore fundamentals course (ChE 201) using distance techniques. This allows two-year transfers to enter into our junior-year curriculum. Formal agreements have been or are being put into place to establish formal Pre-Chemical Engineering programs at Minot State University (ND), Itasca Community College (MN), Hibbing Community College (MN), Minnesota State Moorhead, North Dakota State College of Science, Turtle Mountain Community College (a North Dakota tribal college), and Benedictine College (KS).

## OUR MISSION STATEMENT

It is our vision to offer an unsurpassed, personal, undergraduate chemical engineering education, coupled with a top-tier-quality, research-centered graduate program. The department's primary objective is the education of undergraduate students so that, upon graduation, they are prepared to take responsible, entry-level positions in a wide range of industries. Research and professional activities by members of the faculty, conducted in collaboration with graduate and undergraduate students, provide training for our students on how to succeed as researchers.

## EDUCATIONAL OBJECTIVES

The Chemical Engineering program prepares graduates who, in their professional careers:

1. Have the knowledge and skills required to analyze and solve problems related to the field of chemical engineering and communicate these results in verbal and written form to a diverse audience.

**TABLE 1**  
**The University of North Dakota Chemical Engineering Department – Historical Highlights**

1889	College of Mines and College of Electrical and Mechanical Engineering founded
1916	School of Engineering and Mines formed from merger of the colleges of Mines and Electrical/Mechanical Engineering
1926	Initiation of Chemical Engineering Program at UND
1928	First Degree: Master's of Science in Chemical Engineering
1939	Program with four faculty accredited by the Engineer's Council for Professional Development
1942	Program loses accreditation due to faculty loss brought on by demands of WWII
1946	Program reaccredited with new faculty
1948	ChE moves into brand new building—Harrington Hall
1949	First doctoral degree: Fuel Technology; Charles R. Robertson Lignite Research Laboratory established
1972	Tom Owens receives the 1972 Dow Outstanding Young Faculty Award
1973	Project Lignite sponsored by the U.S. Office of Coal Research; UND Departmental Award for Excellence in Research
1982	Robertson laboratory ownership transferred from federal government to UND and renamed the Energy and Mineral Research Center
1989	Energy and Mineral Research Center merged with Mining and Mineral Resources Institute within the School of Engineering and Mines, and renamed the Energy and Environmental Research Center
1991	New doctoral degree: Energy Engineering; faculty size at five tenure/tenure-track positions
1992	UND Departmental Award for Excellence in Teaching
1993	UND Outstanding Faculty Development Award
1997	Major spring flood devastates Grand Forks and closes UND, final month of semester cancelled; extensive damage was sustained by UND buildings
2000	Tom Owens named North Dakota Teacher of the Year
2005	UND Departmental Award for Excellence in Research; John Erjavec receives UND's Award for Individual Faculty Excellence in Teaching; DOE EPSCoR IIP Award allows addition of sixth tenure/tenure-track faculty member
2006	Darrin Muggli receives UND's Award for Individual Faculty Excellence in Teaching; Michael Mann receives UND's Award for Individual Excellence in Research
2007	UND Departmental Award for Excellence in Teaching; Wayne Seames receives UND's Award for Individual Excellence in Research; research funding level allows the addition of non-tenured faculty member
2008	NSF EPSCoR RII award allows addition of seventh tenure/tenure-track faculty member
2009	Research funding level allows the addition of second non-tenured faculty member

2. Can succeed in entry-level positions in the chemical process and broadly related industries, and demonstrate integrity, responsibility, ownership, and accountability for their work.
3. Have a thorough grounding in fundamentals, allowing them to obtain advanced degrees in chemical engineering or to pursue other professional interests such as medicine or law.
4. Have the teamwork, leadership, and lifelong-learning skills that prepare them for future professional growth in a broad spectrum of careers.
5. Understand the role of chemical engineering as a profession and their role in addressing societal issues, including sustainability, environmental responsibility, and safety.

The program educational objectives and the departmental mission have remained largely unchanged over the past decade. They were developed and have been reaffirmed during that time by involving the departmental students, staff, alumni, key employers, and faculty in a variety of ways—many of them informal.

Alumni are invited to share their perspectives regarding the educational program offered by the department. As a part of our assessment process, we directly contact graduates from the program that have been out of the program for one and three years. Our annual newsletter ([http://www.und.edu/dept/sem/che/pdfs/ChE\\_2009Newsletter.pdf](http://www.und.edu/dept/sem/che/pdfs/ChE_2009Newsletter.pdf)) is our primary method of corresponding with the collective group. Formal processes to canvass employers of our graduates/alumni have been implemented, and we have maintained contact with companies who have traditionally hired our graduates. Alumni from the program frequently relay opportunities for permanent positions, as well as summer and co-operative education positions.

An Alumni/Industrial Advisory Committee has been in place since the early 1980s. The group meets every other year on campus with the departmental faculty. Participants are chosen to represent a range of ages, industries, and terminal degrees and typically include a member from a research-extensive university that is not a graduate of our program. The agendas for the alumni meetings normally include an update of department activities, a review of educational objectives and program-assessment activities, and a recap of proposed changes in the academic program. Those changes may include anything from evolutionary changes in courses to more significant curriculum modifications. We value the perspectives of our alumni advisory committee and have incorporated changes resulting from discussions with them.

Involving students in the process of developing program objectives and in the evolution of courses and degree requirements has been done for more than 30 years. The modest size of the program, both in numbers of students and faculty members, makes it possible to gather opinions of students throughout their studies and upon graduation and gather opinions of graduates as they pursue their various professional careers.

The Chemical Engineering Department performs a full assessment of our programs every year during a retreat. Although this represents a significant time commitment from the faculty, we feel that the benefits warrant the time invested. We use a formal plan that was developed in 1997 and continually updated based on input at our annual assessment meetings. As a part of this retreat, every fact of the program is reviewed. These two- to three-day sessions are used to explore all aspects of the program, to analyze and synthesize data collected during the past year, to evaluate the appropriateness of our objectives, to assess how our program is meeting these objectives, and to identify changes that are needed to ensure we continue to keep our program current based on the needs of our constituents. Material collected from our entire constituency base is used as a part of this evaluation. Major changes to the program are brought before the Alumni/Industrial Advisory Committee for feedback before implementation.

## THE UNDERGRADUATE CURRICULUM

The curriculum is designed as a four-year, 133-hour chemical engineering program that provides exposure to the full breadth of the field. The entire undergraduate experience serves to prepare students for professional success. Classroom training includes an essential-studies component, basic mathematics and science, engineering topics, engineering design, and hands-on laboratories. Research opportunities and co-op or intern employment provide a valuable supplement to the classroom, and all students are encouraged to pursue these opportunities. In addition, teamwork and leadership are best learned by doing, and our curriculum stresses the use of teams in the classroom, in the laboratory, and in homework and project assignments across the curriculum. Students can use both their advanced science and technical electives to build expertise in a selected area. The current curriculum is shown in Table 2.

**Capstone Design.** ChE 412 is our capstone design course. Faculty-selected student teams of three to four members choose a project and develop an implementation plan for their semester's work activities. Each team is assigned a faculty technical advisor who assists the primary course instructor in helping student groups on a one-on-one basis. A full scoping study is prepared that includes at least two fundamentally different process alternatives. The scoping study report includes a budget brief, process description, an I/O diagram, block flow diagrams, process flow diagrams, a preliminary schedule, a preliminary cost estimate, a manufacturing cost estimate, an economic assessment, plus an environmental and safety impact statement. Upon completion of this report, students work on selected portions of the conceptual design including piping and instrument diagrams, plot plans, utility flow diagrams, instrument schedules, piping schedules, equipment specification sheets, and a description of the plant's automation system. Intermediate deliverables include technical review meetings. At

least two faculty members read each intermediate deliverable and participate in the technical review meetings.

The final deliverable is a formal presentation to a panel of the entire faculty, each of whom represents a different job function on a capital project review team (management, finance, process specialist, EHS specialist, etc.). Our senior design projects include multiple-variable constraints and are often performed with industrial partners/mentors. Others are theme-sponsored projects from foundations or governmental agencies. Recent examples include vegetable oil extraction and purification plants (*e.g.*, corn, canola, soybean, cotton), coal gasification with carbon capture, activated carbon from coal, methanol from syngas, renewable diesel from algae for a mission to Mars, and magnesium from seawater.

Faculty participation in the capstone design course provides each faculty member with valuable feedback concerning the assimilation and retention of the key concepts from each of the core recitation courses in the curriculum. We use this feedback to improve our teaching effectiveness in these foundation courses. For example, we found that students were not easily and fluently able to perform complicated mass balances, even though these were covered extensively during the sophomore year. In response we began adding mass-balance problems to various homework sets throughout the curriculum to reinforce the techniques learned earlier. As a result, student performance generating mass balances during the capstone design courses improved significantly. This level of faculty participation also stresses to our students the importance we place on the design component of the curriculum and on the capstone design experience in particular.

**The Laboratory Sequence.** A core value in our undergraduate program is the importance of laboratories to produce a graduate with hands-on experience. In addition to the required labs in chemistry and physics, students must take a four-semester sequence in the department. The early labs are focused on the development of good laboratory techniques, to reinforce fundamental principles, and to introduce software tools. The nature of the experimental problems gradually grows in complexity and rigor as students progress through the sequence. Upper-level labs introduce students to the use of the lab to answer research-based questions and how to use published journal articles as the basis of setting up experiments to answer specific questions. In the final lab, students confront open-ended, vague problem statements where the experiments in the laboratory serve as data-gathering tools used in problem solving. Students determine how to use the laboratory apparatus to generate the data and determine the number of replicate sample sets they need to validate their results statistically. The use of computer tools is incorporated to demonstrate the importance of combining experimental results with simulation.

All laboratory classes are supervised by faculty. We also utilize these labs as a tool to integrate a variety of skills into one experience. It is our philosophy that outside of cooperative education and internships, the laboratory classes, if structured properly, provide the best opportunity to expose students to the set of skills that are best obtained through experiential learning. Therefore, rather than having our laboratory classes focused only on reinforcing chemical engineering principles, we embed a variety of other learning goals. To accomplish

<b>TABLE 2</b>					
<b>The University of North Dakota Chemical Engineering Curriculum</b>					
<b>First Year</b>					
Math 165	Calculus I	4	ChE 102	Intro to ChE	2
Chem 221	Chemistry I	3	Math 166	Calculus II	4
Chem 221L	Chemistry Lab I	1	Chem 222	Chemistry II	3
Engl 110	College Comp I	3	Chem 222L	Chemistry Lab II	1
Arts & Humanities Elective		3	Phys 251	University Physics I	4
Social Sciences Elective		3	Arts & Humanities Elective		3
		<b>17</b>			<b>17</b>
<b>Sophomore Year</b>					
ChE 201	ChE Fundamentals	3	ChE 206	Unit Operations	3
Math 265	Calculus III	4	ChE 232	ChE Lab I	2
Phys 252	Physics II	4	ChE 315	Statistics & Numerical Methods	3
Engr 201	Statics	3	Math 266	Differential Equations	3
Engl 125	Technical & Business Writing	3	Chem 240	Survey of Organic Chemistry	4
		<b>17</b>	Chem 240L	Survey Organic Lab	1
					<b>16</b>
<b>Junior Year</b>					
ChE 301	Transport Phenomena	4	ChE 332	ChE Lab III	2
ChE 331	ChE Lab II	2	ChE 305	Separations	3
ChE 303	ChE Thermodynamics	4	ChE 321	ChE Reactor Design	3
EE 206	Circuit Analysis	3	ChE 340	Professional Integrity	3
Technical Elective II		3	Business/Entrepreneurship Elective		3
		<b>16</b>	Technical Elective I		3
					<b>17</b>
<b>Senior Year</b>					
ChE 408	Process Dynamics & Control	3	ChE 412	Plant Design II	5
ChE 431	ChE Lab IV	3	Arts & Humanities Elective		3
ChE 411	Plant Design I	4	Social Sciences Elective		3
Chem 465	Physical Chemistry II	3	EngSci Elective		3
Advanced Chemical Science Elective		3	Advanced Chemical Science Elective		3
		<b>16</b>			<b>17</b>

these goals we have formally mapped course content with each specific lab. This was done to ensure that the content of each of the labs was consistent with the educational objectives of the department and independent of the faculty teaching the course. The current listing is shown in Table 3.

## DISTANCE EDUCATION

Since 1989, UND has offered its ABET-accredited bachelor's degree program in chemical engineering using a distance delivery program concurrent with our local courses. Designed for working adults who are unable to complete a full-time, on-campus program, the distance program uses the same curriculum as the on-campus program.

Courses are offered asynchronously, which provides great flexibility in accommodating student schedules. As core courses are taught for on-campus learning, they are captured digitally and made available through the Blackboard learning environment, usually within two hours of class completion. This allows students to watch recorded classroom lectures, access course materials, submit assignments, and take tests at the time of day and place of their choice within a time window for each assignment.

The four-lab sequence is consolidated into three two-week, on-campus intensive lab experiences taken over the course of three summers. This provides important face-to-face contact between faculty and students and between students within the same peer group (facilitating group work throughout the curriculum). We also allow local students to participate in these summer labs, which provides useful and exciting synergies between on-campus and distance students.

UND provides extensive student support services, such as online tutoring, library access, tech support, and advising services to ensure that the students can easily and readily access the resources they need for success. In 2004, UND received the WOW Award given by the Western Cooperative for Educational Telecommunications for being on the cutting edge of using technology for distance engineering degree programs.

Distance students are held to the same high standards of excellence as on-campus students. Participants have come from all over North America. We even had one student complete a significant portion of the program while working on an offshore oil platform! Most work in process-related jobs that motivated their interest in a chemical engineering degree but at least one student was a stay-at-home mother of two.

**TABLE 3**  
Mapping of Learning Goals to Laboratory Sequence

Content Area	Lab I	Lab II	Lab III	Lab IV
ChE Principles	mass balances energy balances intro thermodynamics ChE principles	fluid flow heat transfer mass & energy balances intro transport phenomena	separations transport phenomena thermodynamics kinetics	process dynamics process control reactor design separations design
Statistics	mean range significance standard deviation	confidence intervals hypothesis test linear regression	propagation of error simple DOE simple ANOVA linearization residual analysis	nonlinear analysis sources of error response surface method DOE
Data Analysis	data → information identify trends in data	explain trends error analysis (qual/quant) sources of error	empirical modeling error budgets causes of data reasonableness	significance of results factors affecting data fuzzy quantification error testing
Writing	basic writing skills tables figures technical report content	style technical clarity writing instruments editing & revisions	drawings levels of detail audience additional instruments	capstone synthesis standards of excellence
Oral Communication	basic presentation skills content of presentation	style, delivery, clarity methodology of formal talks	informal presentations cohesiveness engagement	impact conclusions recommendations meetings
Teamwork	basic principles of groups team roles manage, coordinate time	group analysis methods priority setting	conflict resolution collaboration, compromise accountability	negotiations
Integrity	plagiarism referencing	manipulation of data presentation of data	doing your share accountability	
Professionalism	levels of attire	working with support personnel	communication etiquette	independence standards of excellence
Safety	formal lab safety training basic lab safety	formal lab safety training safety concerns in reports MSDS	formal lab safety training MSDS PHAs	formal lab safety training operational safety

We recognize the time commitments and family sacrifices that are necessary for these nontraditional students to complete this program (including their summer vacations for three years!). Faculty try to be accommodating with work conflicts and assignment due dates while still moving students toward course and program completion. Faculty and staff try to provide at least the same level of personal attention and accessibility to distance students as to on-campus students. This may involve online dedicated problem solving or review sessions to ensure that distance students can participate in engagement learning methods similar to on-campus students.

## ACCOMPLISHMENTS AND AWARDS

The current faculty members are proud to have maintained the department's long tradition of providing the highest quality education available to undergraduate students in chemical engineering. Annual analysis of data from our assessment

instruments (undergraduate, alumni, and employer surveys; performance on standardized tests; etc.) shows that we are meeting and usually exceeding all of our educational objectives. Our department is accredited by ABET, with our most recent accreditation visit in Fall 2009. The faculty is dedicated to excellence in teaching, and the atmosphere in the department is especially conducive to learning.

- *The department was recognized with UND's 1992 and 2007 Departmental Awards for Excellence in Teaching.*
- *Dr. Tom Owens, then professor and chair (now professor emeritus) received the 1972 Dow Outstanding Young Faculty Award and the 1993 UND Outstanding Faculty Development Award, and was named the state of North Dakota's Educator of the Year in 2000.*
- *Dr. John Erjavec, then associate professor (now professor emeritus) received UND's 2005 Award for Individual Faculty Excellence in Teaching.*

## *The Current Faculty in the University of North Dakota Chemical Engineering Department*



**Michael Mann** (distinguished professor, chair). Research interests: Performance issues in advanced energy systems firing coal and biomass, emission control; renewable and sustainable energy systems; development of energy strategies coupling thermodynamics with political, social, and economic factors.



**Frank Bowman** (assistant professor). Research interests: Atmospheric aerosols; organic aerosol partitioning; mathematical modeling of multicomponent aerosols; air quality modeling; educational technology; assessment of student learning; educational air pollution models.



**Edward Kolodka** (associate professor). Research interests: Polymer reaction engineering; synthesis, rheological, and mechanical properties of polymers; development of polymers from agricultural products; synthesis and characterization of conducting polymers.



**Gautham Krishnamoorthy** (assistant professor). Research interests: Computational fluid dynamics; simulations of combustion reaction flows; carbon capture technologies; radiative heat transfer.

**Wayne Seames** (professor). Research interests: Novel process technologies; renewable fuels and chemicals; advanced combustion technologies; mitigation of the environmental impact of heavy metals; trace element partitioning from combustion and incineration.



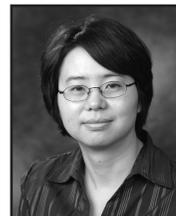
**Brian Tande** (assistant professor). Research interests: Polymer science and engineering with applications in sustainable energy; rheology of complex fluids; block copolymer morphology; neutron scattering; effect of polymer branching on membrane transport; polymers and composites from renewable sources.



**Steve Benson** (professor). Research interests: Efficient and clean utilization of renewable and fossil fuels in gasification and combustion systems; ash formation and fireside ash deposition; carbon products; carbon dioxide separation and capture.



**Yun Ji** (assistant professor). Research interests: Renewable and sustainable energy; chemicals and fuels from renewable sources; biomass pretreatment; biochemical and thermo-chemical of biomass for fuel production, enzymatic hydrolysis; integrated energy and environmental projects; process simulation; forestry biorefinery; pulp and paper technology; lignin utilization.



**Bob Wills** (associate professor). Research interests: Non-thermal drying of solids by chemical dehydration; vegetative oil extraction and product enhancement; increasing process efficiencies in the fermentation industry.



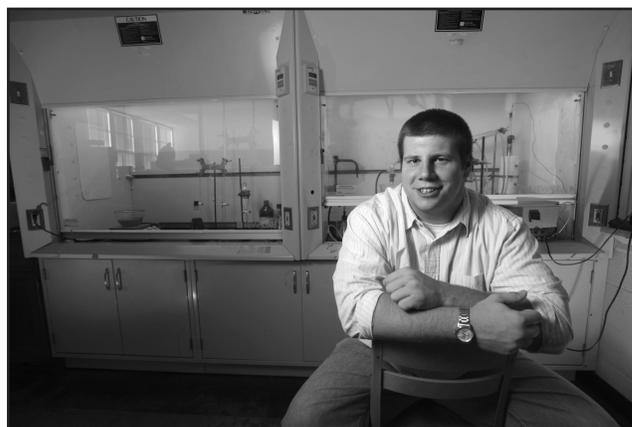
- *Dr. Darrin Muggli, then associate professor (now adjunct), received UND's 2006 Award for Individual Faculty Excellence in Teaching.*
- *Drs. Wayne Seames, Darrin Muggli, Frank Bowman, and Brian Tande were voted by the students as SEM Professor of the Year in 2006, 2007, 2009, and 2010, respectively.*
- *UND ChE student Mitch Braegelmann, BSChE08/MSChE09, was named a Tau Beta Pi Engineering Honor Society Laureate. This prestigious national award has been given to only 60 undergraduate engineering students since it was started in 1982.*

Strong, active research programs have also become a trademark of the department. Five faculty members have been honored in the past three years by the Technology Transfer Office for submitting patents and/or patent disclosures. The number of graduate students currently enrolled has stabilized at around 35 (34 enrolled in Fall 2009 including seven in the Engineering Ph.D. program with ChE advisors). Qualified full-time students are all fully supported on GRAs and GTAs.

- *The department was awarded the Fellows of the University Award of Excellence in Research in 1973 and 2005.*
- *Dr. Michael Mann, then professor (now distinguished professor, chair, and associate dean for research), received UND's 2006 Award for Individual Excellence in Research.*
- *Dr. Wayne Seames, then associate professor (now professor and director of ND SUNRISE) received UND's 2007 Award for Individual Excellence in Research.*
- *Yongxin Zhao, Ph.D., Energy Engineering (advised by ChE professor Michael Mann), received UND's 2006 Outstanding Doctoral Dissertation Award.*
- *April Hoffart (advised by ChE professor Wayne Seames) and Chris Flakker (advised by ChE professor Darrin Muggli) were awarded UND's 2005 and 2008 Outstanding Master's Thesis Awards, respectively.*

## PRINCIPLES AND VALUES

How did a program with a small five-person faculty emerge as one of UND's signature departments? UND ChE's academic excellence is due primarily to a set of principles that govern faculty selection and interaction. Preeminent among these is that the faculty must function as a team. Industry stakeholders are consistent in highlighting the ability to work in teams/groups as one of the most important tools they want chemical engineering departments to teach their students. At UND we do not believe this is feasible unless the faculty members model this behavior. Every new faculty member comes into the department with the understanding that they must function within a team environment. The keys to effective faculty teaming are collaboration, consensus, and communication. Administrators that do not know our department closely are often surprised at the consistency of voice expressed from ChE department faculty. This isn't because faculty do not have different opinions. It is that those differences are expressed within the group in discussions that lead to group consensus.



*UND ChE student Mitch Braegelmann, BSChE08/MSChE09, was named a Tau Beta Pi Engineering Honor Society Laureate.*

Operating as a faculty team also has allowed us to more efficiently use the resources at our disposal. For example, research laboratories and equipment are shared. Faculty do not have designated laboratories but share space as required. Graduate student offices are integrated across all advisors with purposeful mixing of students with different nationalities and different project topics. Co-advising of graduate students and collaborative proposals are the norm, not the exception. Most graduate students have two or three equally responsible faculty co-advisors overseeing their research projects.

A second key principle is that outstanding teachers must have superior communications skills. So in addition to looking for faculty members that will work well in a team environment, faculty recruitment also focuses on oral and written communications skills and the ability of candidates to listen effectively. This emphasis on communications is passed on to our students. UND ChE is known within the university for the quality of communication preparation included in the curriculum. Students are taught that the best ideas are unlikely to be adopted if no one can understand them or if the credibility of the engineer proposing the ideas is questioned. Good oral and written communication skills cannot be taught by those that do not have this ability within themselves. It is also difficult to teach complex concepts and problem-solving skills if the way these concepts are communicated inhibits understanding.

Some other key principles that are adopted by the entire faculty team are:

- *The primacy of education as the department's mission.*
  - *Education should not be compromised for research or service.*
  - *An important element of faculty selection is the candidate's passion for teaching and demonstrated competency in education.*
  - *Engagement teaching methods should be maximized.*

- Every member of the department attends the University of Buffalo's Case Studies in Science workshop to learn how to incorporate case studies and problem-based learning methods into science-oriented courses.
  - Experiential learning is essential. Lab courses are not secondary courses in the curriculum and teaching quality is as important in these courses as in recitation courses. All ChE lab courses are taught by faculty. All lab reports are graded by faculty. Teaching in recitation courses is weighted heavily towards engagement methods rather than lecture.
  - Teaching objectives can be achieved across the curriculum not just within individual courses. This is made possible by teamwork and allows more objectives to be achieved in less class time. Current across-the-curriculum topics are shown in Table 4.
  - Research projects should be student-centered. Research for research sake is not a priority in our department. Rather, we conduct research as a tool to teach students at all levels how to formulate and solve complex problems and to learn deeply in specific topic areas.
  - Faculty members limit travel during the academic year in order to avoid lessening the quality of education. This means that UND ChE faculty are purposely less involved in national conferences and other service activities that take them away from Grand Forks. As a consequence, the department is not as well known outside the local region as would be expected based on the level of research accomplishment achieved.
- Faculty mentoring is the responsibility of experienced members of the faculty.
- In a faculty team, peers are not seen as competitors, they are seen as resources.
  - Informal interactions between faculty lead to improved performance as faculty members share ideas and experiences. This is made effective by the department's teaming philosophy.
  - Senior faculty write collaborative research proposals with new faculty within the first couple of months to help them learn the process and to integrate the new member into the department's research team.
  - Faculty share their course resources when new faculty take over a class so that new faculty have a model for how to teach effectively.
- Students deserve personal attention.
- We employ mandatory faculty advising every semester for every student with the same faculty advisor for their entire program. (Students are free to request a different advisor if they are uncomfortable with their mentor.) This results in high student retention and minimizes graduation requirement issues.
- All faculty have an open door policy rather than posted office hours. Unless there is a compelling reason, all faculty are accessible during normal business hours.
  - We have no interest in retaining students that do not want to stay in the program for valid reasons. On the other hand, we do not want to lose students because of a poor experience in a science or math foundation course giving them the wrong impression about whether or not they will enjoy chemical engineering as a career. We conduct exit interviews with students who took our Fundamentals (ChE 201) class and passed with a C or better but elected not to enroll in the next technical chemical engineering class, Unit Operations (ChE 206). In the 2007-08 academic year, two students transferred to other programs.
  - Our department conducts a senior exit interview. On a scale of 1 to 5, with 5 being very satisfied, our graduating seniors rated the quality of advisement as 4.4. Comments from these interviews are taken seriously and reviewed by all faculty at the annual retreat.
  - Graduate programs are custom-designed for each student. For example, there are no required graduate classes in our ChE master's degree programs. Faculty advisors work with students to develop a program mutually acceptable to both that will best prepare students based on their objectives for obtaining an advanced degree.
- Core values for graduating students.
- We identified the following set of core values that every student graduating from our program should possess:
    - The ability to work in teams,
    - Respect for ethics and integrity
    - A firm understanding of key fundamentals of chemical engineering
    - The ability to communicate effectively
    - Fluency in the use of statistical methods
    - Competency in chemistry
    - Independence and self-discipline
    - An understanding of professional standards of quality in both technical content and personal conduct
  - These values are built into our curriculum and reinforced through multiple learning experiences. For example, they were used to identify our across-the-curriculum themes that are incorporated into individual courses within the program.
- Experience in Applied Engineering.
- There is great value in having a significant fraction of faculty members with applied engineering experience.

- *Most of our undergraduate students will go directly into industry (60-80%). Applications-oriented courses in the curriculum are best taught by those who teach what they know rather than those who teach what they learned.*
  - *In general, applied engineering jobs teach certain skills more effectively than most research jobs, such as teamwork, multitasking, planning, supervising other engineers, commercialization, and communications. Many of these are skills that our stakeholders want to see us teach to our students.*
  - *Applied engineering experience is equally valued to research experience within the faculty team.*
  - *Students are encouraged to participate in cooperative education assignments, internships, and/or undergraduate research. These experiential learning opportunities help students develop insight into what they are studying and motivation to apply themselves in their studies. Although these opportunities are voluntary, almost all UND ChE students participate in at least one of them.*
- *Teaching and research excellence are not mutually exclusive.*
- *Faculty hires must have doctoral degrees and demonstrated competency in research.*
  - *Faculty are mentored in grant writing and project management to increase their effectiveness.*
  - *Reasonable, but nontrivial, published tenure requirements allow faculty the freedom to take risks and reach for excellence. Patents and nontraditional venues for documenting research productivity are valued equally with peer-reviewed publications. For example, initiating a startup company based on faculty research is a valid productivity measure. In fact, in the current environment where universities are expected to be engines for economic development, entrepreneurial activities are highly valued. Four of the current faculty are associated with start-up/spin-off company ventures.*
  - *Faculty are considered full members of the team regardless of their contract status (tenured, tenure-track, nontenure-track). This improves team building and allows faculty resources to be used most effectively.*

## SUNRISE: THE CHEMICAL ENGINEERING-CHEMISTRY PARTNERSHIP

Faculty in ChE began collaborating on research projects with faculty in UND's chemistry department in the 1990s. These collaborations intensified in the 2000-2003 timeframe and in 2004 a decision was made to transform these small-scale collaborations into a more extensive partnership. The two departments established the Sustainable Energy Research Initiative and Supporting Education (SUNRISE) program.

Seeded with around \$1 million in research projects funding from existing collaborations, SUNRISE has since grown to include 33 faculty in 13 departments at both UND and North Dakota's other research university, North Dakota State University. Also participating are two faculty from North Dakota nondoctoral institutions. Working in three principle focus areas—renewable fuels and chemicals, the long-term sustainable use of coal, and harvesting energy from diverse sources—SUNRISE has received over \$32 million in research funding over the past six years.

All of the UND ChE faculty are expected to maintain active research programs and to bring in research funding sufficient to continuously support at least two graduate students. At present, all ChE faculty participate in SUNRISE along with 75% of the UND Chemistry faculty. Due to the ChE department's accomplishments in research, UND agreed to add two tenure-track faculty positions. These positions are funded during their initial three-year period with funding from the North Dakota EPSCoR program, with state-appropriated funding picking up the cost after that time. In addition, due to the level of research funding the department has received we have been able to add three nontenure-track faculty positions, one full-time and one half-time grants and contract officer positions, one instrument technician, two research chemists, three research engineers, and one marketing/outreach administrative assistant. In addition to assisting in the research mission of the department, these extra positions allow us to increase our course offerings and improve our service to the students.

## A WINNING RECIPE

Collaboration, consensus, and communication are the cornerstones of UND's Department of Chemical Engineering. By continually demonstrating their commitment to teamwork, our faculty members consistently prioritize the needs of our students and the industries and universities that eventually employ them. □

<b>TABLE 4</b> <b>Across-the-Curriculum Themes</b> <b>in UND Chemical Engineering</b>
Teamwork
Sustainability
Communication: writing, speaking, listening
Professionalism and Integrity
Environment, Health, and Safety
Instrumentation and Control
Independent Learning
Statistical Analyses of Data
Computational Tools

# GAS PRESSURE-DROP EXPERIMENT

WILLIAM L. LUYBEN AND KEMAL TUZLA  
*Lehigh University • Bethlehem, PA 18015*

For many years, one of the most important experiments in the Lehigh Undergraduate Chemical Processing Laboratory has been a fluid mechanics experiment in which pressure drop through pipes of various diameters is measured over a range of velocities. The working fluid is liquid water, which is pumped from a holding tank by a centrifugal pump. The stream flows through a manual valve, a rotameter, one of three pipes with different diameters, through another manual valve, and back to the tank. Experimental data is used to calculate friction factor vs. Reynolds number, and results are compared to literature Moody diagram<sup>[1]</sup> predictions. Pump characteristic curves are also generated for different motor rotational speeds: pump head vs. flowrate and motor power vs. flowrate.

Regulating the flowrate is usually achieved by positioning the manual valve immediately after the pump. This means that the pipes are at a low pressure since they discharge back into the tank, which is at atmospheric pressure. In fact, under some conditions the pipes can be under vacuum because they are located at an elevation above the tank. This can lead to air being sucked into the impulse lines of the pressure gauges and can give faulty reading.

To prevent this, the valve downstream of the pipes before the tank can be used to set the flowrate. Then the pressure in the pipes is only slightly lower than the pump discharge pressure of about 45 psig.

Several years ago, a group of students took their data using the valve upstream of the pipes (low-pressure operation) and obtained some unreasonable data for pressure drops. The

laboratory instructor suggested that they should have used the valve downstream of the pipes to have positive pressure in the test pipes. The response of the students was that they had to repeat all of their experiments. Of course, this is not true since liquid water is incompressible and pressure drop does not vary with pressure in the pipe.

This misconception by some bright students prompted us to design and build a new experiment in which the density of the fluid can be changed. Density affects both pressure drop and flow measurement, and understanding these concepts is very important to any engineer working with gas streams. In the current era of increasing importance of biomass gasifica-



**William L. Luyben** is a professor of chemical engineering at Lehigh University. He received his B.S. from Penn State and Ph.D. from the University of Delaware. He teaches Unit Operations Laboratory, Process Control, and Plant Design courses. His research interests include process design and control, distillation, and energy processes.

**Kemal Tuzla** is a professor of practice and associate chair

in the Department of Chemical Engineering at Lehigh University. He received his B.S. and Ph.D. from the Technical University of Istanbul. He teaches Unit Operations Laboratory, Fluid Mechanics, and Heat Transfer courses. His research interests include thermal energy storage and heat transfer in two-phase flows.



tion and the hydrogen economy, the chemical engineer must be competent in dealing with gas flows through pipes.

There have been a number of papers discussing experiments in compressible flow systems. Aerospace departments use many experiments to illustrate compressible flow effects in converging-diverging nozzles, usually at high Mach numbers. Lam and Liu<sup>[2]</sup> provide a useful example of a simple laboratory set up. Forrester, et al.,<sup>[3,4]</sup> discuss experiments in which gas discharges from a pressure vessel or is fed into a vessel.

Despite the importance of gas flows in chemical engineering industrial processes, we are not aware of any student laboratory experiments dealing with the flow of compressible fluids through pipes.

## DESCRIPTION OF EQUIPMENT

Figure 1 gives a schematic flowsheet. High-pressure air (85 psig) flows through a pressure regulator. This device holds a constant pressure at the down-stream rotameter, and this pressure can be adjusted to different levels. After passing through the rotameter, the piping consists of two parallel lines. One pipe is 1/4 inches in diameter and the other is 1/2 inches in diameter. There is a manual valve at the inlet of each line that is used to set the flowrate of air through the line in service. At the discharge end of each pipe is a back-pressure regulator that is adjusted to hold different pressures in the test pipe.

For example, suppose the supply pressure is 85 psig. The pressure at the rotameter could be 50 psig. The pressure at the beginning of the test pipe could be 26 psig, and pressure at the end of the pipe in service could be 25 psig due to the 1 psi pressure drop. Pressure gauges measure the total pressures at each end of test pipes, and a differential pressure measurement is made between the inlet and exit of each pipe.

## GAS PRESSURE DROP

The first concept illustrated in this experiment is the effect of density on pipe pressure drop. The first task for students is to measure friction factors and compare the experimental values to Moody's data. Since the pipe is horizontal, the measured pressure drop across the pipe is assumed to be due to frictional pressure losses only. Any effects due to small pressure changes along the pipe associated with compressibility of the gas are assumed negligible.

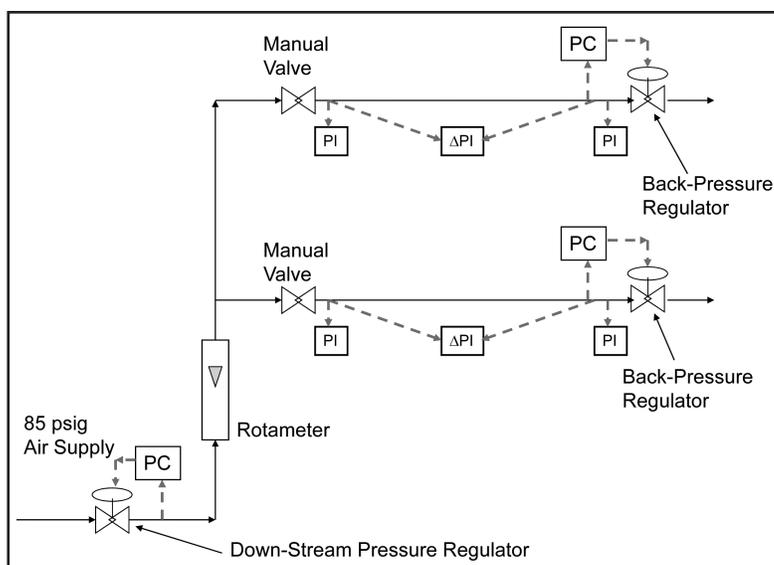


Figure 1. Schematic of experimental test loop.

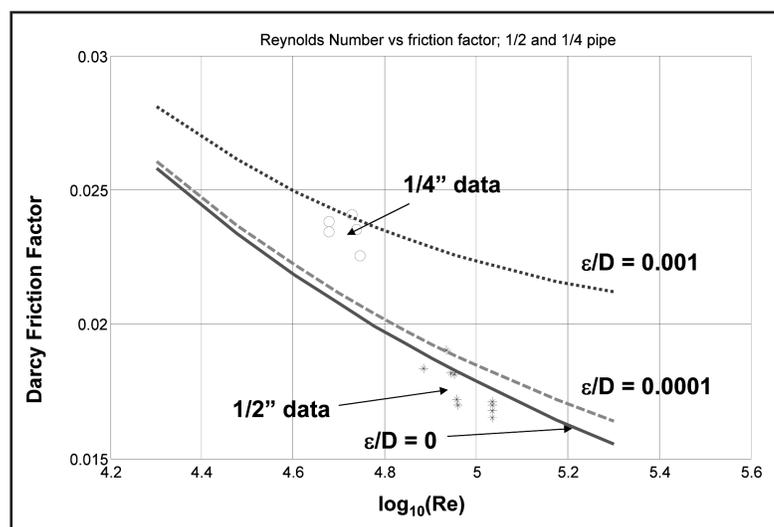


Figure 2. Comparison of experimental data with Moody data for two pipe sizes.

A sample comparison is presented in Figure 2. Experimental data for the 1/4" pipe agree with Moody's data for a roughness ratio of  $\epsilon/D=0.0008$ . The data for the 1/2" pipe shows good agreement with Moody's at zero roughness. There are few points that show friction factors less than a smooth tube, which is obviously due to experimental uncertainty.

The apparatus permits pressure-drop data to be gathered with different pipe pressures. For the same mass flowrate, the pressure drop changes as pressure in the pipe changes. Pressure drop depends on kinetic energy, which is proportional to density ( $\rho$ ) times the square of the velocity ( $V^2$ ).

Higher pressure means higher gas density, but higher density decreases gas velocity. So density increases directly with line pressure, but velocity decreases directly with line pressure. The net effect is a linear inverse relationship between pressure drop and pressure in the pipe.

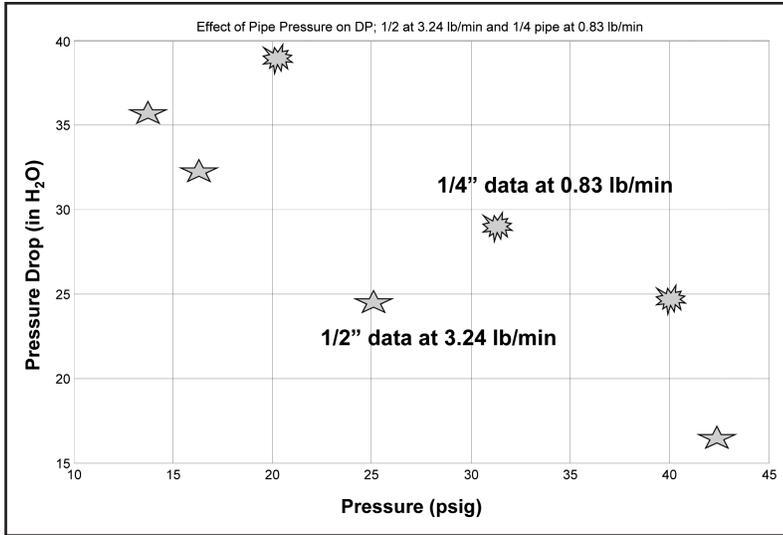


Figure 3. Effect of line pressure on pressure drop at constant mass flowrate.

Students are asked to verify this relationship by carrying out several tests at similar rotameter conditions, (*i.e.*, at same mass flow rate) but different pipe pressures as tabulated in Table 1. Note that there are three gas densities involved in the calculations: density at standard conditions, density in the pipe at pipe pressure, and density in the rotameter at rotameter pressure.

From the data of Table 1, the variation of pressure drop across the pipe is plotted as a function of pressure in the test pipe and is presented in Figure 3. For the 1/2 inch pipe that is 8 ft long, with a mass flowrate of 3.24 lb/min, the pressure drop is 24.5 inches of water when the average pressure in the pipe is 25.5 psig (arithmetic average of the inlet and outlet pressures in the pipe). With the same mass flowrate, the pressure drop decreases to 16.5 inches of water when the pipe pressure is increased to

Pipe: 1/2 inch – Schd. 40.				
ID (inches)	0.622			
Pressure at Rotameter (psig)	50	50	50	50
Gas Density at Rotameter (lb/ft <sup>3</sup> )	0.330	0.330	0.330	0.330
Rotameter Reading (SCFM)	20.6	20.6	20.6	20.6
Pressure at Inlet of Pipe (psig)	14.5	17.0	26.0	42.8
Pressure at Outlet of Pipe (psig)	13.0	15.5	25.0	42.3
Differential Pressure (inches H <sub>2</sub> O)	35.6	32.3	24.5	16.5
Mean Gas Density in Pipe (lb/ft <sup>3</sup> )	0.145	0.158	0.205	0.292
Mass Flowrate (lb/min)	3.24	3.24	3.24	3.24
Velocity in Pipe (ft/sec)	176	162	125	87.7
Darcy Friction Factor	0.0170	0.0167	0.0165	0.0158
Reynolds Number	109,000	109,000	109,000	109,000
Pipe: 1/4 inch – Schd. 40				
ID (inches)	0.364			
Pressure at Rotameter (psig)	45	45	45	
Gas Density at Rotameter (lb/ft <sup>3</sup> )	0.306	0.306	0.306	
Rotameter Reading (SCFM)	5.5	5.5	5.5	
Pressure at Inlet of Pipe (psig)	40.5	32.0	21.0	
Pressure at Outlet of Pipe (psig)	39.5	31.0	19.5	
Differential Pressure (inches H <sub>2</sub> O)	24.5	29.0	39.0	
Mean Gas Density in Pipe (lb/ft <sup>3</sup> )	0.279	0.235	0.178	
Mass Flowrate (lb/min)	0.83	0.83	0.83	
Velocity in Pipe (ft/sec)	68.7	81.4	108.0	
Darcy Friction Factor	0.0235	0.0234	0.0239	
Reynolds Number	47,600	47,600	47,600	

42.5 psig. With the same mass flowrate, the pressure drop increases to 35.6 inches of water when the pipe pressure is decreased to 13.8 psig.

Note that there is a slight curvature in the data shown in Figure 3. In theory, the relationship between pressure drop and pressure should be linear. Pressure drop in a pipe can be calculated from the friction factor  $f$ .

$$\Delta P = f \left( \frac{L}{D} \right) \rho \frac{V^2}{2} \quad (1)$$

where  $L$  and  $D$  are the length and diameter of the pipe,  $\rho$  is density and  $V$  is velocity. When the mass flowrate of gas is constant in a constant-diameter pipe, the Reynolds number is constant. This means the friction factor is constant. Consider two pipes of the same diameter and length that operate with gases having different densities ( $\rho_1$  and  $\rho_2$ ) but with the same mass flowrate. The pressure drops through the pipe ( $\Delta P_1$  and  $\Delta P_2$ ) at these two conditions are

$$\begin{aligned} \Delta P_1 &= f \left( \frac{L}{D} \right) \rho_1 \frac{V_1^2}{2} \\ \Delta P_2 &= f \left( \frac{L}{D} \right) \rho_2 \frac{V_2^2}{2} \end{aligned} \quad (2)$$

Taking the ratio of the pressure drops and expressing velocity as the mass flowrate  $F_{\text{mass}}$  divided by density  $\rho$  and pipe cross-sectional area  $A_{\text{CS}}$  give the effect of density on pressure drop.

$$\frac{\Delta P_1}{\Delta P_2} = \frac{f \left( \frac{L}{D} \right) \rho_1 \frac{V_1^2}{2}}{f \left( \frac{L}{D} \right) \rho_2 \frac{V_2^2}{2}} = \frac{\rho_1 V_1^2}{\rho_2 V_2^2} = \frac{\rho_1 \left( \frac{F_{\text{mass}}}{\rho_1 A_{\text{CS}}} \right)^2}{\rho_2 \left( \frac{F_{\text{mass}}}{\rho_2 A_{\text{CS}}} \right)^2} = \frac{\rho_2}{\rho_1} \quad (3)$$

If the two densities are different only because of differences in pressure (same molecular weight and temperature), the ratio of the pressure drops varies inversely with pressure  $P$ .

$$\frac{\Delta P_1}{\Delta P_2} = \frac{P_2}{P_1} \quad (4)$$

These experiments expose the students to the important observation that the density of the gas affects the pressure drop in the pipe. This knowledge is vital to any engineer involved in a process that handles gas flows. The density of the gas can change with pressure and temperature. Very importantly, it also can change with composition. Fuel gas in a plant is a common example. The fuel gas can come from various sources (purchased natural gas or gas produced in a process, for example hydrogen or propane). Therefore the composition of the gas changes as the flowrates from the various sources change. The laboratory experience provides the students with this important insight.

## GAS FLOW MEASUREMENT

The second important concept illustrated in this experiment is how to correct gas flow meter constants for conditions different than used for their calibration. This is achieved by operating the flow measurement device at different pressures. The mass flowrate changes as the density of the gas in the flow-measuring device changes.

If a turbine meter is used, which is a volumetric device, it is straightforward to find the mass flowrate by simply multiplying the volumetric flow reading from the turbine meter by the actual density of the fluid in the device.

If the device is based on drag force (the case for a rotameter) or on Bernoulli's Principle (the case for the differential pressure in an orifice plate or Pitot tube), the calculation of flowrate is not as straightforward. The correction requires the use of the square root of the ratio of the density at actual flow conditions to the density at calibration conditions. The correction factor relationship is given in Eq. (5).

$$F_{\text{actual}}^{\text{mass}} = F_{\text{cal}}^{\text{mass}} \sqrt{\frac{\rho_{\text{actual}}}{\rho_{\text{cal}}}} \quad (5)$$

The  $F_{\text{actual}}^{\text{mass}}$  is the actual mass flowrate of gas flowing through the meter.

The term  $F_{\text{cal}}^{\text{mass}}$  is the mass flowrate that is calculated by using the flow meter reading (usually in volumetric units  $F_{\text{cal}}^{\text{vol}}$ ) times the gas density at calibration conditions.

$$F_{\text{cal}}^{\text{mass}} = F_{\text{cal}}^{\text{vol}} \rho_{\text{cal}} \quad (6)$$

The gas densities  $\rho_{\text{actual}}$  and  $\rho_{\text{cal}}$  are at the actual and calibration conditions in the flow meter.

In the experiment, only gas pressure changes since the gas is air at ambient temperature. In this case, the correction factor is given in Eq. (7) in terms of pressures.

$$F_{\text{actual}}^{\text{mass}} = F_{\text{cal}}^{\text{mass}} \sqrt{\frac{P_{\text{actual}}}{P_{\text{cal}}}} \quad (7)$$

The students in the laboratory operate the rotameter at different pressures but with the same mass flowrate. They observe that the rotameter reading is different at different pressures because of the change in gas density with pressure. For the same mass flowrate, the rotameter reading increases as the pressure in the rotameter decreases because the lower density increases the gas velocity. The derivation of these equations for the rotameter used in the experiment is appended.

Consider a numerical example. A rotameter is calibrated for air under standard conditions (14.7 psia and 70 °F). The rotameter reading is 20.6 scfm. The flow meter is used with air at room temperature but with a pressure of 50 psig in the rotameter. We want to calculate the mass flowrate through the rotameter.

Assuming ideal gas behavior, the density of air (28.84 lb/lb-mole) at 70 °F and 14.7 psia is

$$\rho_{\text{cal}} = \frac{(28.84 \text{ lb/lb-mol})(14.7 \text{ lb}_f/\text{in}^2)(144 \text{ in}^2/\text{ft}^2)}{\left(1545 \frac{\text{ft lb}_f}{\text{lb-mol } ^\circ\text{R}}\right)(460 + 70^\circ\text{R})} = 0.0746 \frac{\text{lb}}{\text{ft}^3} \quad (8)$$

The mass flowrate at standard conditions would be

$$F_{\text{cal}}^{\text{mass}} = F_{\text{cal}}^{\text{vol}} \rho_{\text{cal}} = (20.6 \text{ scfm})(0.0746 \text{ lb/ft}^3) = 1.54 \text{ lb/min} \quad (9)$$

Using Eq. (7) to find the actual mass flowrate with the same molecular weight and temperature gives

$$F_{\text{actual}}^{\text{mass}} = (1.54 \text{ lb/min}) \sqrt{\frac{14.7 + 50}{14.7}} = 2.97 \text{ lb/min} \quad (10)$$

## CONCLUSION

This paper has described an experiment that illustrates several important issues associated with the fluid mechanics of gas flow in pipes at low Mach numbers, which is found in many chemical engineering processes. The experiment gives the students hands-on experience and understanding that:

- For a given mass flowrate, pressure drop in a pipe varies inversely with gas density.
- Flow measurements using a variable area rotameter or differential pressures (orifice plates or pitot tubes) need to be properly compensated for densities that differ from those used for calibration.

Although students are exposed to these concepts during their classroom studies, our experience shows that this experiment provides very helpful reinforcement for student understanding and retention of concepts.

## ACKNOWLEDGMENT

Initial design work of this experiment was carried out by Lehigh ChE seniors Eric Pukszyn and Alisa Vasilenko. The authors acknowledge their meticulous work and effort.

## REFERENCES

1. Moody, L.F. "Friction Factor for Pipe Flow," *Trans. ASME*, **66**, 67 (1944)
2. Lam, C.Y., and C.Y. Liu, "An Experimental Facility for Compressible Flow," *Int. J. Eng. Ed.*, **15**(1), 58 (1999)
3. Forrester, S.E., and G.M. Evans, "The Importance of System Selection on Compressible Flow Analysis," *Chem. Eng. Ed.*, **32**(4), 399 (1998)
4. Forrester, S.E., A.V. Nguyen, and G.M. Evans, "Compressible Flow Analysis: Discharging Vessels," *Chem. Eng. Ed.*, **38**(3) 29 (2004)
5. Fox, R.W., A.T. McDonald, and P.J. Pritchard, *Introduction to Fluid Mechanics*, 7th Ed., John Wiley & Sons (2009)

## APPENDIX

Derivation of rotameter equations is summarized below. A schematic of a rotameter is shown in Figure A1. Suppose we carry out two experiments with different operating conditions in this rotameter, and the float stabilizes at the same level. Furthermore assume that one of the experiments is under standard calibration conditions (cal) with air (1 atm and 70 °F) at which the rotameter has been calibrated, and the other condition is at a different pressure and temperature (actual) and perhaps a different gas with a different molecular weight.

A force balance on the float would include the drag force, the buoyancy force of the fluid, and the weight of the float;

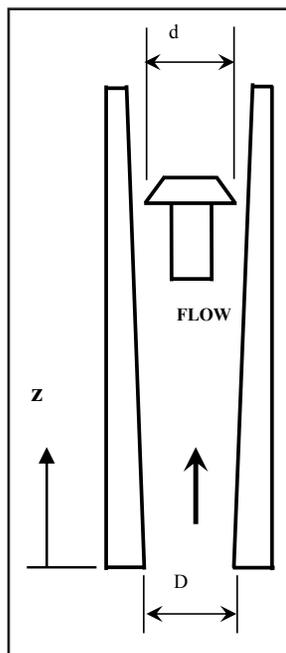


Figure A1. Rotameter schematic.

$$F_D + \rho_{\text{Fluid}} \text{Vol}_{\text{Float}} \frac{g}{g_c} = \rho_{\text{Float}} \text{Vol}_{\text{Float}} \frac{g}{g_c} \quad (A1)$$

where the drag force is defined as;

$$F_D = C_D A_{\text{Float}} \frac{\rho_{\text{Fluid}} (V_{\text{Fluid}})^2}{2g_c} \quad (A2)$$

The drag coefficient,  $C_D$ , consists of both pressure drag and frictional drag. For the geometry of the float with a short aspect ratio, however, frictional drag is negligible for a wide range of Reynolds Numbers (between 1,000 and 250,000), and therefore pressure drag dominates the  $C_D$ . As a result,  $C_D$  becomes a constant, independent of Reynolds Number.

Combining Eqs. (A1) and (A2) gives the velocity and volumetric flow rate.

$$V_{\text{Fluid}} = \left[ \frac{2g \text{Vol}_{\text{Float}} (\rho_{\text{Float}} - 1)}{C_D A_{\text{Float}} \rho_{\text{Fluid}}} \right]^{1/2} \quad (A3)$$

$$F_{\text{Fluid}}^{\text{Vol}} = A V_{\text{Fluid}} = A \left[ \frac{2g \text{Vol}_{\text{Float}} (\rho_{\text{Float}} - 1)}{C_D A_{\text{Float}} \rho_{\text{Fluid}}} \right]^{1/2} \quad (A4)$$

where  $A$  is the annular area between the body of the rotameter tube and the float. When gases are used, the ratio of  $\rho_{\text{Float}}$  to  $\rho_{\text{Fluid}}$  is very large, so the term “-1” on the right-hand side of Eq. (A4) can be neglected;

$$F_{\text{Fluid}}^{\text{Vol}} = A \left[ \frac{2g \text{Vol}_{\text{Float}} \left( \frac{\rho_{\text{Float}}}{\rho_{\text{Fluid}}} \right)}{C_D A_{\text{Float}}} \right]^{1/2} \quad (\text{A5})$$

If we consider the flowrate for two different experimental conditions, one with density at which the rotameter has been calibrated and the other at some other actual density, the ratio of the volumetric flowrates would be as given in Eq. (A6).

$$\frac{F_{\text{actual}}^{\text{Vol}}}{F_{\text{cal}}^{\text{Vol}}} = \frac{A \left[ \frac{2g \text{Vol}_{\text{Float}} \left( \frac{\rho_{\text{Float}}}{\rho_{\text{actual}}} \right)}{C_D A_{\text{Float}}} \right]^{1/2}}{A \left[ \frac{2g \text{Vol}_{\text{Float}} \left( \frac{\rho_{\text{Float}}}{\rho_{\text{cal}}} \right)}{C_D A_{\text{Float}}} \right]^{1/2}} = \left( \frac{\rho_{\text{cal}}}{\rho_{\text{actual}}} \right)^{1/2} \quad (\text{A6})$$

The term  $F_{\text{cal}}^{\text{Vol}}$  is the volumetric flowrate reading from the rotameter based on its meter constant. The  $\rho_{\text{cal}}$  and  $\rho_{\text{actual}}$  are the gas densities at standard calibration conditions and actual conditions in the rotameter, respectively. To calculate the mass flowrates, the corresponding densities are used.

$$\frac{F_{\text{actual}}^{\text{mass}}}{F_{\text{cal}}^{\text{mass}}} = \left( \frac{F_{\text{actual}}^{\text{Vol}}}{F_{\text{cal}}^{\text{Vol}}} \right) \frac{\rho_{\text{actual}}}{\rho_{\text{cal}}} = \left( \frac{\rho_{\text{cal}}}{\rho_{\text{actual}}} \right)^{1/2} \frac{\rho_{\text{actual}}}{\rho_{\text{cal}}} = \left( \frac{\rho_{\text{actual}}}{\rho_{\text{cal}}} \right)^{1/2} \quad (\text{A7})$$

When the temperature and molecular weight of the fluid do not change, the relationship can be expressed in terms of pressures.

$$F_{\text{actual}}^{\text{mass}} = F_{\text{cal}}^{\text{mass}} \sqrt{\frac{P_{\text{actual}}}{P_{\text{cal}}}} \quad (\text{A8})$$

## NOMENCLATURE

- $A_{\text{CS}}$  – cross-sectional area
- $C_D$  – drag coefficient
- $D$  – diameter
- $F_D$  – drag force
- $F_{\text{mass}}$  – mass flowrate
- $F^{\text{Vol}}$  – volumetric flowrate
- $g$  – gravitational constant
- $P$  – pressure
- $Re$  – Reynolds number
- $V$  – velocity
- $z$  – vertical position of rotameter float

## Subscripts

- actual – at operating conditions
- cal – at calibration conditions
- fluid – gas phase
- float – rotameter float

## Greek

- $\rho$  density
- $\varepsilon$  roughness factor
- $\Delta$  difference in property between locations  $\square$

# CREATIVE LEARNING IN A MICRODEVICE RESEARCH-INSPIRED ELECTIVE COURSE

## *for Undergraduate and Graduate Students*

ADRIENNE R. MINERICK

*Michigan Technical University • Houghton, MI 49931\**

It is widely touted that the use of research ideas can create excitement for learning in the classroom.<sup>[5-9]</sup> This paper describes the development of a research-inspired Analytical Microdevice Technology (AMT) course for undergraduates and graduate students at Mississippi State University. Microscale research is a challenging area within which to do this because microscopes are required to observe most phenomena in microdevices. The approaches used in this course were designed to overcome the challenges with directly observing fluid and particle dynamics at the microscale, while still demonstrating the powerful nature of this area of engineering. The primary course goal was to get the students familiar with small-scale technology with a focus on biomedical diagnostic applications. The course covered both theoretical and experimental advances in the realm of chemical, mechanical, optical, and biological analysis. This was accomplished through four activities throughout the semester (15 weeks, MWF class): a lecture, a Survivor game,<sup>[1]</sup> discussions of technical articles,<sup>[2, 3]</sup> and a concept development project.<sup>[4]</sup> Mondays were dedicated lecture days (15 total contact sessions) where the professor came with a structured set of material, in-class activities, videos, etc., to provide a foundation of knowledge for the students. Wednesdays were dedicated to a Survivor game modeled after J. Newell's 2005 article.<sup>[1]</sup> This interactive game had student teams solving knowledge, calculation, concept, and design problems during class. Teams with incorrect answers lost members via a voting mechanism. Fridays were comprised of student presentations and discussions of technical articles and current news articles on Analytical

Microdevice Technology. The fourth activity was a semester-long, open-ended concept development project completed in teams outside of class. These concept development projects included progress reports every two weeks; the intermittent reports built to a fully developed journal-style article outlining a microtechnology concept well-grounded in the research literature and featuring a novel approach or device for a biological analysis. This paper describes the course content and its close influence from the author's research, and concludes with results of student assessment of the four learning tools which have been cross-correlated with the student's preferred Felder-Silverman Learning Style.<sup>[10,11]</sup>

**Adrienne Minerick** is an associate professor of chemical engineering at Michigan Technological University, having recently moved from Mississippi State University, where she was a tenured associate professor. She received her Ph.D. and M.S. from the University of Notre Dame and B.S. from Michigan Tech. At MTU, Adrienne has taught graduate Kinetics. At MSU, she taught the graduate Chemical Engineering Math, Process Controls, Introduction to Chemical Engineering Freshman Seminar, Heat Transfer, and Analytical Microdevice Technology courses. Her research is in medical microdevice diagnostics and dielectrophoresis.



\* Work conducted at: 323 President's Circle, Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS, 39762. Author can be contacted at: 1400 Townsend Drive, Department of Chemical Engineering, Michigan Technological University, Houghton, MI, 49931; Phone: 906-487-2796, Email: minerick@mtu.edu

Electrokinetics and Quantitative Analysis in Microdevices is an active area of research for the author and the development of this course was supported by an NSF CAREER Award. The course counts as a chemical engineering elective in MSU's curriculum, but was widely advertised as open to all majors and even enrolled a biochemistry graduate student. A total of 14 students—nine undergraduates and five graduate students—completed the course. Course content covered both theoretical and experimental advances from the perspective of understanding the fundamental forces dominating at the micron-length scales in both electric fields and small, confined channels. The phenomena were closely tied with known microdevice applications that harnessed those forces for a biomedical diagnostic application. Course content is given in Table 1 with the reference texts listed by author.<sup>[12-21]</sup>

Course objectives were structured to provide undergraduate and graduate students with preliminary research skills as well as a solid background and an enthusiasm for analytical microdevice technology. Surveys of news and corresponding technical articles were intended to empower students with familiarity, skills, and knowledge to envision microdevice applications and apply this in research or in future job pursuits. Upon completion of the course, the students were to demonstrate proficiency in the following topics and skills:

- *Review of micro / nano technology news and critique of corresponding technical publications*
- *Fundamental understanding of micro/nano forces*
- *Materials and methods for microdevice fabrication*
- *Contextualization of existing and future detection tools*
- *Concept plan of a fully integrated device*

The four main learning activities during the semester—lectures, Survivor game, article presentations, and a large concept development project—were drawn from various sources. The lecture content was largely governed by the content given in Table 1. Questions for the game were pulled from each of the other three activities. For article presentations, students were encouraged to actively read the literature as a learning tool and as a supplement to information provided in class. Two facility tours were conducted. The first was of the microfabrication facilities (photolithography, electroplating, and epitaxy) at SemiSouth, Inc., a start-up company from Mississippi State University. The second tour was of MSU's Life Sciences Biotech Institute, a multi-user genomics and proteomics facility that uses a variety of electrophoretic profiling devices. Lastly, the students were arranged into four teams each having a graduate student leader, and each team worked together to develop a concept project, which culminated in a viable draft of a journal article. Each of these activities is discussed in the following sections of this paper. In addition, the course topic of linear electrokinetics is described under each activity to demonstrate how course content was related between the activities.

## ACTIVITY 1: LECTURES

Lectures were held each Monday in order to provide the students a well-organized foundation in the physics of materials at the micro- and nanoscales as well as fundamental knowledge of the optical and electronic tools utilized in microdevices. The topics covered are outlined in Table 1. Lectures were of traditional format with content written on a whiteboard in a sequential fashion. Calculation exercises, videos, and short class activities were interwoven into the lecture. Due to the open atmosphere of the classroom (likely facilitated by the other class activities), students regularly asked questions and began discussions to understand why fluids or particles behaved as they did in the confined geometries. When topics related to biochemistry or biology were included in the lecture, a biochemistry graduate student would frequently add insight and instruction beyond what the professor presented. It was an excellent learning opportunity for the students and professor alike.

For example, linear electrokinetics included coverage of both electrophoresis and electroosmotic flow. Students had previously learned charge interactions and particle behaviors in Section 1 of the course. The introduction included applications of electric fields including the geometry considerations (uniform, non-uniform) as well as energy considerations (Direct Current, Alternating Current). The linear electroki-

**TABLE 1**  
**AMT Course Topics**

1. Intermolecular and Surface Forces, <i>Israelachvili, Probstein</i> <sup>[12,13]</sup>	
	Intermolecular interactions
	Interparticle forces
	Polar (izable) molecules
	Electrostatic forces
2. Microdevice Designs & Considerations, <i>Literature, Rathore</i> <sup>[14]</sup>	
	Shape & materials
	Fabrication techniques & lab tour
	Sample injection / mixing
3. Pressure Driven Flow (micron length scales), <i>Bird, Fournier, Truskey, Literature</i> <sup>[15-17]</sup>	
	COMSOL Multiphysics DEMO
4. Linear Electrokinetics, <i>Rathore, Li</i> <sup>[14,18]</sup>	
	Electrophoresis
	Electroosmotic flow
	Lab tour: Life Science Biotechnology Institute
5. Nonlinear Electrokinetics, <i>Morgan, Delgado Literature</i> <sup>[19,20]</sup>	
	Dielectrophoresis
	Magnetophoresis
	Traveling wave DEP
6. Detection and Quantification of Analytes, <i>Webster</i> <sup>[21]</sup>	
	UV, flow cytometry, fluorescence

netics discussion was limited to uniform geometry and DC electrical configurations. Foundations in both electrophoresis and electroendosmosis were covered as shown in cartoon in Figure 1. The apparent electrokinetic velocity observed in a microchannel is a combination of the electrophoretic (EP) velocity and the electroosmotic (EO) velocity as follows:

$$V_{EK} = V_{EP} + V_{EO} \quad (1)$$

where the particle's electrophoretic velocity is given by:

$$v_{EP} = \frac{q \cdot E}{r \cdot \eta} \quad (2)$$

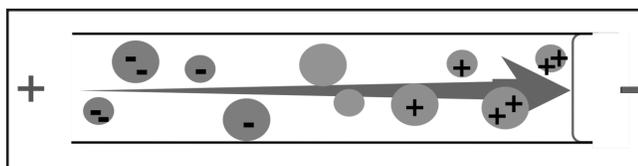
and the electroosmotic flow velocity is given by:

$$v_{EO} = \frac{\epsilon \cdot \zeta \cdot E}{\eta} \quad (3)$$

One concept that is important to keep straight is the difference between mobility and velocity. They are related as

$$\mu = \frac{v}{E} \quad (4)$$

The variables used in these equations are  $v$  as the velocity,  $q$  as the particle charge,  $E$  as the electric field (voltage per distance),  $r$  as the particle radius,  $\eta$  as the fluid viscosity,  $\epsilon$  as the dielectric permittivity,  $\zeta$  as the zeta potential (the effective charge difference between the wall and the bulk fluid in the normal dimension), and  $\mu$  is the mobility. The complex wall charge / fluid charge interactions were examined in detail.



**Figure 1.** In uniform, linear DC electric fields, particles will move due to a combination of the electrophoretic forces acting on the particle as well as the electroendosmotic forces inducing flow of the liquid. This diagram demonstrates the relative mobilities of highly charged small particles down to lowly charged large particles.

	Q1: I learn a great deal from the Survivor Problems.		Q2: I had fun playing Survivor in class.	
	Begin	Middle	Begin	Middle
Strongly Agree	4	6	10	9
Agree	8	6	3	4
Neutral	2	2	1	1
Disagree	-	-	-	-
Strongly Disagree	-	-	-	-

Lectures were interactive in the form that in-class activities were also interspersed throughout the instructor-dominated discussions. Activities and discussions were frequent sources of questions for Survivor the following class period.

## ACTIVITY 2: MICRO-TECHNOLOGY SURVIVOR

A game of Survivor: Classroom was conducted each week and based upon J. Newell's adaptation of this popular TV show in his Mass and Energy Balances class.<sup>[1]</sup> This game served as means for the students to apply the information learned in the lecture and as such replaced a homework component of the class. Three types of questions were asked during the game that roughly corresponded to the levels of Bloom's Taxonomy.<sup>[22]</sup> Level 1 questions primarily queried knowledge and understanding of concepts; these were quicker-answer questions that probed the "remember" and "understand" levels of Bloom's Taxonomy. Level 2 questions ranged from plug-and-chug calculations (equations not provided, students could use notes) to more involved quantitative reasoning questions; these targeted the "apply" domain of Bloom's Taxonomy. Level 3 questions typically were a team effort and involved the novel design of microdevices that capitalized upon the phenomena of interest to achieve mixing, reaction, separation, or other micro-unit operations. These questions targeted the "evaluate" and "create" levels of cognitive development.<sup>[22]</sup>

Two surveys were conducted during the semester to gauge student perception of this game as a learning tool. The first was conducted after the first Survivor game day and was focused primarily for students to provide feedback on questions and logistics of conducting the game in class. The second was conducted halfway through the semester. In both surveys, the students were asked to respond to an open essay question and two questions on a 5-point Likert scale from Strongly Agree down to Strongly Disagree. The responses are compiled in Table 2 and demonstrate positive student feedback to the game. Interestingly, the students recognized that the fun factor was a little greater than the learning factor. There was a slight increase by mid-semester in the number of students who felt they were learning from the Survivor game.

With the feedback from the surveys, a number of modifications were made to the rules of the game. Original rules are available in J. Newell's article<sup>[1]</sup>; AMT class rules differed in the following ways:

- The tribe with fewer members was immune from losing a member the first round. Graduate students were immune for the first three questions.
- Students who were eliminated in any round joined the Peanut Gallery. They were given the task of designing and solving one problem per gaming session with the intention that it might be used in later rounds.
- Peanut Gallery students could also continue to compete independently. If they "won" a round, they could choose to join any team (and earn points). The team they joined then earned immunity from loss of a member for that round.

The ability of members of the Peanut Gallery to answer questions independently helped immensely by keeping those students engaged in the game and learning.

Linear electrokinetics concepts were reinforced during the Survivor game. For this particular topic, level 1 knowledge questions were:

1. “Rank order the mobility of the following particles from slowest to fastest.

- A. Large, highly charged analyte,
- B. Small, highly charged analyte,
- C. Large, barely charged analyte,
- D. Small, barely charged analyte.”

ANSWER: C,D,A,B

2. “What happens to flow if a capillary surface is chemically modified to express densely packed positive charges? Describe the cause / effect relationships that lead to the final electroosmotic flow profile.

ANSWER: The positively charged wall will attract a Debye layer of negative charges. In a DC field, these will pull the fluid toward the anode in the classic flat velocity profile.

Level 2 questions included the following:

1. “What is the electrophoretic mobility of an analyte with a net positive charge of 2 and an effective radius of 50 nm in an aqueous solution?

ANSWER: Note that 1 Coulomb is equal to the charge of  $6.24 \times 10^{18}$  protons.

$$\mu_{EP} = \frac{q}{r \cdot \eta} = \frac{2C / 6.24 * 10^{18}}{50nm \cdot 1cp} = \frac{3.21 * 10^{-19} \frac{kg \cdot m^2}{V \cdot s^2}}{50nm \cdot 1m / 10^9 nm \cdot .1 * 10^{-3} \frac{kg}{m \cdot s}} = 6.4 * 10^{-9} \frac{m^2}{s \cdot V} \quad (5)$$

2. “For a given analyte, does the mobility change if the electric field is doubled?”

ANSWER: No, the mobility is a property solely of the analyte and characterizes the analytes’ ability to move in an electric field. While mobility will not change, its velocity will increase in large electric fields and separations will occur faster.

One level 3 question was asked of the teams.

“Design a microfluidic device that is able to mix two aqueous electrolyte streams using only patterned alternating wall surface charge to accomplish the task. Draw your device and label, then include explanations of what the flow profile will look like.”

While the level 3 problems were the most time intensive and hardest for which to judge team winners, the students who excelled on these questions were not usually the students who answered the level 1 questions that tended to be speed dependent. Also, it was interesting that all questions obtained from Peanut Gallery members for subsequent Survivor games were predominantly level 1 questions with a few level 2 questions and no level 3 questions.

### ACTIVITY 3: CURRENT NEWS AND ARCHIVAL JOURNAL ARTICLE DISCUSSIONS

This section of the class was modeled after the author’s research group’s weekly literature discussion class termed “Journal Club.”<sup>[2]</sup> Article discussions were intended to be a practice forum where one student would lead the class in a discussion of an article of his/her choosing. Undergraduate students were allowed to pull from popular news. Graduate students, however, could scan the science/technology news, but had to secure the archival journal article and present from that. When the student provided the article in advance, it was posted on MyCourses, an online proprietary virtual Blackboard Learning System.<sup>[23]</sup> No incentive or monitoring occurred to see if the other students read the articles in advance, however. The professor did keep track of questions asked and who participated in the discussion in order to give participation points, but strove to not control the progression of the discussion.

Given the number of students in class, each student presented approximately once every three weeks. The students were told that a significant part of engineering research is oral and written communication with tangible depth and conveyance of understanding. As a result, emphasis was placed on the clarity, organization, and understandability of the student’s presentation. It was strongly encouraged to present at the level of the audience such that an involved discussion could develop from the article.

Students were allowed to use any method of delivery they preferred. Most students utilized the document camera to project figures from their paper to the video projection screen. Some students prepared handouts to overcome the awkward maneuvering of the document camera and one student put presentations into PowerPoint.

An example of a linear electrokinetic article discussed was that by Amy Herr, "Electroosmotic Capillary Flow with Non-Uniform Zeta-Potential," published in *Analytical Chemistry* in 2001.<sup>[24]</sup> The student presenting enjoyed discussing the charge-modified capillaries and the creative use of caged fluorophores to image the changing electroosmotic flow profile.

#### ACTIVITY 4: SEMESTER CONCEPT DEVELOPMENT PROJECT

The skills that best serve graduates of engineering programs are not all learned from textbooks. Tangible skills that are harder to teach, but are essential to prepare students to be productive, technical, members of society, include problem-solving skills, information-filtering skills, and logic skills. The traditional classroom does not focus on these skills nor does it usually provide individual practice linking unique concepts together. This semester-long concept development project was a concerted effort to strategically develop these skills in the students enrolled in this course. This activity strove to push students to the highest level of learning in Bloom's Taxonomy.<sup>[23]</sup> This activity, above all others, demonstrated student mastery of material.

The assignment for the project teams was a large, open-ended, concept development project. The students were integrally involved in deciding the small-scale technology that they wanted to pursue that would help address an important biomedical application using either micro- or nanotechnologies. The concept was to build from both theoretical and experimental reported technologies in the realm of chemical, mechanical, optical, and biological analysis. Their resulting virtual microtechnology was to be a novel extension of published work. Upon completion of the project, each team member was expected to be able to conduct an extended discussion of the following topics and skills related to their project:

- *Review of pertinent technology from peer-reviewed publications*
- *Micro- and nanoscale forces acting within their micro / nano device*
- *Materials and methods utilized in their conceptual device (and why chosen)*
- *Why and how their project was novel from existing detection tools*

The output of the effort was to be a concept plan of a fully integrated biomedical technology. The concept was to be articulated in an archival journal paper and presented via a team oral presentation. Progress reports were due throughout

the semester and were designed to sequentially formulate the sections of the final archival journal article. The reports were a) description of proposed novel analytical microtechnology, b) complete literature review on the scientific premises of the proposed analytical microtechnology (> 10 references, fully discussed), c) prototype drawing and accompanying description of the analytical microtechnology, d) final device design and a first draft of complete final report, and e) final archival journal article. The professor provided feedback using a structured assessment template after each report. The student teams were to demonstrate significant improvements guided by this feedback in the final journal article.

The projects included:

1. "*Ricin Dosimetry via Lab-on-a-Chip Antibody-Mediated Detection*" by Daniel Barnes (Grad), Jennifer McCottrill (UG), Parisa Toghiani (UG), and David Quick (UG). *Castor oil from the castor plant is an economically important, international commodity. The castor seed contains around 50% oil by weight but grinding the seed releases an extremely toxic protein, ricin. Ricin has an LD50 of 3 to 5 µg/kg when inhaled, and there is no specific treatment for ricin poisoning. The device described in this paper is designed to detect airborne ricin particles and alert the wearer to the accumulation of dangerous levels in the atmosphere over the course of a 4-hour shift.*
2. "*Carbon Nanotubes as a Drug Delivery System*" by Kaela Leonard (Grad), Miranda Smith (UG), Jason Strunk (UG), and Roberto Velasquez (UG). *Osteosarcoma, bone cancer, is a rare form of cancer that attacks the bone tissue. This paper proposes a novel method specifically for patients suffering from osteosarcoma. Significant comfort and efficacy benefits for the patient are possible if drug delivery occurred directly to the affected area, and if the delivery system could be functionalized to attack only cancerous cells. By utilizing carbon nanotube technology, this paper outlines a plausible system, based upon existing advances reported in the literature, which would effectively deliver the chemotherapeutic drug while simultaneously providing structural reinforcement to the bone tissue remaining after surgery. Carbon nanotubes will be preloaded with micelles containing the anticancer drug cisplatin, which will then be released upon implantation in the bone, (and directed to any remaining cancer cells via folate functional groups on the micelle's outer surface).*
3. "*An Electric Field Gradient Focusing Method for Fluorescent Detection of Immunological Reactions*" by Aytug Gencoglu (Grad), Eric Rutan (UG), and Zach Wynne (UG). *A conceptual design is proposed for a novel microdevice that would be used for the investigation of immunological reactions between proteins found in body fluids and pathogens such as the flu virus is presented. The operation of the proposed microdevice would consist of two consequent phases. The first phase would be the separation of different proteins from a sample prepared from body fluids by electric field gradi-*

ent focusing (EFGF), where an electric field gradient would be formed within a square channel by the use of electrodes with varying potentials along the length of the channel. Control dyes would be used to determine the completion of the first phase. The second phase would be the contacting of the focused protein bands with the fluorescent tagged antigens and detection of reactions using fluorescence. This new technique could reduce the time required for the design of new drugs or vaccines, and could also be adapted to be used as a novel allergy testing technique.

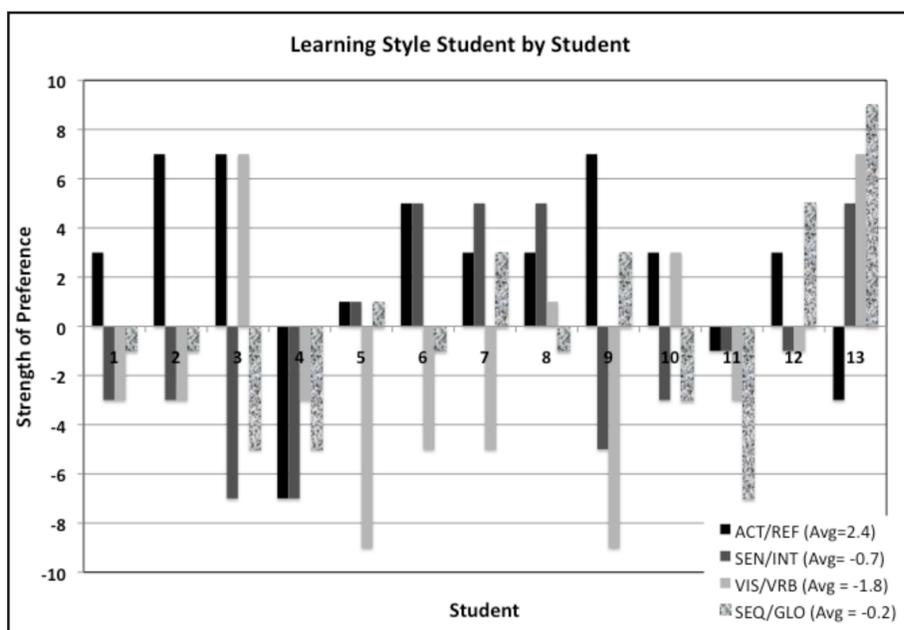
4. "Detection of Metastatic Breast Cancer: Prototype of a Rupturing Microdevice" by Sheena Reeves (Grad), Soumya S. Keshavamurthy (Grad), and Lekeith Terrell (UG). Earlier detection is recommended for preventing the spread of the disease especially for individuals who have had cancer previously. There have been many detection methods developed and explored by researchers over the past years; however, these methods are painful, intrusive, and time consuming for the patient. In this work, blood testing will be explored as a possible method for early detection of metastatic breast cancer. Cancerous cells are softer than the normal healthy cells as demonstrated by researchers. CTCs are found in the bloodstream and are obtainable for testing. Here, rupture rate of normal and cancerous cells will be used as a measure of detection. A device capable of rupturing the cells has been designed in order to quantify the rupture rate. A lab-on-a-chip system will be developed for faster and rapid diagnosis of breast cancer by using flow cytometer assembly with fluorescent markers for easy and early detection. The microdevice makes use of a channel, electrodes, an electric field generator, and flow cytometry. Normal cells rupture at a slower rate compared to cancerous cells since they are much harder than cancerous cells.

The topic ideas were brainstormed and developed by the students with guidance from the instructor. In the following section, the assessment of each of these activities is discussed.

## ASSESSMENT

Students' preferences for each class activity were assessed via a short survey on the final day of the course. The 11-question, instructor-derived survey

**Figure 2.** Learning style preferences for each student who completed the survey. Negative values indicate a preference towards the first of the two modalities. Non-weighted averages are provided in the legend labels.



and the 44-item Soloman-Felder questionnaire<sup>[11]</sup> were approved by MSU's Institutional Review Board (IRB) for the protection of human subjects; the 13 students present in class all signed the consent forms giving permission for their data to be included. The survey was designed to test the hypothesis that the class activity that each student most preferred was influenced by that individual's learning style.

The premise was that everyone has learning-style preferences<sup>[10, 25]</sup> that can be measured on a sliding scale between two extremes in four stages of learning: processing, perception, input modality, and understanding.<sup>[26]</sup> During processing, students favor either **active (ACT)** or **reflective (REF)** learning by introspectively thinking about material. In perception, **sensing (SEN)** learners focus on external input while **intuitive (INT)** learners focus on internal contemplation. Input modality preferences scale between **visual (VIS)** and **verbal (VRB)**. Lastly, learners can achieve understanding in **sequential (SEQ)**, linear logical steps or **globally (GLO)** where information is pieced together into a big picture.

To test this hypothesis, students were directed to the Soloman-Felder online learning styles inventory and asked to complete the 44 questions.<sup>[11]</sup> They then self-reported their scores on the written instructor-derived survey and proceeded to answer the remaining 11 survey questions. In Figures 2 through 4, which incorporate the student's learning style,

	Lecture	Survivor	Articles	Project
Average	7.7	6.5	8.2	8.5
Standard Deviation	1.5	1.3	1.5	1.3

the four stages of learning are reported as ACT/REF with a negative number indicating preference towards active learning while a positive number indicates preference towards reflective learning. The same nomenclature is used for SEN/INT, VIS/VRB, and SEQ/GLO.

Overall student-learning preferences are included in Figure 2 and are slanted towards reflective (REF) with an average of 2.4, slightly sensory (SEN) with an average of -0.7, more visual (VIS) than verbal (VRB) with an average preference of -1.8, and equally balanced between sequential (SEQ) and global (GLO). The SEQ/GLO average is slightly misleading as eight of the 13 students were sequential learners, but did not show as great a preference in this direction. Given that global learners historically have not been known to gravitate into engineering, this is an interesting distribution of students in this course.

The first question asked students to rank their most favorite to least favorite learning activity in this class. The activities were: lecture, Survivor game, article discussions, and concept design project. The most popular activity was the article discussions, which is interesting because this was the activity that students demonstrated the most apprehension over when the concept was introduced. While some students voiced dread over their turn to present, the remaining students became more engaged in the discussions as the semester progressed. Figure 3 cross-correlates the student's preferred class activity with their composite learning style (style preference is summative). The stronger active learners were skewed toward Survivor as the preferred activity (N=4 students) while the weakly active learners and reflective learners preferred the article discussions. Overall, sensory learners preferred article discussions while intuitive learners preferred Survivor. The stronger visual learners had a slight preference for Survivor over article discussions. Overall, global learners preferred article discussions while sequential learners preferred Survivor.

One individual chose lectures as the favorite class activity and their strongest preference was toward sequential. Lectures tended to be quite sequential in concept progression, while the article topics were undirected due to student's freedom of choice to obtain an article. In addition, the Survivor game questions were purposefully randomized.

Students were also asked to score how much they learned during each activity on a scale from 1 to 10 with 10 being "learned a great deal" and 1 being "learned very little." As demonstrated in Table 3, the students felt they learned the

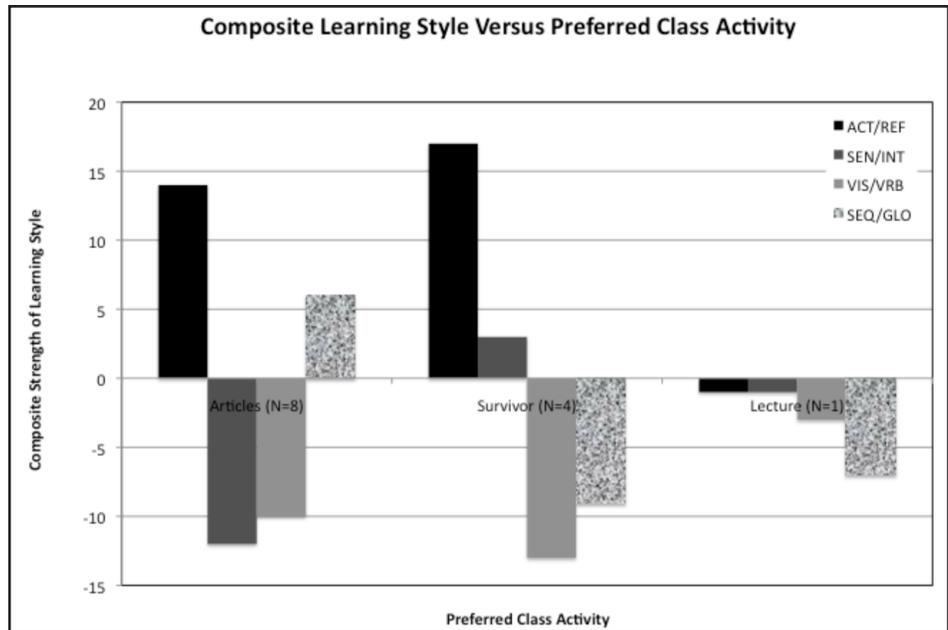


Figure 3. Composite (additive) learning style correlated with preference towards class activities.

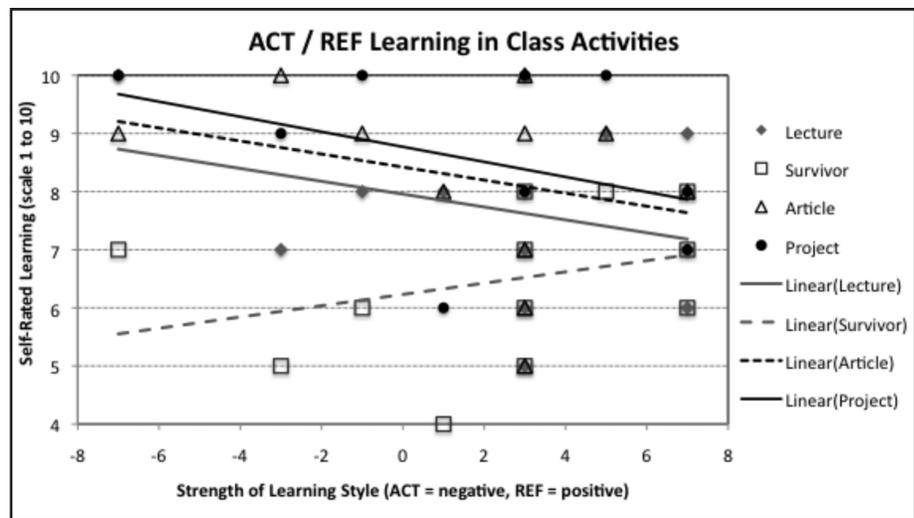


Figure 4. Student ratings of learning value of the four class activities (Lecture, Survivor, Article Discussions, Concept Design Project) cross-correlated with their Active-Reflective (ACT/REF) learning style preference. This trend is presented in line 1 of Table 4 using the normalized covariance.

most from their concept development project followed by their favorite activity—article discussions. The students learned the least from the Survivor game, but it should be noted that the average score here is still greater than neutral (5).

This critique of their own learning was cross-correlated with their learning style and is shown in Figure 4. Trend lines using a least squares method are added to guide the eye for an overall tendency. As shown, active learners felt they learned more from the project, article, and lecture than reflective learners. Reflective learners, however, felt they learned more from Survivor than the active learners, which is surprising given the learning mechanism this modality suggests. In all cases, all types of learners rated Survivor lowest as a learning tool.

Such trends can also be captured using a cross-correlation scheme such as the normalized covariance in a more concise form. For this reason, figures are not included for the other three learning styles and the data is in Table 4: sensory/intuitive (row 2), visual/verbal (row 3), and sequential/global (row 4). Students' learning style,  $l$ , was correlated with their course activity preferences,  $a$ , as follows:

$$C_{l,a} = \frac{\Sigma(1 - \bar{l})(a - \bar{a})}{\sqrt{\Sigma(1 - \bar{l})^2(a - \bar{a})^2}} \quad (6)$$

where  $\bar{l}$  and  $\bar{a}$  denote average learning-style preference and activity preference, respectively. This linear correlation provides an indicator normalized between -1 where the two data sets demonstrate a perfectly linear negative correlation, 0 where the data sets are uncorrelated, to +1 where the two data sets demonstrate a perfectly linear positive correlation. The results are presented in Table 4.

Learning style vs. activity correlations are not particularly strong and given the population size (13 respondents), the numbers could have been skewed by the response of an individual or two. Negative correlations in this case indicate a preference towards the first dimension of the learning style modality, while positive correlation numbers indicate a preference towards the second dimension. For example, intuitive learners and sequential learners equally liked the projects. Other notable trends include that visual learners felt they learned more than verbal learners from the lectures.

Students were also asked if there was a particular combination of learning activities that was instrumental in helping them learn. The two most common combinations mentioned were lecture / Survivor (by 4 of 13) and article / project (by 4 of 13). This result is not surprising given that lecture served to provide a foundation and the Survivor game was a mechanism for students to practice applying this knowledge. Similarly, the article discussions enabled the students to be efficient and use their article presentation to read and present on articles of use to their team concept design project.

**TABLE 4**  
Correlation of Students' Learning Style ( $l$ ) With Preferred Class Activity ( $a$ )

$l \backslash a$	Lecture	Survivor	Article	Project
ACT/REF	-0.29	0.32	-0.32	-0.42
SEN/INT	0.01	-0.14	0.17	0.23
VIS/VRB	-0.41	-0.27	-0.14	0.16
SEQ/GLO	-0.11	-0.10	0.08	-0.22

Newell's Survivor paper<sup>[1]</sup> discussed a model where students had four primary types of motivation. The original work describing this was Biggs and Moore in 1993.<sup>[27]</sup> They summarized the four types as: "**Intrinsic**—learning because of natural curiosity or interest in the activity itself; **Social**—learning to please the professor or peers; **Achievement**—learning to enhance position relative to others; and **Instrumental**—learning to gain rewards beyond the activity itself (better grades, increased likelihood of getting a high-paying job, etc.)" Students were asked to rate themselves against these four motivators on a scale from 1 to 10 with 10 being "very motivated by this" and 1 being "not motivated by this at all." On average, the students felt they were very intrinsically motivated ( $8.8 \pm 2$ ), fairly neutrally socially motivated ( $5.0 \pm 2.2$ ), a little more strongly motivated by achievement ( $6.5 \pm 1.9$ ), and even more strongly instrumentally motivated ( $7.8 \pm 1.5$ ). It should be noted that by directly asking students to rate their motivation, the results might be biased to higher numbers because of the tendency to consciously or subconsciously rate higher.

Student's motivation,  $m$ , was correlated with their preferences for each course activity,  $a$ , using the normalized covariance as follows:

$$C_{a,m} = \frac{\Sigma(a - \bar{a})(m - \bar{m})}{\sqrt{\Sigma(a - \bar{a})^2(m - \bar{m})^2}} \quad (7)$$

where  $\bar{a}$  and  $\bar{m}$  denote average of each activity and motivation, respectively. The results are presented in Table 5.

Intrinsically motivated students equally preferred Survivor and the concept development project. This preference is similar in instrumentally motivated students. Intrinsically motivated students, however, showed a slight preference for the article discussions with no correlation for the lectures while the instrumentally motivated students were the opposite. Most students felt they were not strongly motivated by social factors, which is likely the reason that negative correlations were observed for these against Survivor, article discussions, and the projects. The most surprising dimension of this is the negative correlation between social- and achievement-based motivations and Survivor, which suggests that those with a higher desire to please others and those who want to advance relative to others disliked Survivor. While the Survivor game

provides immediate feedback from the professor and peers, it also tends to favor extroverted individuals (personal observation) and extroversion/introversion is likely not correlated with a desire to please others.

## SUMMARY

A research-focused special topics course on Analytical Microdevice Technology was taught for the first time in Spring 2008 with four different class-learning activities. The activities were lectures, a Survivor game, article discussions, and a concept development project conducted in teams. While the students showed a strong preference towards the article discussions, most felt they learned the most from the projects.

Correlations with student learning styles were compiled and demonstrated that while students have a preference for certain activities, learning is possible with all activities as demonstrated by quantitative learning rankings greater than neutral. Overall, the students rated themselves as intrinsically and instrumentally motivated. Grades were de-emphasized in this course, yet student participation by all except one student was greater than the professor has seen in core chemical engineering courses she has taught. The population size was rather small (13 completed the surveys), yet interesting trends suggest learning merits in each of the four class activities.

Any individual interested in implementing these strategies or who would like course preparation materials may contact the author. The findings from this study can guide future implementations of this course by increasing time dedicated to those activities that most promote student learning. In order, they are projects,<sup>[4]</sup> articles,<sup>[2,3]</sup> and lecture. While the Survivor game was not rated as high in terms of learning merit, it was still rated higher than average (6.5 on a 10-point scale) and should remain included to complement the lectures and to introduce an element of fun into the course. In general, the inclusion of diverse learning tools into a single course is beneficial because one tool isn't sufficient to fully engage students of all learning styles.

## ACKNOWLEDGMENTS

The author would like to acknowledge funding support from the National Science Foundation (CBET 0644538) as well as the hard work and enthusiasm of the students enrolled in this course.

a \ m	Intrinsic	Social	Achieve	Instrument
Lecture	0.01	0.02	0.19	0.25
Survivor	0.64	-0.29	-0.43	0.49
Article	0.18	-0.66	0.03	0.05
Project	0.64	-0.44	0.04	0.62

## REFERENCES

- Newell, J.A., "Survivor: Classroom. A Method of Active Learning That Addresses Four Types of Student Motivation," *Chem. Eng. Ed.*, **39**(3), 228 (2005)
- Minerick, A.R., "Journal Club: A Forum to Encourage Graduate and Undergraduate Research Students to Critically Review the Literature," New Engineering Educators Division - American Society of Engineering Education *Proceedings*, (June 2006)
- Hill, P.J., "Teaching Entering Graduate Students the Role of Journal Articles in Research," *Chem. Eng. Ed.*, **40**(4), 228 (2006)
- Minerick, A.R., and G.T. Thibaudeau, "Use of Concept Development Projects in Science and Engineering Courses," American Society of Engineering Education Southeast Section *Proceedings* (April 2009)
- Maase, E.L., and K.A. High, "Active Problem Solving and Applied Research Methods in a Graduate Course on Numerical Methods," *Chem. Eng. Educ.*, **42**(1), 23 (2008)
- Harrison, R.G., M.U. Nollert, D.W. Schmidtke, and V.I. Sikavitsas, "The Research Proposal in Biomechanical and Biological Engineering Courses," *Chem. Eng. Ed.*, **40**(4), 228 (2006)
- Krantz, W.B., "Membrane Science and Technology in the 21st Century," *Chem. Eng. Ed.*, **38**(2), 94 (2004)
- Lipscomb, G.G., "A Compendium of Open-Ended Membrane Problems in the Curriculum," *Chem. Eng. Ed.*, **37**(1), 46 (2003)
- Newell, J.A., S.H. Farrell, R.P. Hesketh, and C.S. Slater, "Introducing Emerging Technologies into the Curriculum Through a Multidisciplinary Research Experience," *Chem. Eng. Ed.*, **35**(4), 296 (2002)
- Felder, R.M., and L.K. Silverman, *Engr. Education*, **78**(7) 674 (1988)
- Soloman, B.A., and R.M. Felder, "Soloman-Felder Learning Styles Questionnaire," <<http://www.engr.ncsu.edu/learningstyles/ilsweb.html>> Accessed Sept. 22, 2008
- Israelachvili, J., *Intermolecular and Surface Forces: Second Edition*, Academic Press, San Diego (1992)
- Probstein, R.F., *Physicochemical Hydrodynamics: An Introduction*, 2nd Ed., Wiley-Interscience Publication, New York (1994)
- Rathore, A.S., and A. Guttman, *Electrokinetic Phenomena*, Marcel Dekker, New York (2004)
- Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, 2nd Ed., Wiley, New York (2002)
- Fournier, R.L., *Basic Transport Phenomena in Biomedical Engineering*, Taylor & Francis, Philadelphia (1999)
- Truskey, G.A., F. Yuan, and D.F. Katz, *Transport Phenomena in Biological Systems*, Pearson Prentice Hall, Upper Saddle River, NJ (2004)
- Li, D., *Electrokinetics in Microfluidics in Interfacial Science and Technology V. 2*, Elsevier, Amsterdam (2004)
- Morgan, H., and N.G. Green, *AC Electrokinetics: Colloids and Nanoparticles in Microtechnologies and Microsystems Series*, Research Studies Press, Baldock (2003)
- Delgado, A.V., *Interfacial Electrokinetics and Electrophoresis in Surfactant Science Series V. 106*, Marcel Dekker, New York (2002)
- Webster, J.G., *Bioinstrumentation*, John Wiley & Sons (2004)
- Krathwohl, D.R., B.S. Bloom, and B.B. Masia, *Taxonomy of Educational Objectives, the Classification of Educational Goals. Handbook II: Affective Domain*, New York: David McKay Co., Inc. (1973)
- Blackboard Learning Systems, <<http://www.blackboard.com/>>, Accessed Nov. 5, 2009
- Herr, A.H., J.I. Molho, J.G. Santiago, M.G. Mungal, T.W. Kenny, and M.G. Garguilo, "Electroosmotic Capillary Flow with Non-Uniform Z-Potential," *Analytical Chemistry*, **72**(5) 1053 (2001)
- Felder, R.M., "Matters of Style," *ASEE Prism*, **6**(4) 18 (1996)
- National Effective Teaching Institute (NETI), in cooperation with American Society of Engineering Education, <<http://www.ncsu.edu/felder-public/NETI.html>>, Accessed July 19, 2005
- Biggs, J., and P.J. Moore, *The Process of Learning*, Prentice Hall, Englewood Cliffs, NJ (1993) □

# Using Aspen to Teach Chromatographic Bioprocessing: A CASE STUDY IN WEAK PARTITIONING CHROMATOGRAPHY for Biotechnology Applications

STEVEN T. EVANS,<sup>1</sup> XINQUN HUANG,<sup>2</sup> AND STEVEN M. CRAMER<sup>1</sup>

*1 Rensselaer Polytechnic Institute • Troy, NY 12180*

*2 Covidien • St Louis, MO, 63132*

Course projects are an effective way to focus students' attention<sup>[1]</sup> as students learn best when they become actively involved in solving problems.<sup>[2]</sup> Properly chosen projects can serve to prepare engineering undergraduates for industrial settings where specialized process simulators (e.g., Aspen Plus, CHEMCAD, HYSIM, and PROSIM) are used extensively.<sup>[3-6]</sup> Steady-state process simulators in separations and/or design courses are already used in most chemical engineering departments.<sup>[7, 8]</sup> Recently, programs such as Aspen Chromatography allow students to model and solve liquid-phase ion exchange systems that are often operated as unsteady-state processes. Commercial simulators model these sorption processes through the solution of partial differential equations governing heat and mass transfer and algebraic equations describing equilibrium and pressure drop.<sup>[3]</sup>

Many chemical engineering students enter the field of biotechnology and bioprocessing where they are confronted with difficult purification challenges. Monoclonal antibodies represent a large percentage of new biopharmaceuticals and those currently in clinical trials. This important class of proteins often requires several downstream processing steps including: clarification, protein A chromatography, anion exchange chromatography followed by hydrophobic interaction chromatography (or cation exchange chromatography), virus filtration, and finally, ultrafiltration or diafiltration.<sup>[9]</sup> The elimination of even one of these steps can significantly reduce operating costs.

The recent use of weak partitioning chromatography (WPC) in the downstream processing of antibodies by Wyeth BioPharma (Andover, MA) has generated significant attention.<sup>[10-12]</sup> In that process, WPC is employed to purify monoclonal antibodies in anion exchange systems as part of a two-column separation platform (with Protein A chromatography) as compared to traditional three-column separation platforms. WPC is an isocratic chromatographic protein separation method performed under mobile phase conditions where the product

**Steven Evans** received his chemical engineering and chemistry B.S. degrees from the University of California, Irvine, his M.S. from the University of Wisconsin-Madison in chemical engineering, and completed his Ph.D. in chemical engineering at Rensselaer Polytechnic Institute. He joined MedImmune in Gaithersburg, MD, as process biochemistry scientist in the summer of 2009.

**Xinqun Huang** received his B.S. and M.S. from East China University of Science and Technology in chemical engineering and his Ph.D. in chemical engineering from Rensselaer Polytechnic Institute. He is currently a process engineer at Covidien in St. Louis, MO.

**Steven Cramer** received his B.S. from Brown University in biomedical engineering and his M.S. and Ph.D. in chemical engineering from Yale University. He is currently the William Weightman Walker Professor at Rensselaer Polytechnic Institute. In addition to regularly teaching undergraduate and graduate Separations and Bioseparations courses he is also the editor of the journal Separation Science and Technology. His research interests include: design of chemically selective displacers for protein purification; multi-scale modeling of complex chromatographic behavior; molecular modeling of selectivity and affinity in mixed model chromatographic systems; spectroscopic/chromatographic investigation of protein-surface interactions; chromatography on a chip; novel separation systems for proteomics; high-throughput screening for bioprocess development; and chemometrics for process analytical technology.

protein binds weakly to the resin, in contrast to flowthrough operations<sup>[12]</sup> where no binding of the product protein occurs. A major advantage of WPC is that it can enable significantly stronger binding of impurities, resulting in improved purification as compared to the flowthrough mode of operation.<sup>[12]</sup> In addition, product losses are reduced by loading larger amounts of product. Finally, a short wash step can also be employed to attain even higher purity and resin capacity using WPC.

In this paper we describe a project that was used in an advanced chromatographic separations course (15 weeks long, offered every Spring term) taught to senior undergraduate students and graduate students for the past three years. The biotechnology-related separations challenge was derived from the WPC work presented by S. Vunnum<sup>[10]</sup> at the 2006 national American Chemical Society conference and recently published in several papers.<sup>[11-16]</sup> Many of the details of using the commercial simulator employed (Aspen Chromatography) and teaching courses with simulators integrated into lectures have been reported previously.<sup>[3,8]</sup> The course project described in this paper was designed to instruct the students in basic simulator operation and to enable them to apply course material to an important separation challenge from the biotechnology industry.

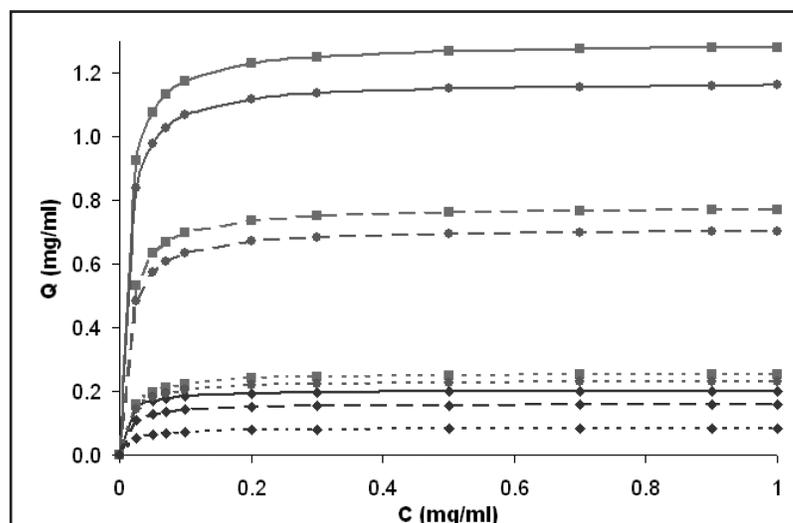
## 2. THE PROJECT

**2.1 Learning Objectives:** The specific learning objectives<sup>[17]</sup> for this project were as follows:

At the end of this project students should be able to 1) generate and interpret adsorption isotherm and partition coefficient plots, 2) use a simulation tool for chromatographic modeling, 3) explain the subtleties of a novel mode of chromatography (WPC) through varying calculations and simulations, 4) illustrate the benefit of fractional factorial simulations as a tool for directing experiments, and 5) apply their chromatographic simulation and optimization experience to modeling other separation processes.

**2.2 Project Goal:** The students were instructed that their goal was to optimize the product yield (recovery) associated with the anion exchange step while satisfying several constraints. The feed mixture for this system consisted of a therapeutic monoclonal antibody (product) and two compounds representing typical impurities in these biological mixtures (e.g., nucleic acids, endotoxins, viruses, or host cell proteins). These impurities are in general more strongly bound than the product of interest under anion exchange

**Figure 1.** Adsorption isotherms for the product (◆), impurity 1 (●), and impurity 2 (■). Isotherms are given for varying NaCl concentrations of 190 (dotted lines), 200 (dashed lines) and 225 mM (solid lines).



chromatographic conditions.<sup>[12, 18, 19]</sup> The process must result in a product yield greater than 90% while satisfying a 95% purity constraint. Further, the process must maximize the production rate (amount purified per unit time) and be accomplished in less than eight hours (typical work shift).

**2.3 Overview:** This project is based on a recent publication describing the WPC process.<sup>[12]</sup> Students were introduced to key WPC concepts, provided with batch adsorption data, instructed to plot adsorption isotherms, and then required to generate partition coefficient plots. Aspen Chromatography was then employed to guide the students through specific column simulations (varying feed loading volume and salt counter-ion concentration). Students were then charged with the open-ended task of optimizing this separation through simulations varying parameters of their choosing (factorial simulation).

**2.4 Introducing Students to the Problem:** The students were given extensive equilibrium adsorption data for the product and the impurities at three different salt concentrations, some of which are shown in Figure 1 as symbols. They were then asked to fit the isotherm data to an extended Langmuir isotherm with counter-ion dependence [Eq. (1)]. This isotherm is readily available in Aspen Chromatography and was chosen for its ability to represent nonlinear chromatographic behavior at different salt concentrations.

$$Q_i = \frac{(IP_{1i}) \exp[-(IP_{2i})(c_b)] (IP_{3i}) \exp\left[\frac{IP_{4i}}{c_b + IP_{5i}}\right] (C_i)}{1 + \sum_{k=1}^{nc} (IP_{3k}) \exp\left[\frac{IP_{4k}}{c_b + IP_{5k}}\right] (C_k)} \quad (1)$$

In this isotherm equation  $Q_i$  is the amount of solute  $i$  bound to the stationary phase and  $C_i$  is the amount of solute  $i$  in the mobile phase. The five isotherm parameters are represented by  $IP_{1i}$  through  $IP_{5i}$  for each solute  $i$ ,  $c_b$  is the salt counter-ion

concentration in the mobile phase, and  $C_k$  in the denominator summation is the mobile phase solute concentration for all solutes (except the salt counter-ion, b).

Once the isotherm plots were generated and the isotherm parameters of the product and the two impurities were obtained, the students were then instructed to determine the effect of varying salt concentration (counter-ion,  $c_b$ ) upon these isotherms. Adsorption isotherms for counter-ion concentrations of 190 (dotted lines), 200 (dashed lines) and 225 mM (solid lines) are shown in Figure 1. The diamonds represent the product, the circles represent impurity 1, and the squares represent impurity 2. The students were asked to comment upon the relative binding affinity of the solutes, how the affinity of each solute changes with the salt concentration, and what their initial thoughts on possible separation strategies might be. Additionally the students were asked to comment on the salt concentration at which the isotherms of all of the solutes begin to overlap corresponding to conditions that would make it very difficult to separate the product from the impurities. For the data given in this problem a salt concentration of 270 mM was sufficient to compress the isotherms such that any process separation would be difficult. Figure 1 and all of the other figures presented in this text are representative of typical student work.

**2.5 Partition Coefficient Plot and Weak Partitioning Chromatography:** The generation of partition or distribution coefficient plots served to introduce students to the WPC mode of chromatographic separation. The partition coefficient [Eq. (2)] is defined as the ratio of solute bound to the stationary phase (Q) to that in the mobile phase (C) as the concentration in the mobile phase approaches zero (corresponding to the linear regime of the isotherm). The calculation of partition coefficient values is straightforward using the isotherm [Eq. (1)] with the fitted parameters.

$$K_p = \left( \frac{Q}{C} \right)_{C \rightarrow 0} \quad (2)$$

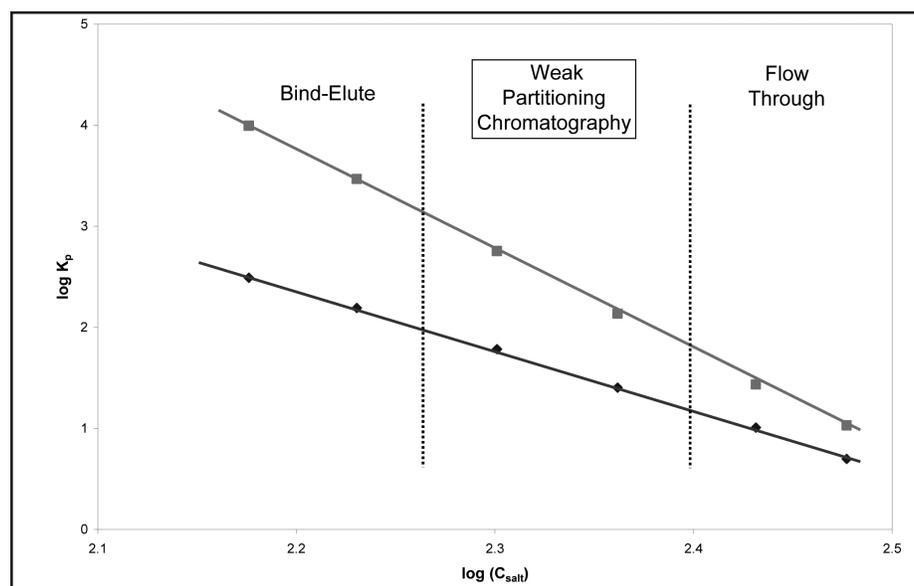
A partition coefficient plot is a log-log plot of  $K_p$  vs.  $C_{\text{salt}}^{[12]}$ . A representative student-generated plot is shown in Figure 2 for the product and most highly retained impurity (note: in this plot the salt concentration ranged from 150 to 300 mM).

To help the students interpret this plot they were informed that protein ion exchange separations are typically operated as either 1) bind-elute or 2) flowthrough separations. For bind-elute separations the product  $K_p$  is high under the column loading condition (often  $>100$ ) while for flowthrough separations the product  $K_p$  is low (usually  $<0.1$ ). WPC separations define the regime in this plot that lies between bind-elute and flowthrough separations. Typical  $K_p$  values for WPC range from 0.1 to 20.

Each of these separation modes (bind-elute, flowthrough, and WPC) has distinct advantages and disadvantages. The choice of chromatographic operation depends upon the solutes in a particular system. Students were instructed to comment on the trends observed in their partition coefficient plots at both high and low counter-ion salt concentrations. They were also asked to rate the potential utility of these three separation modes for this particular feed mixture. This enabled the students to learn about the behavior of WPC as compared to more traditional modes of chromatography and satisfied learning objective 3.

**2.6 Preliminary Project Student Reports:** Prior to employing Aspen Chromatography the students were required to write preliminary reports that included the following: plotted adsorption isotherms, fitted isotherm parameters, isotherms at varying salt concentrations, partition coefficient plots, and written responses to the various fundamental and applied questions mentioned above. These reports should have a detailed discussion of the isotherm and partition coefficient plots and should include the following observations: i) the product is always the least strongly bound component of the feed mixture under all salt conditions, ii) as the salt concentration was increased, the relative decrease in the amount of product bound was less than that observed for the impurities, iii) superior separations may be possible at higher

concentrations of the product and impurities. The plot shows three regions: Bind-Elute (left), Weak Partitioning Chromatography (middle), and Flow Through (right). The product (diamonds) and impurity 2 (squares) show a decreasing trend in  $\log K_p$  as  $\log(C_{\text{salt}})$  increases. The impurity 1 (circles) shows a similar trend but is consistently lower than the other two species.



**Figure 2.** A representative partition coefficient plot<sup>[12]</sup> of  $\log K_p$  versus  $\log C_{\text{salt}}$  for the product ( $\blacklozenge$ ) and the most highly retained species, impurity 2 ( $\blacksquare$ ) for NaCl concentrations ranging from 150 to 300 mM.

Isotherm Parameters	Product	Impurity 1	Impurity 2
1	33.87	66.09	70.55
2	25.56	3.13	3.02
3	7.58	1.16	1.13
4	0.48	2.39	2.40
5	0	$1.08 \times 10^{-3}$	$9.93 \times 10^{-4}$

salt concentrations, and iv) flowthrough or WPC modes of chromatography may result in improved ion exchange chromatographic processes. These exercises served to meet the first and third learning objectives.

Isotherm parameters (Table 1) were then given to students to compare with their obtained values and for use in Aspen Chromatography.

Data and insight gathered were then used in the Aspen Chromatography simulation platform for optimizing this anion exchange separation. From this point forward, each student was told to use the isotherm parameters provided by the instructor (note: the use of inappropriate isotherm parameters could result in simulator non-convergence since solute profiles can become quite steep for these nonlinear isotherms<sup>[3]</sup>). Students were then introduced to the commercial simulator through a hands-on computer laboratory lecture.

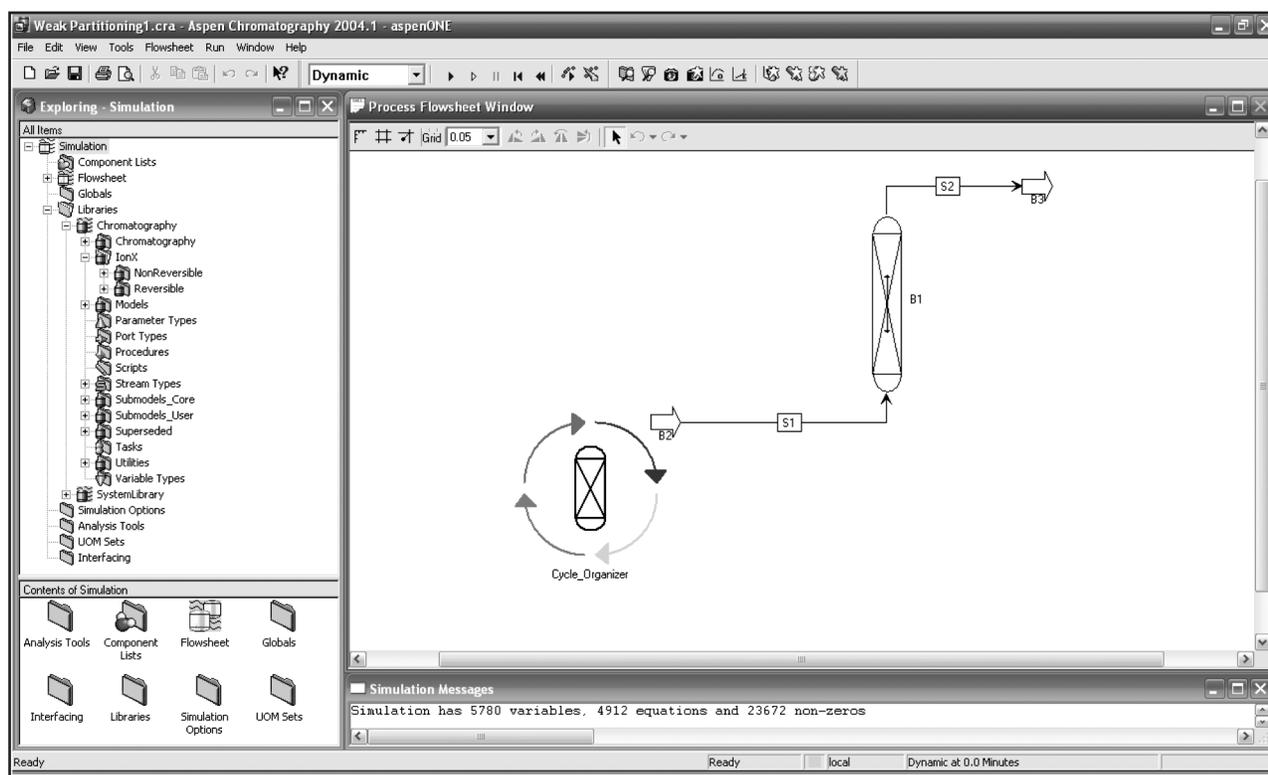
Example problems were reviewed with the students under the guidance of the instructor. In this classroom environment the instructor was able to visit with each student and address the individual questions raised.

### 3. ASPEN CHROMATOGRAPHY

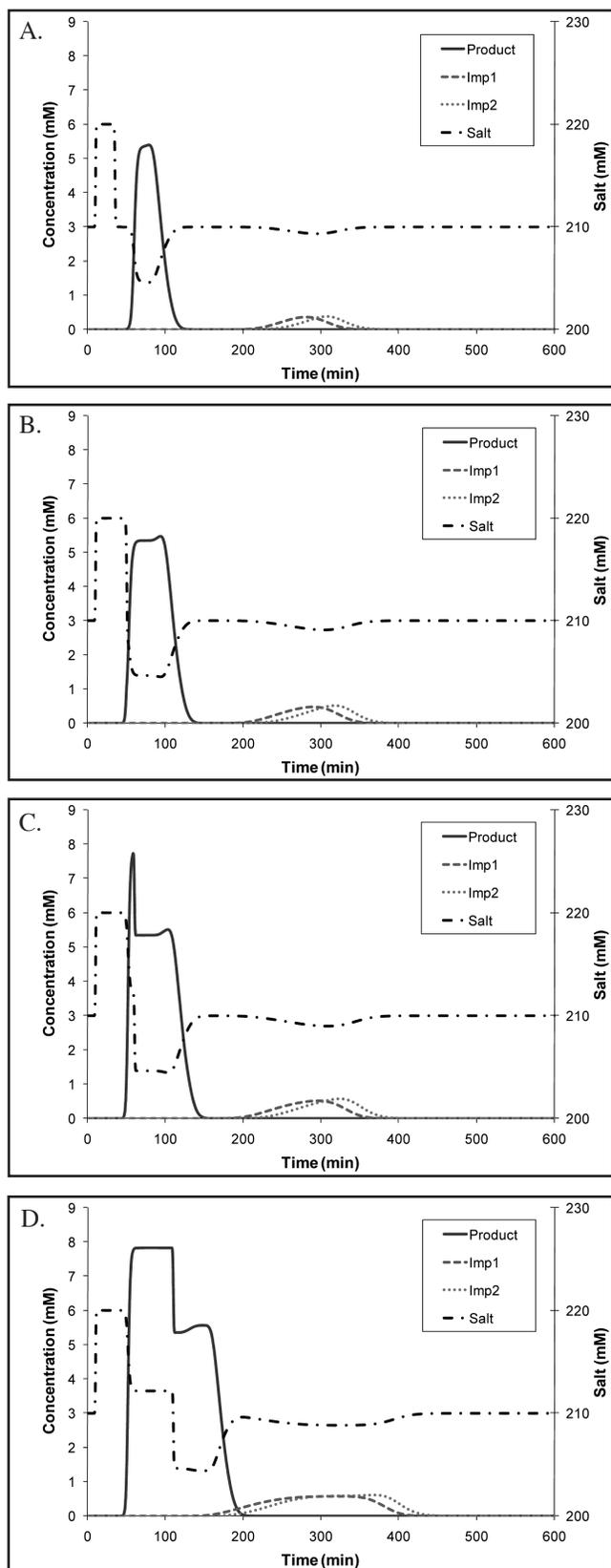
**3.1 Process Flowsheet:** The Aspen Chromatography software was used to generate a model using the isotherm parameters and column properties given below along with appropriate Solver Properties (note: representative solver properties are given in the appendix for those unfamiliar with Aspen). While the commercial simulator has been described in detail elsewhere<sup>[3,8]</sup> it is instructive to briefly introduce it here.

The Templates and Demonstrations given in the Aspen software package are useful for gaining familiarity with the simulation platform. Clicking on “File” then “Template” or “Demonstration” loads process flowsheets for sample problems already stored within the Aspen chromatography simulator. There are brief descriptions of each example flowsheet. After running the simulation, results can be viewed by selecting “Tools,” “Report,” and then “Chromatography\_Report.” These Template and Demonstration files help the user get acquainted with the simulation platform and are easily adapted to a range of other separation problems.

For the students to construct their flowsheets with corresponding models (Figure 3) they were also instructed on how to use the Cycle Organizer. By clicking on appropriate



**Figure 3.** Aspen Chromatography graphical user interface and representative flowsheet.



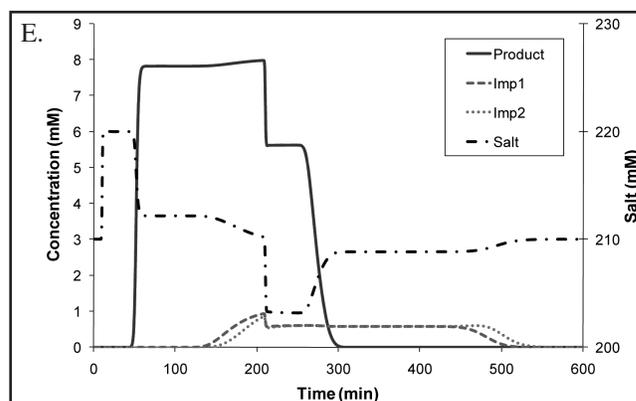
**Figure 4, A through E.** Simulated chromatograms for separations with varying feed volumes at constant inlet NaCl concentration of 210 mM (dash-dot line), flow rate (10 ml/min), and feed concentrations [8 mM product (solid line), 1 mM impurity 1 (dashed line), 1 mM impurity 2 (dotted line)]. Feed loading varied from a) 25, b) 40, c) 50, d) 100, and e) 200 minutes.

directories in the “Exploring-Simulation” window on the left side of Figure 3, they can readily construct the flowsheet and assign appropriate models (e.g., *ionx\_r\_feed*, *ionx\_r\_column*, and *ionx\_r\_product*) to the column.

**3.2 Simulation Parameters:** For the purpose of the simulations a liquid chromatography column (length = 40 cm, Inner Diameter = 2 cm) with a stationary-phase resin (the same used for generating the batch adsorption data and determining the isotherm parameters) having the following properties was used: inter-particle voidage of 0.40, intra-particle voidage of 0.70, bed capacity of 30 M, and 50 micron radius spherical particles.

The following simulation assumptions were used: liquid viscosity of 1 cP, spherical stationary phase resin particles having  $S_{Fac} = 1$  (measure of particle uniformity), constant mass transfer coefficients (MTC) of  $100,000 \text{ min}^{-1}$  for the solutes, material balances assuming convection with dispersion based upon plate numbers (400 plates for the counter-ion and 150 plates for each solute), a solid film model assumption, and a linear lumped resistance kinetic model assumed. The simulations were set to allow varying pressure with constant velocity for the “Pressure Assumption.” The “BUDS” partial differential equation discretization method with 100 nodes was sufficient for the calculations.

Initially the students were instructed to use a feed loading time of 25 minutes and a flow rate of 10 ml/min (about 2 column volumes). The concentrations of the product and impurities in the feed mixture were set to 8 mM product, 1 mM impurity 1, and 1 mM impurity 2. While it is a good assumption that the product comprises between 90-95% of the WPC feed, the product and impurities concentration values were chosen for ease of illustration during instruction. The feed stock counter-ion concentration was always set equal to that of the column running buffer for each WPC simulation as these separations are carried out under isocratic conditions. Through this hands-on computer laboratory lecture the students were then able to independently run Aspen, satisfying learning objective 2.



**3.3 Factorial Simulations:** After appropriately configuring the process flowsheet factorial simulations were employed to optimize the separation. Factorial simulations allow for the study of a given factor's effect upon a response variable as well as interactions between factors. If the number of experiments for a full factorial design is too high, a fractional factorial design may be performed in which some of the possible combinations (usually at least half) are omitted.

As outlined above the process specifications required 90% or greater product recovery (yield) with at least 95% purity. The optimal separation processes should maximize the product purified per unit time while not exceeding a typical eight-hour shift limitation. The students were required to perform factorial simulations using the Aspen Chromatography simulator to vary the feed loading volume and salt concentration in the column running buffer. Further parameters (feed concentration and flow rate) can also readily be examined and were included as an extra-credit option in the present form of this project. Students were initially instructed to approach the problem in an explicitly outlined manner and later asked to optimize the process through more "open-ended" questions.

**3.3.1 Varying Column Loading Volume:** The following simulations were aimed at instructing the students of WPC separation subtleties and illustrating the benefit of factorial simulations, addressing learning objectives 3 and 4. The first process variable the students were asked to study was the effect of the feed loading volume upon the product production rate. Constant pH, salt (210 mM), flow rate (10 ml/min), and feed concentrations (8 mM product, 1 mM of each of the two impurities) were used. For each simulation the salt concentration in the loading buffer was set equivalent to the running buffer. Simulations using feed loading times of 25, 40, 50, 100, and 200 minutes were required of the students. Results from these simulations are shown in Figure 4 A-E. In these figures the concentration (mM) of the product (solid line), impurity 1 (dashed line), and impurity 2 (dotted line) are given on the left hand y-axis, the salt (dash-dot line) concentration (mM) is given on the right hand y-axis, and the separation time is given on the x-axis (minutes).

Figure 4A shows the WPC separation for a feed loading time of 25 minutes. In this plot an induced salt wave is observed early in the chromatogram due to the desorption of salt during solute binding. The product does not reach its plateau concentration and there is sufficient resolution between the product and each of the two impurities that would allow the process engineer to further increase the feed loading time while still satisfying the constraints on the process.

As the feed loading times increased (Figures 4 B-E) the product peak began to broaden (Figure 4B, 40-minute feed load) and develop a spike (Figure 4C, 50-minute feed load). This spike is due to the competitive binding of the induced salt wave and the product.<sup>[20]</sup> Further increases in the feed loading time to 100 minutes resulted in broadening of the concentra-

tion spike into a two-step concentration breakthrough of the product (Figure 4d). Under these conditions, however, the product began to overlap with the impurities adversely affecting the yield and productivity. A further increase in the feed loading time to 200 minutes (Figure 4e) resulted in greater product losses due to overlap with the impurities.

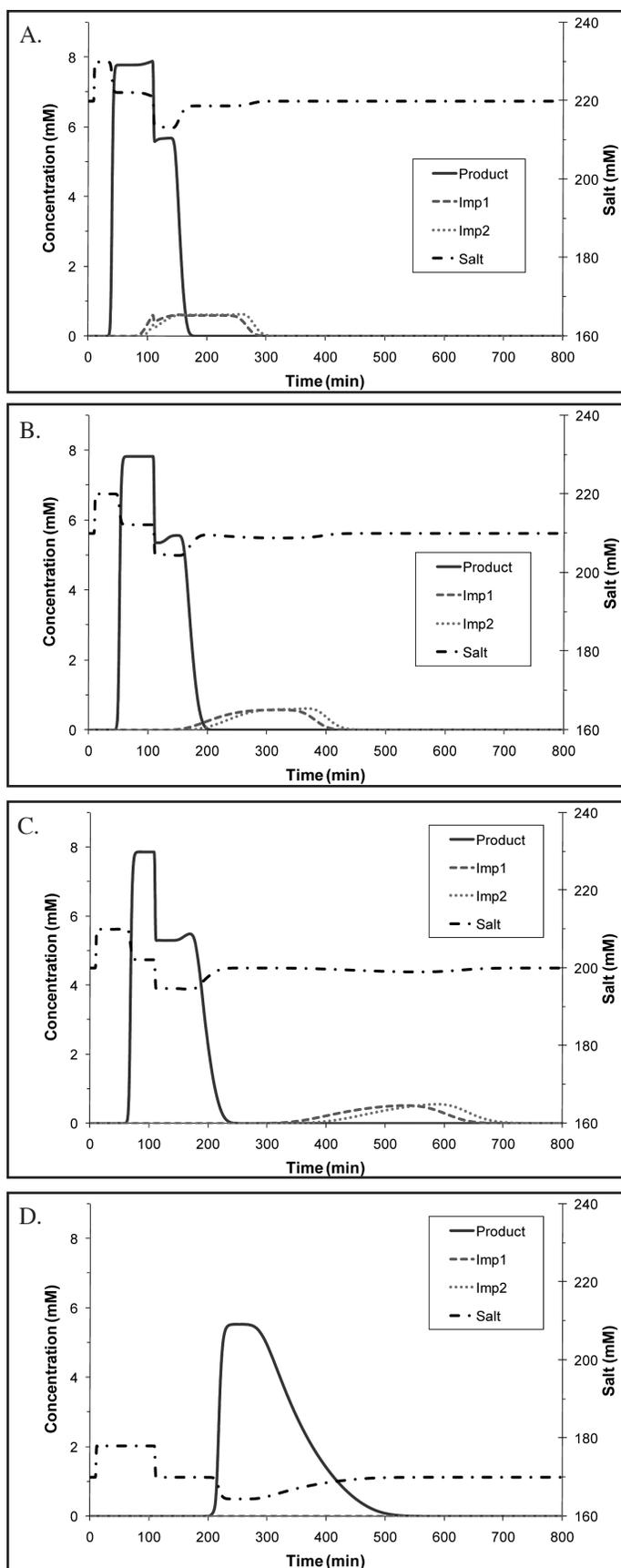
From this set of simulations the students should have noted that there exists an optimum WPC feed loading time for a given salt concentration. Loading times that were too small under-utilize the column capacity available while larger loading times eventually suffer from product losses.

**3.3.2 Varying Salt Concentration:** The students were instructed to study the effect of varying the salt concentration under which the WPC separations are performed. Simulations at specific salt concentrations (220, 210, 200, and 170 mM NaCl) were required of the students. Figures 5 A-D (next page) show chromatograms for these simulations that were performed using a feed loading time of 100 minutes (note: this feed load corresponded to the conditions where the product began to overlap with the impurities in Figure 4). Students were asked to comment on the changes observed for these parametric WPC simulations (breakthrough times of the product and impurities, time required for the entire separation, shapes of the peaks obtained, etc).

As the salt concentration is increased to 220 mM (Figure 5A) and above, the separation becomes more of a flowthrough operation with product yield diminished due to early eluting impurities. In fact, this illustrates the potential advantage of WPC over more commonly used flowthrough operations. As the salt concentration is decreased (Figures 5 B-C) WPC becomes the dominate mode of separation with increased resolution between the product and impurities. At 200 mM salt complete separation is achieved between the product and the impurities even at this elevated feed load of 100 minutes. Further decrease in salt concentration to 170 mM (Figure 5D) resulted in even greater separation between the product and impurities at the cost of significantly longer separation times. A typical shift time for workers in a manufacturing plant (eight hours) would make such long separation processes impractical. Further decrease in the isocratic operating salt concentration would result in product  $K_p$  values characteristic of bind and elute separations. Clearly, as with the feed loading time, there exists an optimum salt concentration for performing WPC separation of a given feed stock.

These simulations illustrated the benefits of factorial simulations and enabled students to learn about the behavior of WPC as compared to more traditional modes of chromatography, satisfying learning objectives 3 and 4.

**3.3.3 Fractional Factorial Simulations:** Data from preliminary project reports along with the parametric simulations carried out (Figures 4 and 5) now positioned the students to solve the open-ended task of optimizing this separation. The



students were asked to use the Aspen Chromatography simulator to determine the optimum separation conditions (maximized product yield per unit time for a given purity constraint) for this system which did not exceed an eight-hour shift limitation typical in industrial settings. Results from a systematic fractional factorial design approach varying the feed loading volume (11 discrete values) and salt concentration (5 discrete values) are outlined below.

The maximum productivity for the system is given by Eq. (3) where  $T_{\text{Total}}$  is the total run time for a given column separation,  $M$  is the amount of product protein loaded (*i.e.*,  $V$  times  $C$ , where  $V$  is the volume and  $C$  is the concentration of protein loaded). Regeneration and re-equilibration times are not included in this since it is expected that these will be the same for all WPC processes for a given feed/column system. Eq. (3) can be rewritten in the form of Eq. (4) where  $F$  is the volumetric flow rate and  $T_{\text{loading}}$  is the feed loading time.

$$f = \frac{M}{T_{\text{Total}}} \quad (3)$$

$$\max : f = \left( \frac{(T_{\text{loading}}) \times (F) \times (C)}{T_{\text{Total}}} \right) \quad (4)$$

The decision variables that can be used to maximize this objective function are the flow rate, feed loading time, concentration of the feed components, and the salt concentration used for the separation. The students were not given explicit separation conditions for these separations but were allowed to vary the parameters as they saw fit as long as the constraints were satisfied.

Simulations performed under these various conditions were then used by the students to produce graphs of the productivity (mass of product per time) as a function of feed loading volume and salt concentration (Figure 6). In this representative productivity bar graph, the data represented by unfilled bars (purity) and half-filled (shift time) did not satisfy the constraints, while the other data (full bars) did.

From this analysis, the students were then asked to select the optimal operating conditions for the purification of this product from the impurities. For example in Figure 6 the optimum result would correspond to a salt concentration

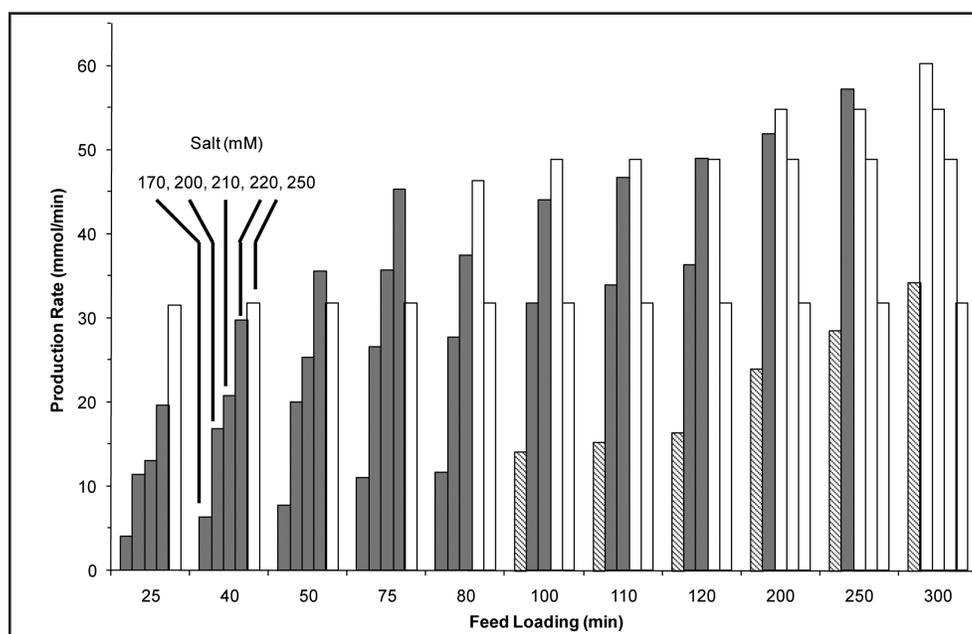
**Figure 5, A through D (all, left).** Simulated chromatograms for separations with varying NaCl concentrations (dash-dot line) at constant feed loading time (100 min), flow rate (10 ml/min), and inlet feed concentrations [8 mM product (solid line), 1 mM impurity 1 (dashed line), 1 mM impurity 2 (dotted line)]. Salt counter-ion concentrations were: a) 220, b) 210, c) 200, and d) 170 mM NaCl.

of 200 mM and a feed load time of 250 minutes. Students were also required to submit representative simulations results illustrating the trends observed in their data and to comment upon how the optimal conditions were obtained. Additionally the students were asked to comment upon the separation conditions for which the constraints were not met. Finally, inspired students were encouraged to take their analysis further by investigating the effect of varying the concentration of the feed components (keeping the relative concentrations constant) and the flow rate (using appropriately modified mass transport coefficients) on the productivity of WPC separations.

#### 4. PROJECT ASSESSMENT

In this section we summarize how learning objectives were satisfied, provide student feedback to various aspects of the project, and provide guidance upon how instructors can assess students through this project. The specific learning objectives<sup>[17]</sup> for this project were as follows: At the end of this project students should be able to 1) generate and interpret adsorption isotherm and partition coefficient plots, 2) use a simulation tool for chromatographic modeling, 3) explain the subtleties of a novel mode of chromatography (WPC) through varying calculations and simulations, 4) illustrate the benefit of fractional factorial simulations as a tool for directing experiments, and 5) apply their chromatographic simulation and optimization experience to modeling other separation processes. Project description handouts provided to the students contained information on current biotechnology separation challenges and taught them about WPC (objective 3). The tasks they were required to perform taught them how to generate and interpret adsorption isotherm and partition coefficient plots (objective 1) and introduced them to the use of simulation tools for chromatographic modeling (objective 2). Further, as the students performed the required

**Figure 6.** Representative productivity bar graph for varying feed loading time and NaCl concentrations. For each feed loading time shown on the x-axis results are given at 5 NaCl concentrations of 170, 200, 210, 220, and 250 mM from left to right. The data represented by unfilled bars (purity) and half-filled (shift time) did not satisfy these particular constraints, while the other data (full bars) satisfied all constraints.



simulations under varying conditions (*e.g.*, feed load and salt concentration) the subtleties of WPC separations became apparent (objective 3). The students were also able to observe trade-offs between maximizing productivity while minimizing the overall process time and satisfying process constraints. The students learned the benefits of fractional factorial simulations (objective 4) during the optimization of their processes. By the end of the project, the students were comfortable and proficient Aspen Chromatography users (objective 5) and they indicated that they felt they had learned the necessary skills to model other separation processes (objective 5).

The student response to the addition of this simulation-based project into the course was quite favorable. While the students had not previously used Aspen Chromatography they had some familiarity with Aspen software through previous chemical engineering courses. The first year that the project was used in the course, the students indicated that more experience with the Aspen simulator in general would have been useful prior to the assignment. This was addressed in the following year by including a hands-on computer laboratory in the lecture sequence. In this studio format, the students were able to get assistance from the instructor and their peers as problems arose, significantly improving the students' experience. Student enthusiasm was apparent, since the entire class stayed well after the instructional period had ended in order to continue learning how to properly use the chromatographic simulator.

Students commented that they enjoyed visualizing the separations that they had been studying earlier in the course and that these exercises significantly strengthened their understanding of chromatographic separations. They also commented that this project enabled them to better understand the implementation of many of the course concepts and theories

for an actual separation process. Finally, several students commented that this simulation module was their favorite part of the course.

Student assessment was based on two written reports that they were required to submit, one prior to using Aspen and one after. The students were assessed for their ability to generate the required data and figures (e.g., isotherm plots, partition coefficient plots, required simulated outlet chromatograms, and simulations performed for the optimization of the process) as well as for their understanding of these processes as evidenced by the discussions in these reports.

## 5. CONCLUSIONS

The commercial simulator Aspen Chromatography was employed to study and optimize an important new industrial separation process, weak partitioning chromatography. This case study on antibody purification was implemented in a chromatographic separations course. Students initially were asked to manipulate adsorption data to determine adsorption isotherm parameters and to study the effect of salt on the isotherm behavior. A preliminary report was turned in at this point that also included their responses to a number of questions to probe their knowledge of the subject matter.

The students were then requested to carry out detailed sets of parametric simulations to investigate the effect of operating parameters (e.g., feed load, salt concentration) on the productivity and yield of this separation process. The course project served to teach students basic simulator operation, apply course material to a separation challenge from the biotechnology industry, and encourage open-ended problem exploration for process optimization.

## ACKNOWLEDGMENTS

This research was supported by NIH Grant 5R01 GM047372. Helpful discussions with Alexander Freed are also gratefully acknowledged.

## REFERENCES

1. Wankat, P., "Efficient, Effective Teaching," *Chem. Eng. Educ.*, p. 92 (2001)
2. Wankat, P.C., "Learning Through Doing: A Course on Writing a Textbook Chapter," *Chem. Eng. Educ.*, p. 208 (1993)
3. Wankat, P., "Using a Commercial Simulator to Teach Sorption Separations," *Chem. Eng. Educ.*, p. 165 (2006)
4. Ge, M., C. Li, and S. Ren, "ChemCAD Software and Application in Chemical Engineering Course Design," *Jisuanji Yu Yingyong Huaxue*, **21**(5), 781 (2004)
5. Smith, C.A., and F.W. Villaescusa, "Simulating Chromatographic Separations in the Classroom," *J. of Chem. Educ.*, **80**(9), 1023 (2003)
6. Haddad, P.R., M.J. Shaw, J.E. Madden, and G.W. Dicinowski, "A Computer-Based Undergraduate Exercise Using Internet-Accessible Simulation Software for the Study of Retention Behavior and Optimization of Separation Conditions in Ion Chromatography," *J. of Chem. Educ.*, **81**(9), 1293 (2004)
7. Rockstraw, D.K., "Aspen Plus in the ChE Curriculum," *Chem. Eng. Educ.*, **39**(1), 68 (2005)

8. Wankat, P.C., "Integrating the Use of Commercial Simulators in Lecture Courses," *J. of Eng. Educ.*, **91**(1), 19 (2002)
9. Kelley, B., "Very Large Scale Monoclonal Antibody Purification: The Case for Conventional Unit Operations," *Biotechnology Progress*, **23**(5), 995 (2007)
10. Vunnum, S., M. Switzer, R. Godavarti, T. Iskra, P.R. Brown, S. Tobler, J. Coffman, B. Costigan, C. Kha, D. Wright, K. Sterl, and B. Kelley, "Anion Exchange Purification of Monoclonal Antibodies: Principals of Weak Partitioning Chromatography," *Abstracts of Papers*, 232nd ACS National Meeting, San Francisco, CA (2006)
11. Tobler, S.A., A. Noyes, P.R. Brown, M. Switzer, and B. Kelley, "Removal of HMW Species Using AEX in the Weak Partitioning Mode for Antibodies and Related Proteins," *Abstracts of Papers*, 234th ACS National Meeting, Boston, MA (2007)
12. Kelley, B.D., S.A. Tobler, P. Brown, J.L. Coffman, R. Godavarti, T. Iskra, M. Switzer, and S. Vunnum, "Weak Partitioning Chromatography for Anion Exchange Purification of Monoclonal Antibodies," *Biotechnology and Bioengineering*, **101**(3) 553 (2008)
13. Coffman, J.L., J.F. Kramarczyk, and B.D. Kelley, "High-throughput screening of chromatographic separations: I. Method development and column modeling," *Biotechnology and Bioengineering*, **100**(4) 605 (2008)
14. Kramarczyk, J.F., B.D. Kelley, and J.L. Coffman, "High-Throughput Screening of Chromatographic Separations: II. Hydrophobic Interaction," *Biotechnology and Bioengineering*, **100**(4), 707 (2008)
15. Wensel, D.L., B.D. Kelley, and J.L. Coffman, "High-Throughput Screening of Chromatographic Separations: III. Monoclonal Antibodies on Ceramic Hydroxyapatite," *Biotechnology and Bioengineering*, **100**(5), 839 (2008)
16. Kelley, B.D., M. Switzer, P. Bastek, J.F. Kramarczyk, K.L. Molnar, T.N. Yu, and J. Coffman, "High-Throughput Screening of Chromatographic Separations: IV. Ion-exchange," *Biotechnology and Bioengineering*, **100**(5), 950 (2008)
17. Felder, R.M., and R. Brent, "Objectively Speaking," *Chem. Eng. Educ.*, **31**(3), 178 (1997)
18. Champion, K.M., J.C. Nishihara, I.S. Aldor, G.T. Moreno, D. Andersen, K.L. Stults, and M. Vanderlaan, "Comparison of the *Escherichia coli* Proteomes for Recombinant Human Growth Hormone Producing and Nonproducing Fermentations," *Proteomics*, **3**(7), 1365 (2003)
19. Van Dyk, D.D., D.R. Misztal, M.R. Wilkins, J.A. Mackintosh, A. Poljak, J.C. Varnail, E. Teber, B.J. Walsh, and P.P. Gray, "Identification of Cellular Changes Associated With Increased Production of Human Growth Hormone in a Recombinant Chinese Hamster Ovary Cell Line," *Proteomics*, **3**(2), 147 (2003)
20. Gallant, S.R., A. Kundu, and S.M. Cramer, "Modeling Nonlinear Elution of Proteins in Ion-Exchange Chromatography," *J. of Chromatography A*, **702**(1-2), 125 (1995)

## APPENDIX

DIAGNOSTICS (Solver reporting level: low; Properties reporting level: none; Watch group: 0; Watch torn sub-group: 0; Check procedure derives: off; Relative checking tolerance: 0.001; Absolute checking tolerance: 0.001; Check the list variables in equivalences for highest variable steps and residuals).

TOLERANCES (Absolute variable tolerance: 1e-007; Relative variable tolerance: 1e-007; Absolute equation tolerance: 1e-007; Variable change tolerance: 1e-007; Numerical derivative absolute perturbation: 1e-005; Numerical derivative relative perturbation: 1e-005; Explicit event tolerance: 1e-005; Uncheck Solver scaling; Check Eliminate equivalence equations; Check Use Group Decompositions).

TEARING (Procedure tearing: Update; Tear update strat-

egy: Direct; Relative tear tolerance: 1e-005; Absolute tear tolerance: 1e-005; Maximum number of tear iterations: 100).

INTEGRATOR (Integration method: Gear; Maximum order: 5; Absolute integration error tolerance: 0.0005; absolute tear error tolerance: 1e-005; relative integration error tolerance: 0.0005; relative tear error tolerance: 1e-005); Uncheck include sensitivity errors; Uncheck reconverge torn variables; Select that the integration error test includes States only; Variable Initial step size of 0.001; Minimum variable step size: 0.0001; Maximum variable step size: 0.1; Variable step reduction factor: 0.5; Uncheck Always enforce minimum step size; Check Interpolate communication time; Uncheck Locate model discontinuities; Uncheck Re-initialize after variable step-change; Check Use initial step size after variable step-change; Show 0 highest integration errors; Show 0 highest tear integration errors).

LINEAR SOLVER (Name: MA48; Drop tolerance: 0; Re-analyze threshold: 2; Pivot tolerance: 0; Re-analyze FLOPS window size: 0; Re-pivot every 0 factorizations; Solver searches 3 columns for pivots; Uncheck use transpose).

NON LINEAR SOLVER (Mode: Standard; Method: Mixed

Newton; Convergence criterion: Residual; Maximum divergent steps: 20; Maximum step reductions: 20; Maximum iterations: 500; Maximum fast Newton steps: 8; Uncheck Dogleg method; Maximum range fraction tolerance: 0; Maximum approach to bound: 1; Absolute perturbation: 1e-005; Singularity perturbation: 0.01; Maximum variable step: 50; Clip factor: 1e-006; Highest variable steps: 0; highest residuals above tolerance: 0; Print linear algebra for groups of size > 0; Uncheck Enabled homotopy).

ESTIMATOR (Estimator: Least Squares; Solver: NL2SOL; Reporting level: High; Solution convergence tolerance: 0.0001; Maximum iterations: 2000; Relative function tolerance: 0.0001; Absolute function tolerance: 0.0001; False convergence tolerance: 0).

OPTIMIZER (Optimizer: FEASOPT; Reporting level: Medium; Maximum iterations: 100; Solution convergence tolerance: 0.0001; Maximum relative step: 10; Maximum absolute step: 10).

HOMOTOPY (Initial homotopy step: 0.1; Maximum homotopy step: 1; minimum homotopy step: 0.01; Step size increment factor: 10; Step size decrement factor: 0.5). □

# A GRAPHICAL REPRESENTATION

## For the Fugacity of a Pure Substance

NEIL L. BOOK AND OLIVER C. SITTON

Missouri University of Science and Technology • Rolla, MO 65409

The traditional development presents the fugacity<sup>[1]</sup> of a pure substance as a mathematical translation to the Gibbs energy.

$$f_i \equiv P_R \exp\left(\frac{G_i - G_{i,R}^\circ - \Delta G_{i,\Delta T}^\circ}{RT}\right) \quad (1)$$

The most frequent expression is the equivalent implicit form or a variant thereof:

$$G_i = G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ + RT \ln\left(\frac{f_i}{P_R}\right) \quad (2)$$

For example, Smith, Van Ness, and Abbott,<sup>[2]</sup> Tester and Modell,<sup>[3]</sup> and Kyle<sup>[4]</sup> use nomenclature of the form:

$$G_i \equiv \Gamma_i \{T\} + RT \ln(f_i) \quad (3)$$

The function of system temperature is:

$$\Gamma_i \{T\} = G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ - RT \ln(P_R) \quad (4)$$

The inclusion of the reference pressure term in the temperature function leaves the defining equation with an apparent infeasibility since fugacity has units of pressure and the argument of the logarithm must be dimensionless. Prausnitz, Lichtenthaler, and de Azevedo<sup>[5]</sup> use nomenclature of the form:

$$G_i - G_{i,R} = RT \ln\left(\frac{f_i}{f_{i,R}}\right) \quad (5)$$

The values at the reference point are:

$$\begin{aligned} f_{i,R} &= P_R \\ G_{i,R} &= G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ \end{aligned} \quad (6)$$

Others (Winnick,<sup>[6]</sup> Kyle,<sup>[4]</sup> and Elliott and Lira<sup>[9]</sup>) define fugacity in differential form at constant temperature:

$$dG_i = RT d \ln(f_i) \quad (7)$$

Integration from the arbitrary reference point at the system temperature gives the Prausnitz, et al. form. Sandler<sup>[7]</sup> defines

the fugacity as a transformation to the residual Gibbs energy:

$$f_i = P \exp\left(\frac{\bar{G}_{i,P}}{RT}\right) \quad (8)$$

All authors use this equation as the basis for computing the value of the fugacity. This equation does not contain the reference state or the ideal gas Gibbs energy change.

A graphical representation of the rigorous mathematical definitions is described that explains the relationship between fugacity and Gibbs energy for a pure substance. The graphical representation provides students with a visual interpretation that aids in their comprehension of the definitions and the methods for determining the value of the fugacity.

### PG DIAGRAM FOR A PURE SUBSTANCE

A PG diagram demonstrates the physics underlying the definitions for the fugacity. Figure 1 is a semi-logarithmic PG diagram for argon. The PG diagram was developed using data from the NIST Chemistry WebBook (<<http://webbook.nist.gov/chemistry/>>). The solid lines are the solid/liquid and the liquid/vapor coexistence curves. The vapor/liquid coexistence curve ends at the critical point (150.687 K and 48.630 bar). The solid/liquid and vapor/liquid coexistence curves would intersect at the triple point (83.8 K and 0.689 bar). The solid squares represent the data for the critical isotherm (150.687 K). The solid diamonds and solid circles are data on the 135 K and 120 K subcritical isotherms, respectively, in the vapor and liquid regions. The solid triangular data points represent the 180 K supercritical isotherm.

**Neil Book** is an associate professor of chemical and biological engineering at the Missouri University of Science and Technology (formerly University of Missouri – Rolla). He received his B.S. in 1972 from the University of Missouri-Rolla and Ph.D. in 1976 from the University of Colorado. His research is in the areas of process modeling and alternative sources of energy.

**Oliver Sitton** is an associate professor of chemical and biological engineering at the Missouri University of Science and Technology (formerly University of Missouri – Rolla). He received his B.S. in 1975 and Ph.D. in 1979 from the University of Missouri – Rolla. His research is in the areas of bioengineering and bioprocess design.

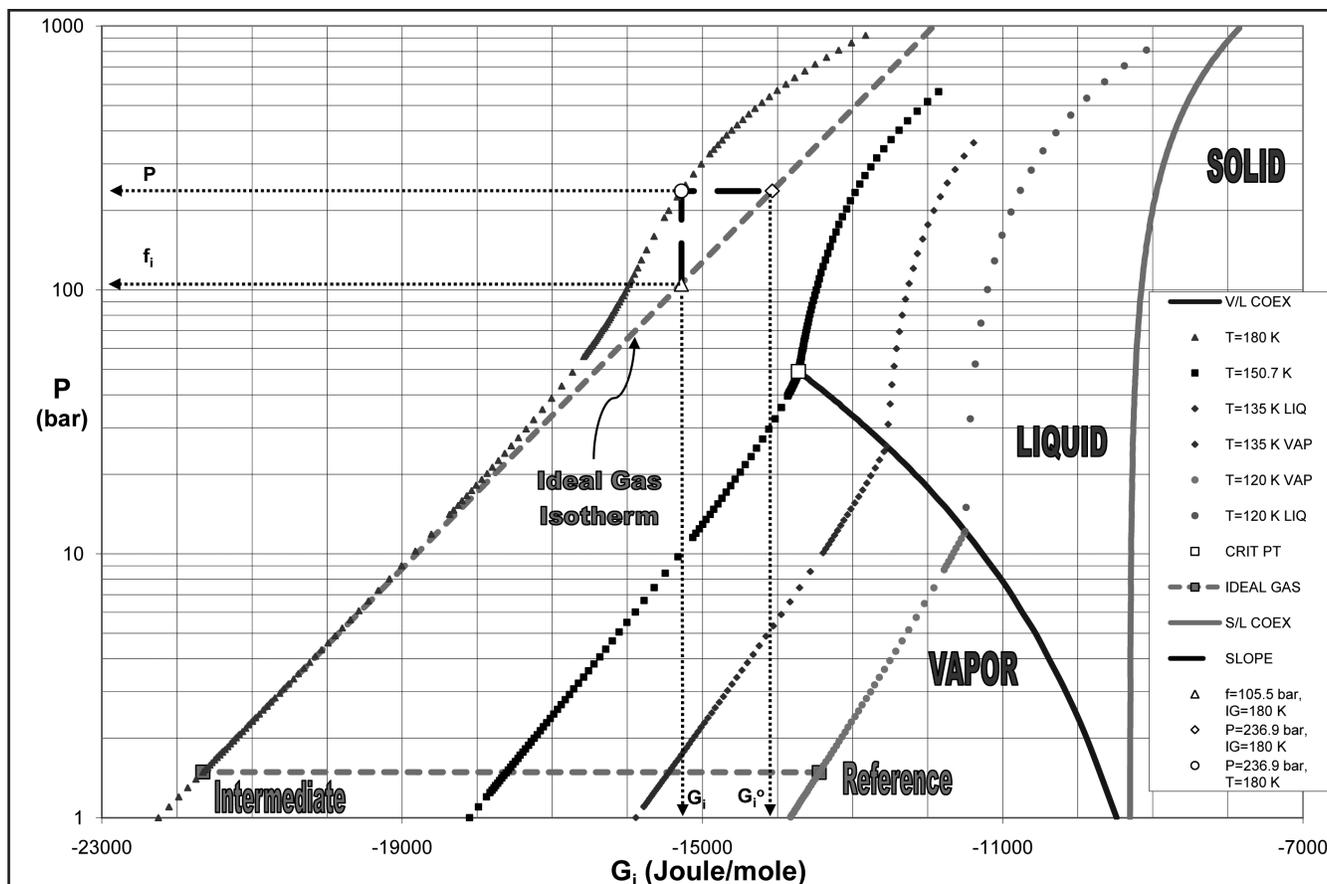


Figure 1. PG diagram for argon.

Suppose that the fugacity of the unfilled circular point at 180 K and 236.9 bar with Gibbs energy of -15,280 Joule/mole is to be determined.

$$G_{AR, 180 \text{ K}, 236.9 \text{ bar}} = -15,280 \frac{\text{Joule}}{\text{mole}} \quad (9)$$

### GIBBS ENERGY FOR A SUBSTANCE BEHAVING AS AN IDEAL GAS

The Gibbs energy of a substance behaving as an ideal gas can be determined at any temperature and pressure provided that:

*The absolute (or standard) entropy of the ideal gas is known at some reference state, and*

*The ideal gas heat capacity is known over the range from the reference temperature to the system temperature.*

Gibbs energy is a state (point) function. As such, any convenient path between two states determines the difference in the Gibbs energy. Select a path from the ideal gas reference state to a hypothetical ideal gas state that is composed of: 1) an isobaric step at the reference state pressure from the reference state temperature to the ideal gas state temperature (details of the ideal gas reference state and the computation

of the Gibbs energy change for the isobaric step are contained in the Appendix) and 2) an isothermal step at the ideal gas state temperature from the reference state pressure to the ideal gas state pressure.

$$G_i^\circ - G_{i,R}^\circ = \Delta G_{i,\Delta T}^\circ + \Delta G_{i,\Delta P}^\circ \quad (10)$$

Rearranging:

$$G_i^\circ = G_{i,R}^\circ + \Delta G_{i,\Delta T}^\circ + \Delta G_{i,\Delta P}^\circ \quad (11)$$

The fundamental property relationship for the Gibbs energy is:

$$dG = -SdT + VdP \quad (12)$$

For the isothermal step, the Gibbs energy change is:

$$\Delta G_{i,\Delta P}^\circ = \int_{P_R}^P V^\circ dP = \int_{P_R}^P \frac{RT}{P} dP = RT \ln \left( \frac{P}{P_R} \right) \quad (13)$$

Rearranging:

$$\ln \left( \frac{P}{P_R} \right) = \frac{\Delta G_{i,\Delta P}^\circ}{RT} = \frac{G_i^\circ - G_{i,R}^\circ - \Delta G_{i,\Delta T}^\circ}{RT} \quad (14)$$

The isotherm for a pure substance behaving as an ideal gas

is a straight line with slope of  $1/RT$  on the semi-logarithmic PG diagram. It is a fundamental axiom of thermodynamics that all substances behave as an ideal gas as the pressure approaches zero on an isotherm, therefore, every isotherm becomes asymptotic to a straight line with this slope as the pressure approaches zero. Note that the four isotherms on Figure 1 become asymptotic to a straight line at low pressure and that the slope of the line decreases with increasing temperature. The dashed line, asymptotic at low pressure to the 180 K isotherm, is the 180 K isotherm for argon behaving as an ideal gas. At 180 K and 236.9 bar, argon has a significant deviation from ideal gas behavior (unfilled circle for argon as a real gas and unfilled diamond for argon as an ideal gas).

Suppose that the Gibbs energy for argon as an ideal gas at 180 K and 236.9 bar relative to the ideal gas reference state taken to be 120 K and 1.5 bar with an ideal gas absolute entropy of 132.35 Joule/mole K and Gibbs energy of -13,444 Joule/mole is to be determined. The ideal gas reference state is not on the 120 K isotherm for argon. It is an ideal gas reference state, therefore it is located on the 120 K isotherm for argon behaving as an ideal gas that is asymptotic to the real isotherm as the pressure approaches zero. At the low pressure of the reference state, there is little difference between the real isotherm and the ideal gas isotherm.

The two-step path is depicted on Figure 1 by a dashed line that begins at the reference state and proceeds horizontally (isobaric) to an intermediate state on the 180 K isotherm for the ideal gas and then proceeds from the intermediate state along the ideal gas isotherm to the ideal gas state (unfilled diamond). The Gibbs energy of argon behaving as an ideal gas at 180 K and 236.9 bar is -14,070 Joule/mole.

$$G_{\text{Ar},180\text{ K},236.9\text{ bar}}^{\circ} = -14,070 \frac{\text{Joule}}{\text{mole}} \quad (15)$$

Substituting for the isothermal step and rearranging:

$$G_i^{\circ} - G_{i,R}^{\circ} = \Delta G_{i,\Delta T}^{\circ} + \Delta G_{i,\Delta P}^{\circ} = \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{P}{P_R} \right)$$

$$G_i^{\circ} = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{P}{P_R} \right) \quad (16)$$

## RESIDUAL GIBBS ENERGY

The residual Gibbs energy at constant pressure is the difference between the Gibbs energy of the system and the Gibbs energy of a system of the same chemical composition and at the same temperature and pressure but behaving as an ideal gas.

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ} \quad (17)$$

An important attribute of residual properties is that the calculation only requires PVT data and/or equations of state applicable on the system isotherm from a pressure that approaches zero to the system pressure. These calculations do not require heat capacity or absolute entropy. On the PG diagram, the residual Gibbs energy for argon at 180 K and 236.9 bar represents a process from

the 180 K ideal gas isotherm at 236.9 bar (unfilled diamond) to the real 180 K isotherm at 236.9 bar (unfilled circle). The residual Gibbs energy for argon at 180 K and 236.9 bar is:

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ} = -15,280 - (-14,070) = -1,210 \frac{\text{Joule}}{\text{mole}} \quad (18)$$

## PHYSICAL DEFINITION OF THE FUGACITY FOR A PURE SUBSTANCE

The fugacity of a pure substance at a temperature and pressure is the pressure at which the substance behaving as an ideal gas at the same temperature has the same Gibbs energy as the system. On Figure 1, the Gibbs energy of a system containing argon at 180 K and 236.9 bar is -15,280 Joule/mole. The pressure of argon behaving as an ideal gas at 180 K that has a Gibbs energy of -15,280 Joule/mole is 105.5 bar. This is the fugacity of argon at 180 K and 236.9 bar. The fugacity is easily determined on Figure 1 as the pressure where a vertical line through the point at 180 K and 236.9 bar intersects the 180 K ideal gas isotherm (unfilled triangle).

$$G_{\text{Ar},180\text{ K},105.5\text{ bar}}^{\circ} = -15,280 \frac{\text{Joule}}{\text{mole}} \quad (19)$$

The fugacity is a point located on the ideal gas isotherm. The two-step path from the reference state gives the implicit form for the definition.

$$G_i = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{f_i}{P_R} \right) \quad (20)$$

## DETERMINING THE FUGACITY FOR A PURE SUBSTANCE

Consider the Gibbs energy changes for a three-step process from the reference state to the system state that is composed of: 1) an isobaric step for the substance behaving as an ideal gas at the reference state pressure from the reference state temperature to the intermediate state at the system temperature, 2) an isothermal step for the substance behaving as an ideal gas at the system temperature from the reference state pressure to the system pressure, and 3) an isobaric step from the ideal gas isotherm to the real isotherm. The first two steps are the Gibbs energy changes for the two-step process from the reference state to the ideal gas state at the system temperature and pressure (unfilled diamond for a system at 180 K and 236.9 bar). The Gibbs energy change for the third step is the residual Gibbs energy.

$$G_i^{\circ} = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{P}{P_R} \right)$$

$$\hat{G}_{i,P} \equiv G_i - G_i^{\circ}$$

$$G_i = G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{P}{P_R} \right) + \hat{G}_{i,P} \quad (21)$$

Equating with the implicit form for the definition of the fugacity gives the Sandler definition:

$$\begin{aligned}
G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{f_i}{P_R} \right) &= G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{P}{P_R} \right) + \widehat{G}_{i,P} \\
RT \ln \left( \frac{f_i}{P} \right) &= \widehat{G}_{i,P} \\
f_i &= P \exp \left( \frac{\widehat{G}_{i,P}}{RT} \right) \quad (22)
\end{aligned}$$

This is the equation that is used to compute the value of the fugacity of a pure substance. The residual Gibbs energy at constant pressure is determined from PVT data and/or equations of state for the pure substance. Since the ideal gas reference state is not specified, the absolute entropy at the reference state is not required. The isobaric ideal gas Gibbs energy change cancels and this eliminates the need for the ideal gas heat capacity.

At 180 K and 236.9 bar, the residual Gibbs energy is -1210 Joule/mole. Substitution gives the fugacity:

$$f_i = P \exp \left( \frac{\widehat{G}_{i,P}}{RT} \right) = 236.9 \text{ bar} \exp \left( \frac{-1210 \frac{\text{Joule}}{\text{mole}}}{\left( 8.3143 \frac{\text{Joule}}{\text{mole K}} \right) 180 \text{ K}} \right) = 105.5 \text{ bar} \quad (23)$$

The PG diagram also reveals this definition for the fugacity. Rearranging:

$$\frac{\ln \left( \frac{P}{f_i} \right)}{-\widehat{G}_{i,P}} = \frac{1}{RT} \quad (24)$$

The slope of the ideal gas isotherm is equal to the “rise” over the “run.” The slope of the 180 K isotherm for argon behaving as an ideal gas at 180 K and 236.9 bar is indicated on the diagram. The rise on the semi-logarithmic PG diagram (unfilled triangle to unfilled circle) is the numerator and the run (unfilled circle to unfilled diamond) is the denominator. The residual Gibbs energy and the fugacity are measures of the deviation from ideal gas behavior. The fugacity is a measure of the vertical distance (on a logarithmic scale) from ideal gas behavior to the system state. The residual Gibbs energy is a measure of the horizontal distance (on a linear scale) from ideal gas behavior to the system state.

## PHASE COEXISTENCE FOR A PURE SUBSTANCE

The temperature, pressure, and Gibbs energy of a pure substance must be equal in each phase for two or more phases to coexist.

$$G_{i(\alpha)} = G_{i(\beta)} \quad (25)$$

The implicit form for the definition of the fugacity produces the equivalent requirement for fugacity.

$$\begin{aligned}
G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{f_{i(\alpha)}}{P_R} \right) &= G_{i,R}^{\circ} + \Delta G_{i,\Delta T}^{\circ} + RT \ln \left( \frac{f_{i(\beta)}}{P_R} \right) \\
f_{i(\alpha)} &= f_{i(\beta)} \quad (26)
\end{aligned}$$

Since the fugacity can be determined from PVT information for a substance, it is more convenient for phase coexistence calculations than Gibbs energy. Lewis<sup>[1]</sup> used this requirement coupled with the low pressure limit as the definition when developing the concept of fugacity.

## STUDENT COMPREHENSION

Lewis described the concept of fugacity that he developed as “abstruse” and most students in the intervening century would agree. The PG diagram demonstrates the equivalence of the various definitions and gives insight to the advantages of fugacity over Gibbs energy. Students prefer the physical definition for fugacity that is also demonstrated on the diagram. It explains why two quantities with the same units but different values, pressure and fugacity, are equal when two phases of a pure substance are in equilibrium. Fundamental comprehension leads to increased confidence and fewer errors when applying fugacity.

## CONCLUSIONS

The semi-logarithmic PG diagram for a pure substance with superimposed isotherms for the substance behaving as an ideal gas provides physical descriptions for the equations used to define and compute the value of the fugacity. The PG diagram clearly demonstrates that the fugacity of a pure substance at a temperature and pressure is the pressure at which the substance behaving as an ideal gas at the same temperature has the same Gibbs energy as the system. This physical definition eliminates much of the “abstruse” nature<sup>[1]</sup> of the fugacity.

## NOMENCLATURE

- $C_{P,i}^{\circ}$  Ideal gas heat capacity at constant pressure for the pure substance
- $f_i$  Fugacity of the pure substance at the system temperature and pressure
- $f_{i,R}$  Fugacity of the pure substance at an arbitrary reference point at the system temperature
- $G_i$  Gibbs energy of the pure substance at the system temperature and pressure
- $G_{i,I}^{\circ}$  Gibbs energy for a hypothetical ideal gas at the intermediate state (system temperature and reference state pressure)
- $G_{i,R}$  Gibbs energy of the pure substance at the arbitrary reference point at the system temperature
- $G_{i,R}^{\circ}$  Gibbs energy for a hypothetical ideal gas at the reference state for the Gibbs energy relative to the reference state for the enthalpy
- $G_{i(\alpha)}$  Gibbs energy of pure substance in phase  $\alpha$
- $G_{i(\beta)}$  Gibbs energy of pure substance in phase  $\beta$
- $G_i^{\circ}$  Gibbs energy of the pure substance as a hypo-

theoretical ideal gas at the system temperature and pressure

$\Delta G_{i,\Delta P}^\circ$  Ideal gas Gibbs energy change at constant temperature from the reference state pressure to the system pressure

$G_{i,R}^\circ$  Gibbs energy at the ideal gas reference state

$\Delta G_{i,\Delta T}^\circ$  Ideal gas Gibbs energy change at constant pressure from the reference state temperature to the system temperature

$\widehat{G}_{i,P}$  Residual Gibbs energy at constant pressure

$H_{i,R}^\circ$  Enthalpy for a hypothetical ideal gas at the reference state for the Gibbs energy relative to the reference state for the enthalpy

P Absolute pressure of the pure substance

$P_R$  Absolute pressure at the ideal gas reference state

R Gas constant

$S_{i,R}^\circ$  Absolute entropy for a hypothetical ideal gas at the reference state for the Gibbs energy

T Absolute temperature of the pure substance

$T_R$  Absolute temperature at the reference state for the Gibbs energy

$\Gamma_i\{T\}$  A function of system temperature

## REFERENCES

- Lewis, G.N., "The Law of Physico-Chemical Change," *Proceedings of the American Academy*, **37**(4), 49, (1901)
- Smith, J.M., H.C. Van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 7th Ed., McGraw-Hill (2005)
- Tester, J.W., and M. Modell, *Thermodynamics and Its Applications*, 3rd Ed., Prentice-Hall (1996)
- Kyle, B.G., *Chemical and Process Thermodynamics*, 3rd Ed., Prentice-Hall (1999)
- Prausnitz, J.M., R.N. Lichtenthaler, and E.G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Ed., Prentice-Hall (1999)
- Winnick, J., *Chemical Engineering Thermodynamics*, John Wiley (1997)
- Sandler, S.I., *Chemical, Biochemical, and Engineering Thermodynamics*, 4th Ed., John Wiley (2006)
- Poling, B.E., J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, 5th Ed., McGraw-Hill (2000)
- Elliott, J.R., and C.T. Lira, *Introductory Chemical Engineering Thermodynamics*, Prentice-Hall (1999)

## APPENDIX

### Ideal Gas Reference State

The value of the fugacity can be determined without specifying the ideal gas reference state, however, development of the PG diagram requires a reference state where the absolute entropy is known. The definition for the Gibbs energy is:

$$G \equiv H - TS \quad (27)$$

The Gibbs energy and the enthalpy are relative quantities however the temperature and entropy are absolute quantities. The absolute entropy (relative to the perfect crystalline state at a temperature of absolute zero) for the substance behaving as an ideal gas is required to determine the Gibbs energy at the ideal gas reference state.

$$G_{i,R}^\circ = H_{i,R}^\circ - T_R S_{i,R}^\circ \quad (28)$$

Gibbs energy and enthalpy are relative quantities but are not independent. The definition of the Gibbs energy ties the value of one to the arbitrary reference state for the other. In like fashion, the definitions for the internal energy and the Helmholtz energy make all four quantities interdependent.

The NIST database reports the absolute entropy of argon as an ideal gas at 298.16 K and 1 bar to be 154.84 Joule/mole K. Extensive tabulations of data for absolute entropies do not exist, thus, one of the driving forces to replace Gibbs energy with fugacity. Standard entropies may be reported for the pure substance as a solid or liquid. In principle, the absolute entropy at an ideal gas reference state can be determined from condensed state data. This makes the definitions of the fugacity based on an ideal gas reference state general.

Poling, Prausnitz, and O'Connell<sup>[8]</sup> provide methods for estimating absolute entropies in the absence of data.

## ISOBARIC GIBBS ENERGY CHANGES FOR A PURE SUBSTANCE

The first step to determine the Gibbs energy change for an ideal gas is an isobaric process. The Gibbs energy change for the process is:

$$\Delta G_{i,\Delta T}^\circ = G_{i,I}^\circ - G_{i,R}^\circ \quad (29)$$

The definition of the Gibbs energy at the intermediate state is:

$$G_{i,I}^\circ = H_{i,I}^\circ - T S_{i,I}^\circ \quad (30)$$

The ideal gas enthalpy at the intermediate state is determined from the ideal gas heat capacity:

$$H_{i,I}^\circ = H_{i,R}^\circ + \int_{T_R}^T C_{p,i}^\circ dT \quad (31)$$

Determination of the value for the absolute entropy at the intermediate state also requires a correlation for the ideal gas heat capacity.

$$S_{i,I}^\circ = S_{i,R}^\circ + \int_{T_R}^T \frac{C_{p,i}^\circ}{T} dT \quad (32)$$

Tabulations of parameter values for correlations of data for the ideal gas heat capacity of pure substances are extensive and there are several group contribution methods<sup>[8]</sup> to estimate the heat capacity in the absence of correlations. □

## THE LINK BETWEEN RESEARCH AND TEACHING

### 2. How to Strengthen Each Without Weakening the Other

RICHARD M. FELDER

North Carolina State University

#### RECAP OF PART 1<sup>[1]</sup>

**R**esearch productivity is the dominant criterion for tenure and promotion at most research universities in the United States, and it's becoming increasingly important at institutions that used to have only teaching missions. This policy has hurt the quality of education at many universities by denying some outstanding teachers tenure, and it has also led to a lot of mediocre research.

The usual justification for the policy is an assertion that research and teaching are inextricably linked, to an extent that only active researchers can be effective teachers. While research activity is no doubt an important qualification for teaching and mentoring graduate students, its connection to undergraduate education is far from obvious. Prince, *et al.*,<sup>[2]</sup> recently surveyed the literature on the connection and found that while disciplinary research can support teaching in principle, it generally doesn't in practice. Significant positive correlations have not been found between individual faculty research productivity and teaching effectiveness, or between institutional research productivity and student learning and satisfaction. (In fact, most correlations of both types have been negligible and sometimes negative.) Most faculty members do not integrate their research into their undergraduate courses, and many who attempt it waste valuable class time on material irrelevant to the course objectives or too advanced for the students' backgrounds. Undergraduate research does provide benefits, such as improving retention of some student populations and influencing some students to pursue graduate study.

As a rule, however, only a small subset of the student body participates in research, the participants often function more like unpaid lab assistants than real researchers, and research activity has not been shown to significantly enhance students' learning and skill development. (See Reference 2 for citations of the studies that produced these findings.)

#### STRENGTHENING THE LINK

Prince, *et al.*,<sup>[2]</sup> offer several proposals for strengthening the research-teaching nexus, including these:

- *Encourage faculty members to use inductive teaching methods (e.g., inquiry-based, problem-based, and project-based learning).*

An instructor may effectively promote learning by teaching in a manner that emulates elements of the research process. Inductive methods such as inquiry-based, problem-based, and project-based learning do that. When implemented correctly,

**Richard M. Felder** is Hoechst Celanese Professor Emeritus of Chemical Engineering at North Carolina State University. He is co-author of *Elementary Principles of Chemical Processes* (Wiley, 2005) and numerous articles on chemical process engineering and engineering and science education, and regularly presents workshops on effective college teaching at campuses and conferences around the world. Many of his publications can be seen at <[www.ncsu.edu/effective\\_teaching](http://www.ncsu.edu/effective_teaching)>.



they facilitate students' attainment of high-level thinking and problem-solving skills<sup>[3]</sup> and can reach more students at a lower cost than undergraduate research can.

- *Engage a substantial percentage of the student body in meaningful research.*

The impact of undergraduate research is limited if only a relative handful of students participate in it, while involving many students can add considerably to the quality of a department's teaching program. Simply giving students projects is not enough, however; for undergraduate research to be effective, the advisor must really mentor the students and not just treat them as additional pairs of hands to help out in the lab.

- *Formally recognize and reward faculty members who successfully integrate teaching and research.*

Successful integration might involve relevant incorporation of the instructor's research into course lectures, assignments, and exams; using inductive teaching methods and demonstrating their effectiveness; and guiding students through well-conducted research projects. If such activities are explicitly included in annual faculty performance evaluations and they count in tenure and promotion decisions, they will eventually become part of the academic culture.

## **STRENGTHENING BOTH RESEARCH AND TEACHING**

Strengthening the linkage between research and undergraduate teaching can improve the latter, but only to a limited extent. As long as excellence in research is routinely rewarded with tenure and promotion and excellence in teaching is occasionally recognized with an award, teaching quality will be well below what it could be. The following two steps should improve an institution's teaching program dramatically without sacrificing its research productivity and quality.

- *Make sure each department has some faculty members (at least 10%) who specialize and excel in teaching and educational scholarship.*
- *Treat performance in teaching/educational research and disciplinary research identically when tenuring, promoting, and rewarding faculty members.*

The idea is not to reverse the positions of research and teaching in the faculty reward system to make teaching dominant. Frontier research is critical to the future of our society, and it is vitally important for universities to keep doing it since industry has largely abandoned research that doesn't promise a quick payoff. But just as not every teacher has the aptitude to be an excellent researcher, not every researcher is capable of

being an excellent teacher. Some professors manage to excel at both—almost every department has a few—but there are not nearly enough of them to populate all department faculties.

So, in addition to hiring and promoting people who are outstanding disciplinary researchers and adequate teachers, every academic department should make room for some outstanding teachers and educational scholars who do little or no disciplinary research. Those individuals will keep up with innovations in pedagogy and instructional technology and share their knowledge with interested colleagues to help them improve their teaching. They will teach important undergraduate courses (such as the engineering lab and capstone design course) that most research-oriented faculty members have little interest in teaching, and help students acquire critical professional skills (communication, teamwork, ethical awareness, etc.) that traditional faculty are often reluctant to include in their courses. There is also a somewhat self-serving argument. Being outstanding teachers, the specialists will motivate their students to learn and inspire them to grow. Alumni tend to remember such teachers fondly throughout their lives, and when they are asked for discretionary donations or endowments of scholarships, named chairs, and new labs and buildings for their alma mater, those memories often lead to generous responses. (All universities have such stories.)

Administrators commonly fear that hiring and promoting education specialists will cause a reduction in institutional research productivity, but that doesn't have to happen. Some traditional faculty members freed from unwanted responsibilities will find the time to write additional proposals, and the education specialists should bring in some of the millions of dollars of funding awarded every year for research on teaching and learning. Having education specialists on the faculty will allow most research and teaching to be done enthusiastically and expertly by people who enjoy and excel in those activities. As long as the specialists are held to the same high performance standards for tenure and promotion that are applied to traditional research faculty and they are rewarded equally for success, everybody wins.

## **REFERENCES**

1. Felder, R.M., "The Link Between Research and Teaching. 1. Does It Exist?" *Chem. Eng. Ed.*, **44**(2), 109 <<http://www.ncsu.edu/felder-public/Columns/Nexus1.pdf>> (2010)
2. Prince, M.J., R.M. Felder, and R. Brent, "Does Faculty Research Improve Undergraduate Teaching? An Analysis of Existing and Potential Synergies," *J. Eng. Educ.*, **96**(4), 283 <[http://www.ncsu.edu/felder-public/Papers/Teaching-Research\(JEE\).pdf](http://www.ncsu.edu/felder-public/Papers/Teaching-Research(JEE).pdf)> (2007)
3. Prince, M.J., and R.M. Felder, "Inductive Teaching and Learning Methods: Definitions, Comparisons, and Research Bases," *J. Eng. Educ.*, **95**(2), 123 <<http://www.ncsu.edu/felder-public/Papers/InductiveTeaching.pdf>> (2006) □

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

# YOUTUBE FRIDAYS: Engaging the Net Generation in 5 Minutes a Week

MATTHEW W. LIBERATORE

Colorado School of Mines • Golden, Colorado 80004

The majority of students pursuing undergraduate degrees are digital natives (sometimes called the Net Generation). These men and women are characterized by being born in the 1980s or 1990s and by having “grown up digital.” They have had access to computers and the Internet from a very young age. The ubiquity of laptops, cell phones, digital music players (*e.g.*, iPods), and other electronic devices has this generation plugged into technology continuously throughout a typical day. The advantages enjoyed by technology-savvy students are numerous. The near instantaneous access to course-related information can be used to look up unit conversions, find physical properties, or verify an equation within seconds. The integration of technology in the classroom, *e.g.*, using Tablet PCs to promote student engagement,<sup>[2]</sup> is almost expected by the digital natives.

There are many technology-driven behaviors that challenge faculty in higher education today, however. For example, the free flow of information has revolutionized how students communicate (and sometimes cheat<sup>[3]</sup>), including the wide availability of solutions manuals for textbooks that are only intended for instructors. Also, handheld technologies allowing students to send text messages or “Tweet” have contributed to shorter student attention spans. Text messages truncate the English language to a series of abbreviations and “Tweets” are limited to just 140 characters (about the length of this sentence). Myriad books, blogs, and wikis discuss topics related to the growing population of digital natives<sup>[4-7]</sup>; however, this

paper focuses on a simple classroom exercise to encourage students to use the seemingly endless information around them to enhance their college educations.

Active learning is a key component of many different teaching techniques used to engage students.<sup>[8]</sup> The use of multimedia (*e.g.*, audio, video, PowerPoint presentations) is one way to maintain student interest throughout a class period and during the duration of a quarter or semester. Student participation and even leadership is critical when finding successful active-learning strategies. Therefore, for an activity to truly qualify as active learning, students’ enthusiasm is needed.

YouTube Fridays began as a way to show the students about my area of research (rheology of complex fluids) as part of the first class period of Introduction to Engineering Thermodynamics. The fact that a professor is both teacher and researcher is important to emphasize to undergraduate students.



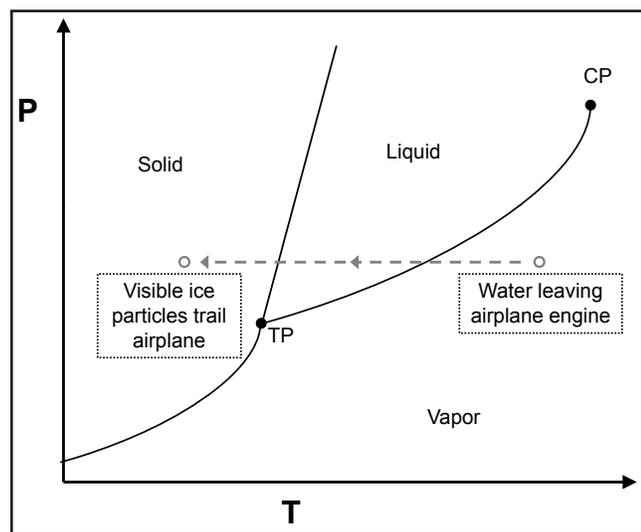
**Matthew W. Liberatore** is an assistant professor of chemical engineering at the Colorado School of Mines. He earned a B.S. degree from the University of Illinois at Chicago and M.S. and Ph.D. degrees from the University of Illinois at Urbana-Champaign, all in chemical engineering. His current research involves the rheology of complex fluids especially traditional and renewable energy fluids, entangled polymer solutions, and surfactant-polymer mixtures.

© Copyright ChE Division of ASEE 2010

Seeing the interesting problems their professor works on piques their interest and motivates them to get the most out of their studies. After watching a video of people “walking on water” (actually a pool of corn starch, a shear thickening fluid), the students wanted to know how a corn-starch pool worked and if they could build one.<sup>[9]</sup> I chose another video, about viscoelastic fluids,<sup>[10]</sup> the second week of class, and the students wanted to know if there would be videos every week. I consented, on the condition that the students do the work and find the videos and relate them to the course. Thus, YouTube Fridays started its transition from a fun way to start class at 8 a.m. on Fridays (and to bolster Friday attendance) to a quantifiable teaching technique.

## IMPLEMENTATION

YouTube Fridays have been piloted as part of two courses (Table 1). Introduction to Engineering Thermodynamics, a sophomore-level class for students in chemical engineering, engineering physics, and civil engineering, was where YouTube Fridays began. A more formal YouTube Fridays pilot was completed the next semester as part of a Material and Energy Balances class, a sophomore-level course for chemical engineering students. The students were required to relate their chosen video to the topic of the course, namely



**Figure 1.** Schematic of a pressure-temperature phase diagram of a pure fluid. Overlaid points represent the two phases of water present in the videos.

thermodynamics in the first pilot and the field of chemical engineering in the second. The evolution of the topics of the videos and the “new” course material related to the videos will be discussed in the context of each pilot. A section on how YouTube Fridays were evaluated precedes the concluding remarks and summary of how to adopt YouTube Fridays in other courses.

### Pilot 1: The Birth of YouTube Fridays

Introduction to Engineering Thermodynamics introduces basic concepts including units conversion, reading steam tables, the first law of thermodynamics (energy conservation), and the second law of thermodynamics (entropy). During the first few sessions of a semester, the class is split into groups of three or four students (of the 40 total students), which are affectionately called “Thermo Teams”; these teams are primarily used to work problems during class. The active learning exercises of working problems in Thermo Teams constitute approximately half of the class time throughout the semester, and many groups work together inside and outside of class.

The videos chosen by the Thermo Teams covered a range of thermodynamics-related topics; the most popular topics included phase changes and blowing things up. Relating the video to class material solidifies the relevance of thermodynamics to the students. For example, one of the first student-selected videos was a series of clips showing water condensing behind a jet engine (sometimes called a contrail).<sup>[11]</sup> Concurrently, the students were learning about phase diagrams of pure fluids, especially water. Therefore, at the conclusion of the video, a sketch of a pressure-temperature diagram was placed on the board. The starting condition of the water in the air was labeled (*i.e.*, vapor). The final condition and the independent intensive variable that changed were quickly discussed in teams before the final solutions were sketched on the board (Figure 1). The video and accompanying discussion were a perfect lead-in to the class material for the day.

Using the videos to create quantitative homework problems or open-ended questions (or “Engineering Estimates”) is a great way to overcome the perceived irrelevance of textbooks by the technology-centric students. One example video was an at-home experiment performed by two young siblings, estimated to be about 11 and 7 years old.<sup>[12]</sup> Here, a plate of green-dyed water has a candle sitting in the center. Three

**TABLE 1**  
Outline of the Two Pilots of YouTube Fridays

Pilot	Course (n=number of enrolled students)	Semester	Student-Selected Videos	Written Report	University Course Evaluation	YouTube-Specific Evaluation
1	Introduction to Engineering Thermodynamics (n=40)	Fall 2008	Yes	No	Yes	No
2	Material and Energy Balances (n=55)	Spring 2009	Yes	Yes	Yes	Yes

pennies are placed on the plate, the candle is lit (with parental supervision), and a glass cup is placed over the candle. The cup rests on the pennies to allow water to flow in or out of the cup. As the cup was placed over the lit candle, I stopped the video and asked the class what they expected to happen. The overwhelming consensus was that the water level in the cup would rise. The video continued and the class's intuition was proven to be correct. A quantitative engineering estimate problem based on the video (Figure 2) required the students to complete a force balance.

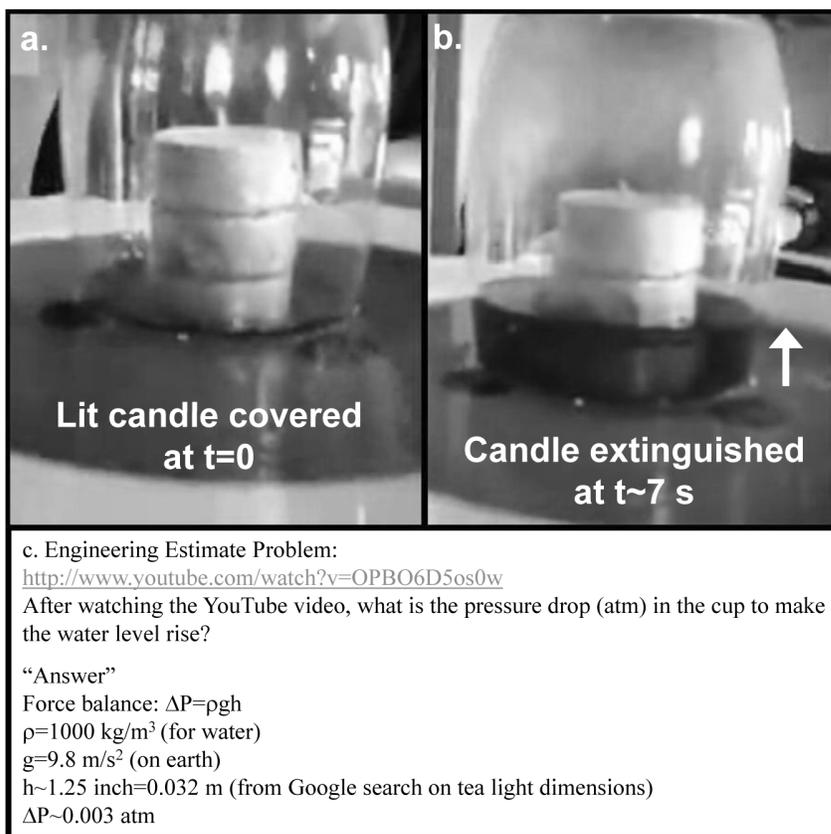
Overall, the first pilot of YouTube Fridays successfully demonstrated a way to engage students of the Net generation. Videos were used to reiterate recent class material, demonstrate the robustness of the first law energy balance, and even introduce the students to advanced topics beyond a sophomore-level first course in thermodynamics. One such topic was the idea of nucleation. The video involves some young people with a clear glass bottle of beer subcooled to a temperature below the freezing point.<sup>113)</sup> They show the beer is still liquid and then tap the bottle on a concrete floor to initialize nucleation. The entire bottle of beer freezes in just seconds to the wonder of the people in the video and the class. (I think many of the students attempted this trick the following weekend.)

### Pilot 2: YouTube Fridays and Chemical Engineering

Material and Energy Balances is the first core course in the chemical engineering curriculum at Colorado School of Mines. The Spring 2009 class contained 55 students and groups of five were assigned randomly. The formal YouTube Friday assignment was given during the second week of class. Students were asked to select videos related to chemical engineering (jobs, products, benefits of, etc.). In addition to choosing the video and giving a short oral description in class, the students were now required to complete a short written assignment as well. The written document provides an avenue for the students to analyze their chosen video. The objective of the written report was to address one or more of the following questions: How does the video relate to chemical engineering, biochemical engineering, or large-scale chemical production? What is the chemical reaction involved? How is the chemical reaction or product scaled up? What company produces the chemical(s) in the video? Does the video involve a chemical engineering job you would like to have? How does chemical engineering influence our daily activities? The written document

needed to be signed by each member of the group. Overall, the quality of writing and depth of thinking demonstrated was better than I had anticipated.

To give the students an idea of the length (less than 5 minutes) and content of the video, I chose a student-created video titled "A World Without Chemical Engineering" for the first Friday of the semester.<sup>114)</sup> The various scenes of the video demonstrate that fireworks, gasoline, cars, mass-produced medicines, etc., would not exist without chemical engineers. Based on the example video, the student-selected topics included blowing things up (again), the difficulty of being a chemical engineering student, and the jobs that a chemical engineer might perform. The mix of information on chemical engineering with humor was common throughout the semester. In total, videos created by chemical engineering students were very popular (including those from South Dakota School of Mines and Technology, Brigham Young University, University of Minnesota, the students in the pilot class at Colorado School of Mines, Tufts University, and Northwestern University). Detailed discussions of a few of the videos demonstrated the basic understanding of the field of chemical engineering and provided a first exposure to more advanced topics that will be seen during the final two years of the students' undergraduate education.



**Figure 2.** Screenshots of a video made of an at-home experiment (a. and b.) and the course-related problem derived from the video (c.).

One of the more humorous videos of the semester also proved to be one of the most instructive of the semester. A video titled “CSTR” is a parody of The Village People’s “YMCA” complete with costumed performers and chemical engineering-centric lyrics (Figure 3).<sup>[1]</sup> While the whole class enjoyed the video and likely picked up one or two facts about CSTRs, the five students who selected the video clearly learned even more, as they wrote a detailed report containing information that was not even in the video. First, the group defined “CSTR” as a continuously stirred tank reactor. Obviously CSTR is not part of the texting vernacular. Next, the basic assumptions of perfect mixing, steady state operation, constant density, isothermal, and irreversibility were stated as conditions needed to understand the function of a CSTR. In addition, current course content was reiterated in the students’ write-up: “CSTRs have the same mass flow rate in as out, which is important so that the reactor does not overflow.” Finally, the students identified Dr. Scott Fogler as the author of *Elements of Chemical Reaction Engineering*, “a book that we use for one of the classes we must take during our curriculum.”

Six of the 11 videos focused on education and jobs related to chemical engineering. Having an understanding of mathematics, physics, chemistry, and biology was mentioned in multiple videos as well as several of the written reports. The difficulty of being a chemical engineering student was ubiq-

uitous and one video was quoted as saying half of the students fail “thermo and diffusion.” Another common observation was that chemical engineers are problem solvers. The many sub-fields of chemical engineering are mentioned in the videos and by the students. Most prevalent areas of future need for chemical engineers were clean energy, nanotechnology, and biotechnology. The excellent pay of chemical engineers was mentioned as one reward of the difficulty of obtaining a chemical engineering degree. The problem-solving skills of chemical engineers allow them to pursue other fields such as law, management, and entrepreneurial positions. The central themes of a chemical engineering education and the profession of chemical engineering were certainly covered over the course of one semester. The educational value for the students will be discussed in the evaluation section below.

Since chemical engineering is a broad field and the assignment was open-ended, it was not surprising a subset of the videos were related to chemical reactions and physiochemical changes. Two videos were segments from the show *Myth-Busters* involving the combustion of non-dairy creamer<sup>[15]</sup> and walking on a corn-starch pool.<sup>[16]</sup> The corn-starch pool introduced the students to the idea of non-Newtonian fluids and the concept of shear thickening (also covered during the first pilot course). The report on the corn-starch pool discusses applying a force quickly, which causes thickening, vs. slowly, in which one would sink into the fluid—an excellent



**Figure 3.** CSTR hand/body motions (parody of the song “YMCA”).<sup>[1]</sup>

example of kinetics (another advanced topic covered later in the curriculum) outside of a reaction engineering setting. The concept of kinetics was also prevalent in a video of a recorded lecture contrasting the rate of reaction and the heat of reaction. During the middle of the semester, a group of students in the class took the initiative and made their own video and posted it to YouTube.<sup>[17]</sup> The enthusiastic group naturally chose to find a chemical reaction that would blow something up. The group mimicked other videos on YouTube by combining toilet bowl cleaner (*i.e.*, concentrated hydrochloric acid) and aluminum foil. The reaction created hydrogen gas. First, a plastic soft drink bottle was destroyed by the reaction in less than a minute. Then, a Nalgene bottle was used as a sealed reactor. The bottle did not explode; the top was simply blown off. The students' report noted the different strengths of two "plastic" bottles and the need for safety measures (venting) when producing aluminum chloride on an industrial scale. Overall, the breadth of chemical engineering was captured in the videos and a significant amount of critical analysis of the videos was included in the written reports.

## EVALUATION

The assignments were graded at the conclusion of both pilot courses, and the points were added to the participation/web-based quiz portion of their grade (5% of total grade for the semester). Overall, the selection and discussion of the video contributed between 0.5 and 1% of the semester grade. During the second semester, the grading rubric was broken down into four categories: 1. length and content appropriateness of the video; 2. video provides new and/or interesting information about chemical engineering or being a chemical engineer; 3. length and content appropriateness of the written document; and 4. the written document addresses one of the questions in the assignment or related information. With few exceptions, the students did an excellent job selecting appropriate, interesting, and entertaining videos. In the future, a peer-review component will also be added to the grade. The peer evaluation will hopefully circumvent the problem of just one or two of the students (out of groups of four or five) completing the assignment. I expect more uniform participation throughout

the semester with the peer review component making up 20% of the assignment's grade.

After the first pilot, feedback was collected via comments on the back of the university's course evaluations. One student commented that YouTube promoted his learning. The curious statement "YouTube Fridays FTW!" appeared in the written comments on another student's evaluation; as someone with no text-messaging experience, I went to class the day after reading the evaluation (which was from the previous semester) and naively asked the students what the statement meant. A Google search defined FTW as "for the win." The students, after laughing at their professor for a minute, assured me that FTW is a very positive statement, basically saying that YouTube Fridays were great.

In addition to the university's course evaluation, a one-page evaluation of YouTube Fridays was given at the end of the second pilot. The evaluation was completed during class and the students' names were required. The multiple-choice section allowed for four levels of response. Two free-response questions and an area for additional thoughts/questions/comments/concerns completed the evaluation form. The assessment of students' opinions, both positive and negative, will lead to a more student-centered activity in future semesters.

Overall, the students gave YouTube Fridays favorable remarks, which are summarized below. The evaluations should be taken in context. The goal of pilot 2 was to introduce the students to chemical engineering and what chemical engineers do, which was very successful based on the written reports and the data collected from the evaluations. YouTube Fridays were not designed to improve their learning of material and energy balances during pilot 2, which also was corroborated by the evaluations.

Five multiple-choice questions were ranked on a scale of "strongly agree," "agree," "disagree," or "strongly disagree." The questions focused on whether YouTube Fridays promoted learning new things about chemical engineering and jobs for chemical engineers, the effectiveness of videos vs. websites, and the value of the class time throughout the semester. The students' responses are summarized in Table 2. An ~80% posi-

**TABLE 2**  
Students' Percentage Responses to Five Survey Statements at the End of the Second Pilot Course

Statements	Strongly Agree	Agree	Disagree	Strongly Disagree
I have a better understanding of the field of chemical engineering from participating in YouTube Fridays.	11	69	20	0
I know more about the jobs available to chemical engineers from participating in YouTube Fridays.	9	73	18	0
YouTube videos teach me more about chemical engineering than websites about chemical engineering.	7	32	61	0
I think it is valuable to use 5 minutes of class time each week (~3% of total class time) to watch YouTube and not cover class material.	24	56	18	2
I think YouTube Fridays helped me learn the material in ChEN 201 this semester.	0	18	71	11

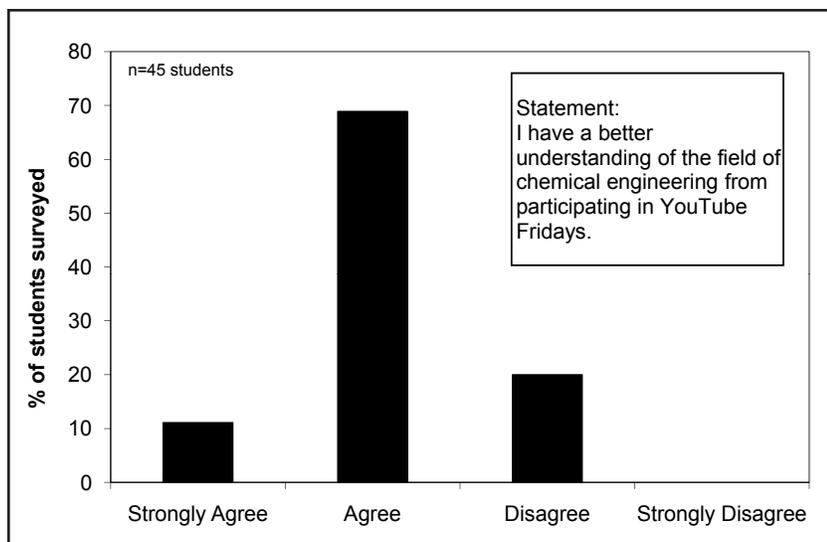


Figure 4. Sample of the assessment data from Material and Energy Balances course (pilot 2).

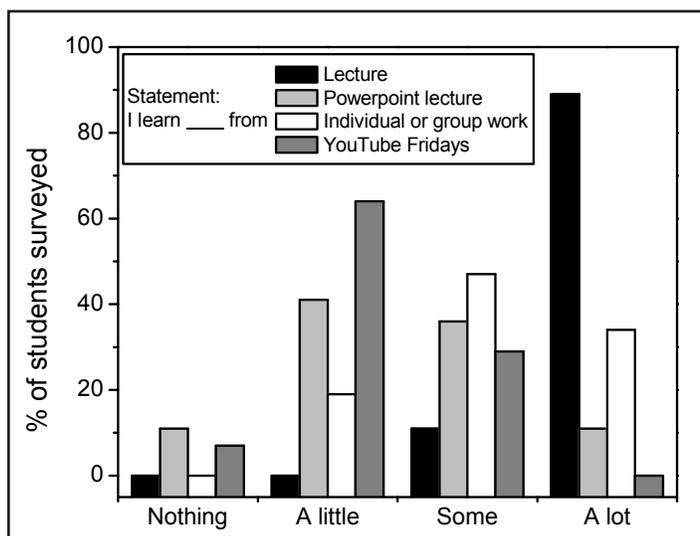


Figure 5. Evaluation data from Material and Energy Balances course (pilot 2).

tive response (“agree” or “strongly agree”) was reported for learning about chemical engineering, learning about chemical engineering jobs, and using a small fraction of class time for YouTube instead of class material (Figure 4). The students believed, however, that they learn more about chemical engineering from websites (*e.g.*, <aiche.org>, <chemicalengineering.org>) than from watching YouTube videos.

Another set of questions investigated the students’ perceived learning from four major classroom teaching styles. The responses to these questions were ranked “nothing,” “a little,” “some,” and “a lot” (Figure 5). All of the students said they learned some or a lot from lecture at the board and ~80% feel they learned some or a lot from individual or group work in class. The efficacy of using PowerPoint slides as a pedagogical method received very mixed

response. Finally, 42 out of 45 students stated they learned a little or some from YouTube Fridays. The response of learning “a little” or “some” seems appropriate since the activity only consumes 5 minutes of class time per week.

The final multiple-choice questions asked how many times the student accessed my website to find the videos shown in class. Only eight of the 45 respondents said they visited my website to watch the videos from class again. This response may be deceiving as I have had several inquiries from students about re-watching the videos. The website of the current and past videos will be given on the assignment at the beginning of future terms. The course website (*e.g.*, within Blackboard) will be used instead of the faculty’s personal laboratory site.

The free-response questions of the evaluation asked 1) for one fact about chemical engineering the students learned from the video their group selected, and 2) for one other fact the students learned about chemical engineering from YouTube Fridays. A sampling of the responses (Table 3) demonstrates the students’ affinity for YouTube Fridays. The most common written comment centered on the diversity of chemical engineering and the jobs chemical engineers do (60% of the class). Other common responses reiterated the exciting future chemical engineers have with the global energy, water, and pollution issues. The extreme difficulty of being a chemical engineering student was also mentioned several times. The need for better sound equipment on which to hear the videos (beyond the laptop’s speakers) was also mentioned several times. Overall, the written feedback was overwhelmingly positive toward having YouTube Fridays as a “break” from normal class time.

A few reflections from my perspective will improve the activity in the future. The written assignment needs to state that the video cannot repeat videos on the list from all past semesters, or the content may become stale (as was the case some weeks during pilot 2). YouTube lists related videos right on the screen as you are watching a video. For a small fraction of the videos selected, the video chosen for the subsequent week came from this list. The students of the Net generation, however, seem to pride themselves on originality when selecting videos. In addition, the open-ended nature of the topic each semester may need refining at one or two points during a semester. For example, instead of chemical engineering as the open topic for the entire term, focus on three topics such as chemical engineering jobs at the beginning of the semester, material/mass balances and

reactions in the middle of the term, and energy balances at the end of the semester.

## CONCLUDING REMARKS

YouTube Fridays only take a small fraction of class time and are an effective way to engage the Net generation and to expand the content of the course in a dynamic way. The organization and execution of this activity are summarized in Table 4. All of the student selected videos from both pilots are included on the author's faculty webpage.<sup>[18]</sup> Technology in the classroom will continue to change in the coming years and YouTube will become obsolete. The ability to integrate "new" technology that is readily assimilated by current and future generations, however, is necessary to continually engage the increasingly technology-savvy student.

## ACKNOWLEDGMENTS

The author would like to acknowledge Ron Miller for help with evaluation and manuscript preparation.

## REFERENCES

1. CSTR. [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=AkM67QsTq3E>>
2. Kowalski, S.E., F.V. Kowalski, and T.Q. Gardner. "Lessons Learned When Gathering Real-Time Formative Assessment in the University Classroom Using Tablet PCs," in *Proceedings of the 39th ASEE/IEEE Frontiers in Education Conference*, San Antonio, TX (2009)
3. Choi, C.Q., "The Pull of Integrity," *Prism*, **18**(7) 28 (2009)
4. Tapscott, D., *Grown Up Digital* [electronic resource]: *How the Net Generation is Changing Your World*, New York: McGraw-Hill (2009)
5. Palfrey, J., and U. Gasser, *Born Digital: Understand the First Generation of Digital Natives*, Basic Books, New York (2008)
6. *Digital Natives*, <<http://www.digitalnative.org>>, access date: June 16, 2009
7. Pletka, B., *Educating the Net Generation: How to Engage Students in the 21st Century*, Santa Monica Press, Santa Monica, CA (2007)
8. Prince, M., "Does Active Learning Work? A Review of the Research," *J. Eng. Ed.*, p. 223, (July 2004)
9. "A Pool Filled with Non-Newtonian Fluid," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=f2XQ97XHjVw>>
10. "Leaping Shampoo," [cited July 14, 2009]; Available from: <[http://www.youtube.com/watch?v=GX4\\_3eV\\_3Mw](http://www.youtube.com/watch?v=GX4_3eV_3Mw)>
11. "F18 Hornet Surface Flyby," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=v8zP5s9vdX0&feature=related>>
12. "An Experiment with Air Pressure," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=OPBO6D5os0w>>
13. "Brainiacs' Beer-Freezing Technique," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=iWCsQP7xhKc>>
14. "A World Without Chemical Engineering," [cited July 14, 2009]; Available from: <[http://www.youtube.com/watch?v=hX\\_HXO3-0P4](http://www.youtube.com/watch?v=hX_HXO3-0P4)>
15. "MythBusters—Creamer Cannon," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=yRw4ZRqmxOc>>
16. "MythBusters—Walking on 'Water'," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=5GWhOLorDtw&feature=related>>
17. "Toilet Boil Cleaner + Aluminum Foil = Homemade Bomb," [cited July 14, 2009]; Available from: <<http://www.youtube.com/watch?v=Iqs4o1ePbhc>>
18. Liberatore, M.W., Rheology of Complex Fluids Laboratory Home Page, [cited July 14, 2009]; Available from: <<http://inside.mines.edu/~mliberat/index.html>> □

**TABLE 3**  
Samples of Written Comments from Students  
Upon Completion Of Pilot 2

I "heart "YouTube Fridays.
ChemE's make bad "gangster" raps.
YouTube Fridays were very valuable and helped to give a reason for some people to come to class on Fridays.
I've learned that mixing chemicals can cause dangerous explosions.
Good to work in groups so we can meet the other students in our class.
That chemical engineers are able to go into many different fields, and most people don't know what a chemical engineer does on a day-to-day basis.
The whole group summary thing was not really helpful because one person usually did it.
I learned that there are a lot more careers available for chemical engineers than I thought there were.
I learned that chemical engineering is such a broad field (and people often devote their degrees to other work).
MEB (Material and Energy Balances) can be difficult and watching these videos helps to remind us all why we are going through this. It shows our future worth.
More work than it needs to be—very hard to get four people together (when) you don't know/trust (them at first).

**TABLE 4**  
Summary of Implementing YouTube Fridays for a  
Semester (16-week) Course

Week 1	Show a video appropriate for the topic of the semester, form groups of three or four students, distribute assignment with timeline, expectations, and grading rubric.
Weeks 3-15	Watch videos once per week. Collect written reports.
Weeks 15-16	Grade all videos and reports. Collect student feedback.
Post-Semester	Reflect upon previous semester's activity and plan refinement and improvement of the activity for future semesters.

# POLYMERIZATION SIMULATOR

## *For Introductory Polymer and Material Science Courses*

WILLIAM M. CHIRDON

*University of Louisiana at Lafayette • Lafayette, LA 44130*

One of the fundamental challenges in teaching a polymer science course is to develop the student's intuition regarding how this class of materials behaves. Professors often describe polymers as entangled masses of spaghetti or kite string to explain the unique behavior of polymers. The reason this is commonly done is that if students can visualize how polymer chains interact and function through tangible examples, then they are better able to understand many of the basic concepts in polymer science and engineering. Near the end of my graduate polymer engineering course, I tell my students that they are prepared for the final exam when they are able to "think like a polymer." Stated in a more didactic fashion, students must be able to visualize and understand the models used in polymer science in order to interpret microstructures, predict effects on properties, and derive the corresponding equations.

One important topic in polymer science is the kinetics of polymerization reactions. Modeling polymerization reactions does not typically require a detailed knowledge of the organic chemistry involved, since most polymerization reactions follow one of several motifs. For instance, in a typical stepwise growth polymerization, there are two monomer types such that each "type A" monomer will react with two "type B" monomers. Each type B monomer will react with two type A monomers, and each monomer does not react with its own

type. A stoichiometric reaction at high conversion will result in long polymer chains of alternating monomer types. A classic example of this reaction is the synthesis of polyester from a monomer with two alcohol groups and a second monomer with two carboxylic acid groups. Modeling the kinetics of the molecular weight development does not require knowing the details of the chemistry, except for knowing the aforementioned bonding rules.

With these thoughts in mind, two polymerization simulators were developed for two different polymerization types: stepwise growth and free-radical chain polymerizations. In these simulators, the details of the chemistry are neglected, and computer models of polymerization are created by

**William M. Chirdon** is an assistant professor at the University of Louisiana at Lafayette in the Chemical Engineering Department. He received his Ph.D. in macromolecular science and engineering at the University of Michigan. Dr. Chirdon also serves as the faculty advisor for the local chapter of the American Institute of Chemical Engineers. His research interests include the modeling of heat generation and transfer in cementitious composites, simultaneous thermal property determination in exothermic solids, thermal analysis of polymers, appearance properties of translucent composite materials, and nanoscratch modeling for polymer surfaces.



considering monomers as simple spheres of different types that obey defined bonding rules. These simulators allow for students to quickly obtain an understanding of how these polymerization reactions occur and the differences between the two. For instance, at moderate conversions, the step-growth polymerization will result in a variety of oligomers, while the free-radical chain polymerization will result in a few long polymers along with unreacted monomers, as seen in Figure 1. An instructor can demonstrate these concepts more effectively and expeditiously with a computer simulation rather than with a blackboard. The simulators featured in this article are also convenient for instructors and institutions because they are free to use for academic, noncommercial purposes.

## TARGET AUDIENCE

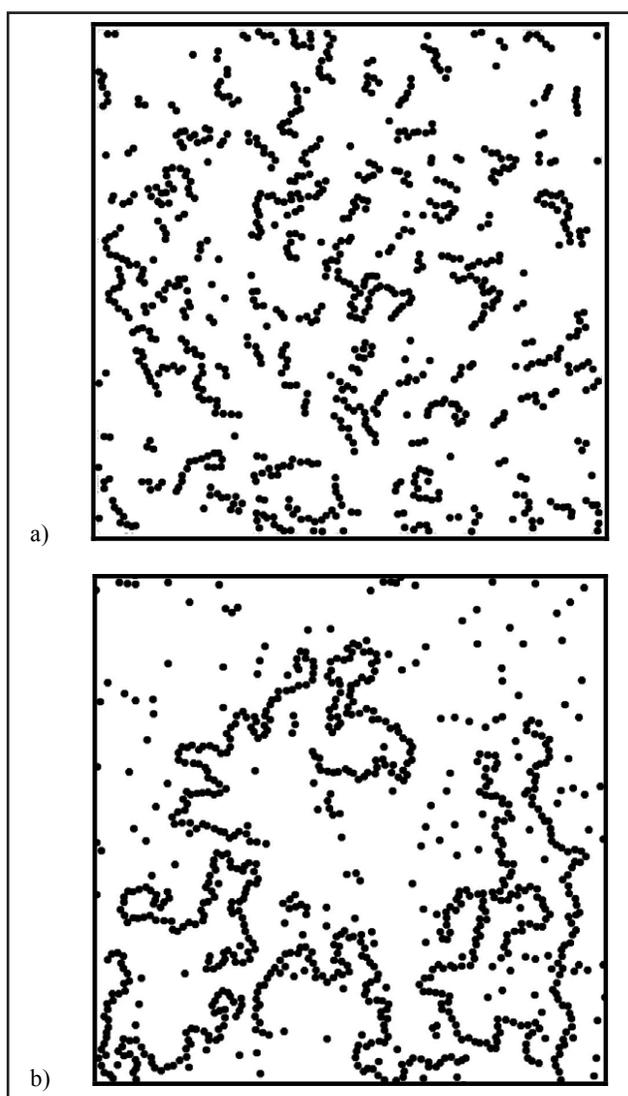
This simulator is an ideal tool for introducing polymerization reactions or simply the concept of a polymer. It has been found to be useful for at least two student groups. First, this module has been found to be effective in a basic materials science/engineering class to introduce polymer materials. Instead of simply giving the definition of a polymer, introducing polymers with the use of this simulator allows for the students to quickly develop an appreciation for what polymers are and how they are made.

The full potential of the simulator, however, can be realized in a graduate-level introductory polymers course, where basic polymer concepts and formulae can be quantitatively analyzed by the students by exporting their acquired data into spreadsheets. Students are likely to become more engaged in a class when there are live demonstrations of polymerizations, such as the “Nylon Rope Trick,”<sup>[1]</sup> or if they can use processing or characterization equipment themselves. These simulators offer much of the visual stimulus of a live demonstration with the convenience of a PowerPoint presentation, and they allow students to conduct their own simulated experiments.

From the students’ perspective, the simulators represent an easier mechanism for learning the material that is more contemporary, visual, and interactive. One major benefit is that this method of instruction allows students with different learning styles that are less receptive to lectures to grasp the key concepts by executing their own model experiments. Surveys conducted at the end of my graduate polymer engineering courses confirm that the simulations help the students visualize and understand polymerization reactions and develop new insights as shown later in the “Results” section. Most professors have known some individuals who were rather lackluster students, yet they excel in more hands-on activities such as laboratory work, independent research, or future employment in industry. Similarly, instructors may find these students that do not respond well to passive learning in lectures may have a chance to excel if they are given an opportunity to perform their own model experiments and analyze the data that they collect.

## MOLECULAR SIMULATION MODELS

The simulators demonstrated in this paper were developed as an Etonica molecular simulation module. These modules are available online, coded in Java, and free for purposes of academic research and instruction. The modules are publicly available at <[www.etonica.org](http://www.etonica.org)>. From the home page, the polymerization simulator can be found by navigating to “Modules” and then selecting the “Polymerization” module. The polymerization module may also be accessed directly at <<http://rheneas.eng.buffalo.edu/wiki/Polymerization>>. The module is designed to be self-explanatory with the essential background material included on the website with examples and problems. The module is even more effective when coupled with a formal polymer course, however.



**Figure 1.** Molecular simulation of a) a stepwise growth polymerization and b) a free-radical chain polymerization. Both simulations are at 80% conversion. Figures are reproduced in black and white, but the monomer types are color-coded in the simulation.

In these models, the average speed of the particles is determined by the system temperature. The temperature can be controlled using a “thermostat” which will change particle speeds to obtain the set temperature for the system. The user is able to set adiabatic or isothermal conditions and change the temperature while the simulation is running. This allows the students to see the effects of temperature on polymerization reactions. The bond energy is also programmable, which affects both the strength of the bond and the heat released during reaction. Users can then monitor the number- and weight-average molecular weights, chain-length histogram, temperature, and conversion over time.

## STEPWISE GROWTH SIMULATION

Stepwise growth polymers are created by reacting at least two different monomer types. In the simplest case, there will be a type A and a type B monomer, where each monomer will react and bond twice with the other type but not its own type. Monomers that form two bonds are known as di-functional. Specific chemical mechanisms are neglected in this simulation, but the monomers are given names for clarity. The type A monomers are di-functional alcohols, annotated as di-ols. The type B monomers are di-functional carboxylic acids, annotated as di-acids. Mono-ols and Mono-acids are mono-functional groups that act as end-capping agents. A tri-functional acid is also available as a cross-linking agent. The di-ols, di-acids, and cross-linking agents are represented as red, blue, and green dots, respectively. Using this simple model, a variety of basic concepts in stepwise growth polymerization can be demonstrated as discussed in the “Student Activities” section.

## FREE-RADICAL CHAIN ADDITION SIMULATION

Free-radical chain addition is an entirely different mechanism of polymerization that has completely different reaction kinetics and results in a different distribution of molecular weights. The first step in a free-radical chain addition simulation is known as the initiation step, where an initiator molecule forms free radicals. In this simulation, the initiator is considered to behave as a typical peroxide initiator, which splits to form two free radicals when heated. This simulation models each initiator as two particles that are not reactive when they are together. The initiators are held together by a finite bond energy, however, so that as the temperature is increased, more bonds are spontaneously broken by the thermal energy. When an initiator splits, it forms two free radical species, each of which can react with a monomer. Once the free radical reacts with a monomer, the formerly reactive particle permanently bonds to the monomer, which then becomes reactive towards other monomers, and the initiation step is complete.

The initiation step results in the nucleation of a growing polymer chain and leads to the second stage in this polymerization: propagation. In the propagation stage, monomers are

added one by one to the growing chain. Each time a monomer is added, the radical (reactive) nature of the chain is passed to the newly added monomer so that the unit on the end is the only chemically active unit in the chain. The last stage of this polymerization is termination, where the propagation is terminated in one of two ways when the active ends of two propagating chains collide. In termination by combination, the active ends will bond with each other, effectively doubling the average molecular weight in this step. Alternatively, the chains can terminate by disproportionation, where the radical is transferred from one chain to the other, killing the reactivity of both chains and resulting in two polymer chains with the same average molecular weight as before the termination step. The probability of combination vs. disproportionation is an input parameter.

## STUDENT ACTIVITIES

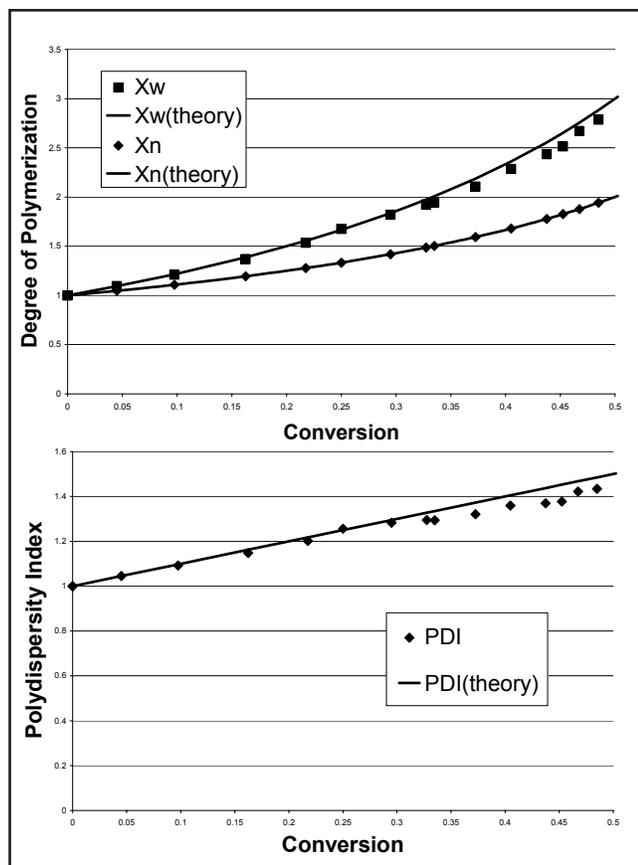
These computer simulations can serve to teach students over a range of levels from a sophomore materials science course through a graduate-level introduction to polymers. Since the detailed reaction mechanisms have been replaced by simple bonding rules, the level of chemistry included in the corresponding lecture can be tailored to fit the learning objectives of the course.

For a materials science course where the students have never been formally exposed to polymer science or organic chemistry, the details of the chemistry can be neglected and only the bonding rules of the monomers need to be discussed. This may be particularly advisable if the course includes a significant number of students from disciplines other than chemistry or chemical engineering. These simulations will still serve to give the students a firm, intuitive grasp of what is a polymer and how they are formed. After a demonstration in front of the class, which may take less than 30 minutes, the students should be able to describe how initiator concentration affects the conversion rate and the final molecular weight of a polymer, the three basic steps of a free-radical chain polymerization, effects of termination mechanism on molecular weight, effects of temperature, the importance of stoichiometry in stepwise growth polymerizations, the effect of mono-functional groups, and the concept of gelation. These critical concepts can be covered quickly and effectively by using this simulation as a visual aid. After this brief tutorial, students will be better prepared for polymer work in undergraduate research projects, industrial internships, or graduate-level polymer courses. The students can then be referred to the website if they wish to learn more about polymerization reactions.

The full potential of the simulation can be used in a graduate-level polymers course. The simulations are not ideal for advanced graduate work or for research purposes since they are two-dimensional, contain a small number of molecules (with respect to the statistics of large numbers of polymers), and the

specific chemical mechanisms are neglected. This simplicity, however, makes the simulations ideal for illustrative purposes for an introductory polymer science or engineering course, because most of the fundamental polymer formulae still apply. The students can then use the simulations to collect their own data, copy the data to a spreadsheet, analyze the data, interpret the results, and discuss how their results agree or disagree with theoretical predictions.

Students in a polymer science course should be able to quantitatively predict the results of the given polymerization from the concentrations of the reactants. For instance, in an unbalanced step-wise growth polymerization consisting of two di-ols for each di-acid monomer, a student should predict that the maximum number-average degree of polymerization would be three, which is verifiable by the simulation. Furthermore, the simulation would also help the student visualize that while the number-average degree of polymerization approaches three, there is significant polydispersity. Students should also be able to quantitatively predict the effect of mono-functional groups. The number- and weight-average molecular weights can be pasted into a spreadsheet, plotted



**Figure 2.** a) Simulation results for number- and weight-average degrees of polymerization plotted vs. conversion and compared to theory. b) Polydispersity index of simulation plotted vs. conversion and compared to theory.

as in Figure 2, and compared to theoretical predictions from the following equations.<sup>[2]</sup>

$$\bar{X}_n = \frac{1}{1-p}, \quad \bar{X}_w = \frac{1+p}{1-p}, \quad \text{PDI} = 1+p \quad (1)$$

where  $\bar{X}_n$ ,  $\bar{X}_w$ , PDI, and  $p$  represent number-average degree of polymerization, weight-average degree of polymerization, polydispersity index, and conversion, respectively.

In a free-radical chain polymerization, the students should be able to predict the final number-average molecular weight for a polymerization reaction if the initiator-to-monomer ratio and termination mode are given.

Gelation can be modeled by using the step-wise growth simulator. Gelation occurs when the polymer network reaches an infinite average molecular weight, which can be easily visualized with the periodic boundary condition by pressing “1” as seen in Figure 3 (next page). If the average monomer functionality,  $f$ , is greater than two for a stoichiometric mixture of reagents, then gelation will typically occur at a high conversion. The critical conversion at which gelation will occur (where a polymer of infinite size appears) can be predicted as  $p_c = (f-1)^{-1/2}$  for a large number of monomers in a stoichiometric, 3-D system.<sup>[3]</sup> Since the simulator features a relatively small number of monomers in a 2-D system for visualization purposes, however, this equation only works as an approximation.

The effects of temperature on the polymerization can also be observed. The simulations can be run under isothermal or adiabatic conditions, and students can plot the conversion over time for both conditions. Under adiabatic conditions, the heat of reaction will raise the temperature during the polymerization reaction, resulting in faster reaction rates. In the stepwise growth simulator, however, the reactions are reversible, so the larger temperatures generated in the reaction will cause depolymerization, which will result in a lower final molecular weight. This auto-acceleration is a real effect as is the thermal degradation which can result at high temperatures. One unrealistic aspect, however, is that the thermally broken polymer chains are able to reform bonds. In reality, thermally degraded polymers typically result in chain ends that are not reactive with monomers or other polymer ends.

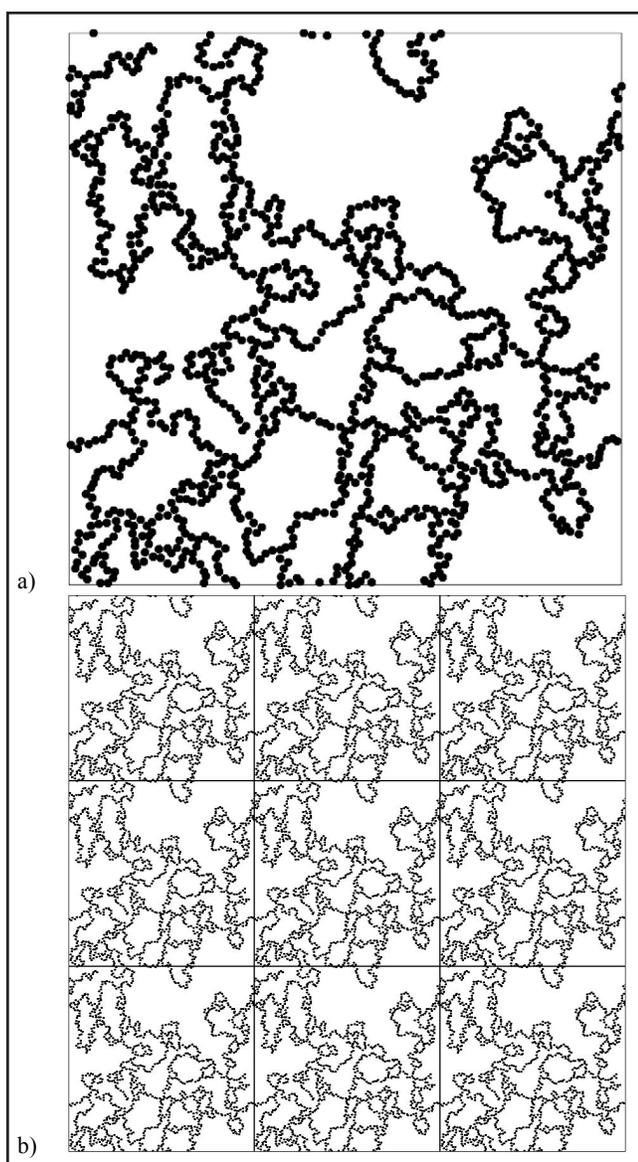
A student can copy the conversion data over time by right-clicking on the plot and then pasting the data into a spreadsheet where the reaction rate kinetics can be analyzed. A reaction rate equation for the consumption of monomer can be pro-

posed such as  $\frac{d[M]}{dt} = -k[M]^n$ , where  $M$ ,  $t$ ,  $k$ , and  $n$  are the monomer concentration, time, rate constant, and order of reaction, respectively. The student can perform his/her own analysis to then determine the values for the rate constant and the order of reaction. The student can also investigate the effect of temperature on the rate constant.

Acid catalysis causes the reaction order for many stepwise polymerizations to be third order ( $n = 3$ ).<sup>[4]</sup> Since acid catalysis is not included in the simulation mechanism, however, a second-order reaction is expected, which has a solution of the form:

$$\frac{1}{M} = \frac{1}{M_0} + kt$$

where  $M_0$  is the initial monomer concentration.<sup>[5]</sup> From this equation,  $k$  can be readily calculated by taking the slope of  $1/M$  plotted over time as shown in Figure 4a. A model of

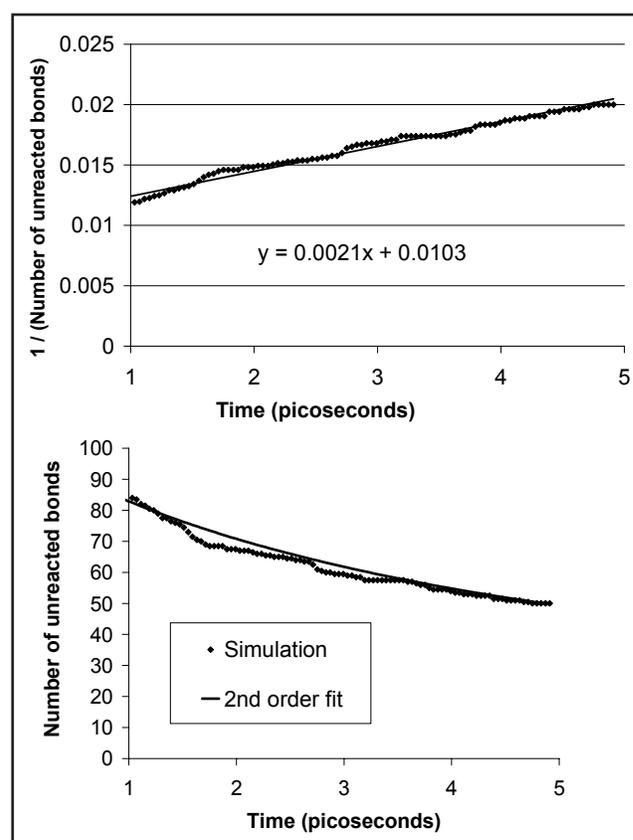


**Figure 3.** a) Simulation of gelation caused by tri-functional monomers. b) View of the simulation with the periodic boundary condition showing  $3 \times 3$  unit cells. Note that the chain continues from one unit cell to the next and is of infinite size after gelation.

the second order reaction using the fitted  $k$  value is shown in Figure 4b. Students can alternatively fit  $k$  and  $n$  without assuming a reaction order.

For a multidisciplinary polymer engineering course, a minimum amount of organic chemistry may be included in the course. In my CHEE 417(G): “Polymer Engineering” course, I remind the students that alcohols react with carboxylic acids to form esters, which leads to showing how a di-ol and a di-acid can react to form a long chain of polyester. At minimum, this amount of chemistry is required to understand polymer nomenclature, because a student may have some difficulty in understanding what a polyester is and how it is made without the basic understanding of an esterification reaction. Students should similarly be able to identify common polymers and the types of monomers used to synthesize them. This will help the students become conversant in polymer terminology so that they may better comprehend research papers and presentations relevant to polymers later in their careers.

In a graduate-level polymer chemistry course with an organic chemistry prerequisite, the chemistry mechanisms would be an essential element of the corresponding lectures. In such a course, the students might be asked to critique this



**Figure 4.** a) The inverse of the number of unreacted monomer bonds is plotted vs. time to find  $k$ . b) The fitted reaction constant can be used to compare the 2nd order kinetics equation to the simulation data.

polymerization model by discussing some of the unrealistic ramifications of removing the chemical mechanisms. For instance, the students may predict how the removal of the acid-catalysis mechanism in the polyesterification reaction affects the order of the reaction. An instructor might also explain how polymer chains may thermally degrade through a beta-scission mechanism or discuss other unfavorable side reactions.

## RESULTS

The use of these simulations had a positive impact on the effectiveness of instruction. As an instructor, I found this was an enjoyable variation from the usual PowerPoint and chalkboard lectures. The students welcomed this change in the medium of instruction even more so. This alternation in medium alone can help an instructor avoid “Death by PowerPoint” as described by Felder and Brent.<sup>[6]</sup> Furthermore, the students garner other benefits through doing their own simulated experiments, analyzing their own data with spreadsheets, and performing the critical thinking required to interpret the results and compare them to theoretical predictions. Incorporating these tasks is also valuable for achieving accreditation outcomes and improving course evaluations.

Instructors should find, as with any model or simulation, that some theoretical equations will work exactly, some approximately, and others not at all due to the assumptions and approximations of the model and how it fails or succeeds in representing reality. One unrealistic aspect of the simulation is that all of the monomers in the simulation were given a molecular weight of 1 g/mole. Therefore, the degree of polymerization is equal to the molecular weight. This was done for the sake of simplicity; however, it was found that it could be confusing to the students when the terms “degree of polymerization” and “molecular weight” are used interchange-

ably. Emphasizing this caveat early in the introduction of the simulation briefly, but clearly, should alleviate this issue.

Equations derived specifically for 3-D systems may only work as approximations in this simulation. Equations derived based strictly on stoichiometry and extent of conversion should work exactly, however. Allowing students to predict which equations will work or fail with this model exercises their critical-thinking skills and will give them a deeper understanding of the equations and their implied assumptions.

Beyond my anecdotal observations, an anonymous survey consisting of 49 questions (38 multiple choice and 11 open response) was taken by an independent party to evaluate the effectiveness of this model for the CHEE 417(G): “Polymer Engineering” course in the Fall of 2008. A sub-selection of the questions is shown in Table 1 for brevity. The class only had seven students, which is excellent for instruction and discussion, but poor for survey statistics even with all seven students responding. Regardless, the feedback was very positive for all of the students. The survey data for the questions in Table I was collected again in the Fall of 2009 with 12 out of the class of 18 students responding with similarly positive results.

In addition to the quantitative survey data, the students were asked open-ended questions regarding the simulation and its implementation. These results were similarly favorable. Many of the students found the simulations aided their ability to visualize the polymerization reactions and found the simulator easy to use. Some students also appreciated the opportunity to practice spreadsheets skills in the analysis of the kinetics. While most students found the interface easy to understand and use, especially with the supporting documentation and examples on the website, it was recommended that the instructor take time at the start to explain the features to be controlled using the interface. Some students have suggested

**TABLE 1**  
Survey Results of the Simulation Module for CHEE 417(G): “Polymer Engineering”

#	Statements	Fall 2008 Average	Fall 2009 Average
1	The computer simulation was an effective use of my time.	4.14	4.25
2	I find this computer simulation helped me visualize molecular motion better than I could before.	4.43	4.50
3	This simulation was a valuable experience.	4.43	4.25
4	This computer simulation allowed me to study a problem in a way not possible with a conventional experiment.	4.14	4.13
5	The use of this module aided in my understanding of the material.	4.43	4.08
6	I believe this module should be used next year.	4.71	4.25
7	The use of this simulation module was a valuable use of class time.	4.43	4.00
8	The content covered in the simulation was appropriate to the course.	4.71	4.17
9	The computer simulation provided me insights I had not had before.	4.29	4.25
10	I feel the computer simulation was effective in increasing my understanding of molecular motion.	4.29	4.25
The individual responses were scored as: 5–Strongly Agree, 4–Agree, 3–Neutral, 2–Disagree, 1–Strongly Disagree. The averages of the responses are shown.			

the model should be more complex, featuring more realistic chemical mechanisms, larger numbers of monomers, and making the simulation three-dimensional. This would necessarily make the simulator more complicated to setup and slower to run, however. There was a fair balance of comments that the simulator was too simplistic vs. being too complicated to set up, which seems to indicate that a good balance has been achieved for students at this level. A trial version of a 3-D simulator was partially developed, but it was not used, because the molecules and interactions were harder to see, even though it was more aesthetically impressive.

Some students would prefer the assignments be assigned to small groups; however, an equal number of students preferred working individually. Running multiple simulations to high conversions can take a considerable amount of time, so allowing data sharing among groups might be a reasonable option if large take-home projects are assigned. Instructors, as in any experiment or assignment, are advised to conduct the simulations themselves before assigning them to make sure that the time demands are reasonable and that the expected results are produced. This simulator was primarily used in individual take-home assignments to ensure that each student had an equal opportunity to use the simulator and received an individual assessment of their work. The ability to work in teams is an important career skill and accreditation outcome, however, and this could be an opportunity to implement a team-based project in a polymer course.

## CONCLUSIONS

Courses generally benefit from tangible visual aids, demonstrations, and laboratory experiments. Unfortunately, many of these course supplements are not implemented due to the material cost, preparation time, safety considerations, or laboratory space required. The simulations presented here allow students to accrue most of the benefits of running their own experiment as they set experimental parameters, collect and analyze data, exercise spreadsheet skills, and then interpret their own results. The only investment required is a small amount time by the instructor to become familiar with the simulator and to make sure that the students have access to a computer.

Overall, the simulations were found effective in explaining the fundamentals of polymerization in a 30-minute demonstration for a materials science and engineering course. The simulations were also successful for teaching a polymer engineering graduate course over the course of the month in which lecture topics, demonstrations, and assignments were conducted and reviewed using the simulations and spreadsheets. An instructor can use these simulators as a brief qualitative introduction to polymer science or as an opportunity for rigorous derivation, analysis, and testing of polymer equations, or any intermediate between these extremes that fits the learning objectives of the course.

## ACKNOWLEDGMENTS

The development of this and other molecular-simulation-based education modules<sup>[7]</sup> was supported by grant DUE-0618521 from the National Science Foundation to the CACHe (Computer Aids for Chemical Engineering) Corporation.<sup>[8]</sup> The author proposed the polymerization module including the basic algorithm and developed the supporting documentation. Prof. David Kofke of the University at Buffalo manages the module development project with algorithm implementation and coding provided by Dr. Andrew Schultz. Additional software support has been provided by Robert Ressler. Phil McLaury conducted the assessment of the simulation under the supervision of Prof. George Bodner of Purdue University.

## REFERENCES

1. Painter, P.C., and M.M. Coleman, *Fundamentals of Polymer Science*, 2nd Ed., Technomic Publishing, Pennsylvania (1997)
2. Sperling, L.H., *Introduction to Physical Polymer Science*, 4th Ed., Wiley-Interscience, New Jersey (2006)
3. Odian, G., *Principles of Polymerization*, 3rd Ed., Wiley-Interscience, New York (1991)
4. Sun, S.F., *Physical Chemistry of Macromolecules*, Wiley-Interscience, New York (1994)
5. Noggle, J.H., *Physical Chemistry*, HarperCollins Publishers, USA (1989)
6. Felder, R.M., and R. Brent, "Death By PowerPoint" *Chem. Eng. Ed.*, **39**(1), 28 (2005)
7. Etomica: Molecular Simulation API, <<http://www.etomica.org>>
8. CACHe, <<http://www.cache.org>> □

# EHRENFEST'S LOTTERY — TIME AND ENTROPY MAXIMIZATION

**“Why don’t you call it entropy? ... no one understands entropy very well, so in any discussion you will be in a position of advantage.”**

– John von Neumann’s name suggestion to Claude Shannon  
for missing information in information theory.<sup>[1]</sup>

HENRY S. ASHBAUGH

*Tulane University • New Orleans, LA 70118*

The conservation of energy dictated by the First Law of Thermodynamics is an intuitively appealing concept. Simply put, energy is neither created nor destroyed, but is just transformed from one form to another—kinetic energy transformed into potential energy, electrostatic energy transformed into gravitational energy, etc. The challenge of applying the First Law of Thermodynamics then reduces to an accountant’s job, maintaining a balance sheet for energy in its different forms. Tracking down apparent discrepancies in the First Law can serve as a tool for scientific discovery, having played a vital role in the development of relativity, quantum mechanics, and particle physics. Despite the power of the First Law, it does not tell us how systems change with time when they are freely allowed to evolve (*e.g.*, a locking pin is removed from a piston or an ice cube is placed in a hot cup of coffee) and what the final state is, despite our intuitions (the piston moves to equate pressures and the ice cube melts). Simply put, the First Law of Thermodynamics is insufficient to determine equilibrium.

Thermodynamic equilibrium is determined by the introduction of the concept of entropy, which unlike the energy is not a conserved property but obeys a maximization principle encapsulated by the Second Law of Thermodynamics. According to this law, the entropy change of an isolated system is greater than or equal to zero for any spontaneous process, and the entropy is maximized at thermodynamic equilibrium. The Second Law of Thermodynamics identifies a time direction by equating time spontaneously moving forward as the direction in which entropy increases. In difference to other natural laws which are time reversible, like Newton’s laws of motion, the arrow of time is unique to the Second Law of Thermodynamics. Indeed, it has been asserted that all phenomena

that behave differently in one time direction can ultimately be linked to the Second Law of Thermodynamics.<sup>[2]</sup>

It is usually at this point in an introductory thermodynamics class that reversible and irreversible processes are introduced, and the differential change in entropy ( $dS$ ) is equated with the reversible heat that crosses a closed system’s boundaries ( $dQ_{\text{rev}}$ ) divided by the absolute temperature ( $T$ ),

$$dS = \frac{dQ_{\text{rev}}}{T}, \quad (1)$$

following Clausius’ historical development. While this classical statement of the entropy change is true, the connection between an idealized reversible process that takes an infinite amount of time to complete and real observable changes in properties that occur over finite time scales is somewhat abstract. To help solidify this concept, it is helpful to provide physically motivated examples of the entropy in action and the approach to equilibrium.

From his studies of gas dynamics and equilibrium, Ludwig Boltzmann proposed an alternate entropy formulation that draws connections between macroscopic observables and the

**Henry S. Ashbaugh** is an associate professor of chemical and biomolecular engineering at Tulane University. He holds chemical engineering degrees from North Carolina State University (B.S. '92) and the University of Delaware (Ph.D. '98). Hank joined Tulane after research appointments at Lund University in Sweden, Princeton University, and Los Alamos National Laboratory. His research interests are in the application of statistical thermodynamics and molecular simulations towards advancing self-assembly for understanding nanostructured materials.



molecular nature of matter. Boltzmann's entropy formula,

$$S = k \ln \Omega, \quad (2)$$

is famously engraved above his bust at his grave marker in Vienna.<sup>[3]</sup> The macroscopic entropy in this expression is identified as proportional to the logarithm of the number of available molecular states of a system,  $\Omega$ , where the constant of proportionality  $k = R/N_A$  is Boltzmann's constant, and is equal to the ratio of the ideal gas constant to Avogadro's number. Interestingly from a historical point of view, Planck was the first to articulate Eq. (2) in resolving the black body radiation problem, building upon Boltzmann's earlier work on the connections between entropy and probability.<sup>[4,5]</sup> Following Eq. (1), Boltzmann's entropy formula directly links the addition of heat to an increase in the number of accessible molecular states. Boltzmann's entropy formula underlies the popular conceptualization of entropy as disorder or randomness. A literal interpretation of entropy as disorder can be problematic, however, due to gut feelings of what constitutes disorder,<sup>[6,7]</sup> and alternate interpretations that equate entropy with energy dispersal.<sup>[8]</sup> Adding to the confusion, a first principles derivation of Eq. (2) is unavailable and its justification is ultimately empirical, resting on its predictive power.

A better understanding of the Second Law of Thermodynamics necessarily requires students to work through examples and thought experiments. To familiarize students with the connections between their personal expectations for equilibrium and maximization of the entropy with increasing time, I describe a series of games that can be played out in class or on a computer. The student assumes the role of a Bingo-like caller transferring numbered marbles between urns based on the outcomes of spins of a lottery wheel. The relationships between entropy, time (*i.e.*, spins of the wheel), and increases in the number of states are shown to be applicable to engineering concepts like diffusion and the derivation of equations-of-state. By establishing entropy maximization in terms of familiar concepts, I hope to form a stronger foundation for explaining the connection between the Second Law of Thermodynamics and equilibrium, and show how this principle pervades problems outside the traditional thermodynamics curriculum.

## EHRENFEST'S LOTTERY

Paul and Tatiana Ehrenfest proposed a simple thought experiment to explore the connections between probability, entropy, and time.<sup>[9]</sup> The experiment is played out as a lottery obeying the following rules (Figure 1): You are given two urns and  $N$  **sequentially numbered** marbles. Initially, the first urn is filled with  $n_1$  marbles, while the second urn is filled with the remaining  $n_2$  marbles. At regular time intervals,  $\Delta t$ , a lottery wheel is spun, randomly producing a number between 1 and  $N$ . The randomly selected marble is then located, taken from the urn it is in, and placed into the other urn. The wheel is

then spun again and the process is repeated *ad infinitum*. On the molecular level the marbles can be thought of as representing individual gas molecules, while the urns correspond to discrete volume units. While the correspondence between the lottery's random-transfer dynamics and molecular motions may appear tenuous, this model has been shown to provide an accurate description of gas mixing.<sup>[10]</sup>

After describing the lottery, the class may already have a number of intuitive expectations about the evolution of urn occupancy trends, including:

- 1) *After playing the game for a sufficiently long time, the number of marbles in both urns will average  $N/2$ .*
- 2) *The relative time sequence of different occupational states can be, roughly, worked out given the number of marbles in each urn. For example, say you are told  $N = n_1 = 100$  marbles, and that at one point in the spin sequence there are  $n_1 = 47$  and  $n_2 = 53$  marbles distributed between the urns, while at another point there are  $n_1 = 84$  and  $n_2 = 16$  marbles in the two urns. It is most reasonable to expect then that the second instance occurred before the first in the sequence.*

The first expectation reflects the limiting probability for a fair game so that each marble has a 50/50 chance of being in either urn. The second expectation, while perfectly reasonable, is not as easy to justify based only on gut feelings. In the long time limit, the probability distribution of urn occupational probabilities approaches a binomial distribution. For large  $N$ , the binomial distribution is sharply peaked about the 50/50 occupational probability, but it does not rule out the observation of a heavily skewed distribution such as 84 and 16 marbles. The probability of observing this configuration for a well-mixed system is approximately  $10^{-12}$ , small but finite. These skewed distributions become exceedingly rare with increasing  $N$ , so that in practice they can be neglected. We note that this omission provides a potential entry for Maxwell's demon to wreak havoc, getting usable work by waiting for unlikely events. While outside the scope of this article, it may be useful to segue into a discussion of Maxwell's demon after introducing Ehrenfest's lottery.<sup>[11]</sup>

The relationship between Boltzmann's entropy and the urn occupational states can be evaluated by counting the number of ways of randomly choosing  $n_1$  marbles to be placed in urn 1 and  $n_2$  marbles in urn 2 independent of the specific numbering of the individual marbles. To calculate the number of ways of divvying up the marbles between the two urns we draw a hypothetical random sequence of all the marbles, and then place the first  $n_1$  marbles in urn 1 and the remaining  $n_2$  marbles in urn 2. The number of ways of arranging all the marbles in a random sequence is  $N!$  following standard combinatorial arguments. The order in which the first  $n_1$  marbles are placed in urn 1, however, does not change the final state of the system, which is only specified by the number of marbles in each urn but not their identities. The number of ways of

choosing  $n_1$  marbles to be placed in urn 1 is therefore over counted by the number of ways of randomly selecting this subset of marbles,  $n_1!$ . A similar over counting holds for the marbles designated for urn 2. The number of ways of randomly dividing  $n_1$  and  $n_2$  marbles between the two urns is then

$$\Omega = \frac{N!}{n_1!n_2!}. \quad (3)$$

A perceptive student may notice that Eq. (3) implies that each marble is indistinguishable from one another, but in fact we have indicated that the marbles are numbered from 1 to  $N$ . When the marbles are distinguishable the number of ways of putting specified marbles in each urn is exactly one. For example for a 4-marble system we could specify that marbles 1 and 4 are in the first urn and marbles 2 and 3 are in the second, and there is only one way to achieve this distribution. The numbering scheme, however, is only a matter of convenience for the purpose of choosing a marble to move, and we are free after each spin to renumber the marbles for

the next spin without changing the probabilistic distribution of marbles in the lottery. So, returning to our 4-marble example we could renumber the marbles 1 and 2 in the first urn and 3 and 4 in the second without changing the equilibrium outcome of the game. From the game's point of view, only the number of ways of distributing the  $n_1$  and  $n_2$  marbles matters, not the numbered identities of the individual marbles. The same can be said for mixing identical molecules in a volume, where only separations of chemical species, rather than specified individual molecules, can be achieved by manipulating the vastly smaller number of macroscopic thermodynamic state variables like temperature and pressure.<sup>[12]</sup>

The entropy of a configuration of indistinguishable marbles can be evaluated by substituting Eq. (3) into Boltzmann's entropy formula, yielding

$$S = k \ln \left[ \frac{N!}{n_1!n_2!} \right] \approx -k \left[ n_1 \ln \frac{n_1}{N} + n_2 \ln \frac{n_2}{N} \right]. \quad (4)$$

In this expression the factorial terms were simplified by applying Stirling's approximation, *i.e.*,  $\ln X! \approx X \ln X - X$ .<sup>[13]</sup> When all the marbles reside entirely in either urn 1 or 2 ( $n_1 = N$  or 0) there is only one way to generate this configuration and the entropy is zero. When the marbles are evenly distributed between the urns ( $n_1 = n_2 = N/2$ ) the entropy is a maximum and equal to that  $S_{\max} = kN \ln 2$ . Between the two extremes, the entropy is a monotonically increasing function.

The expectation that the entropy of the system increases on average with each spin of the lottery wheel can be verified by considering the marble transfer probabilities. The average change in the entropy as the result of a lottery spin is determined by summing over all possible transfer moves the probability of choosing to transfer a marble from one urn to the other (*i.e.*,  $p(\text{urn 1} \rightarrow \text{urn 2})$  or  $p(\text{urn 2} \rightarrow \text{urn 1})$ ) multiplied by the change in the entropy associated with each move (*i.e.*,  $\Delta S(\text{urn 1} \rightarrow \text{urn 2})$  or  $(\text{urn 2} \rightarrow \text{urn 1})$ )

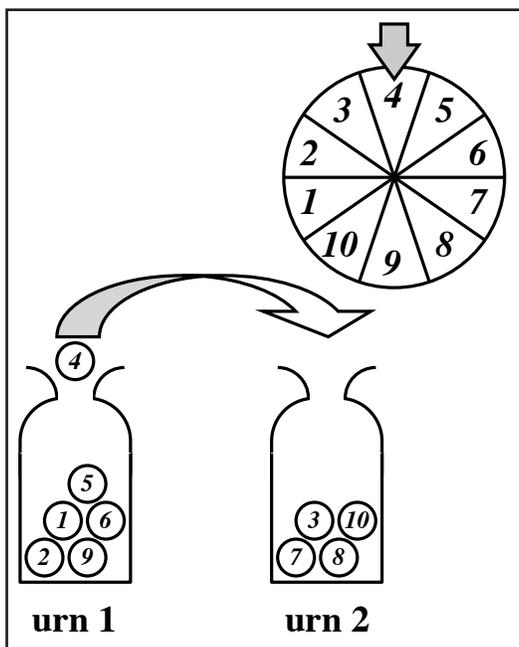
$$\langle \Delta S \rangle = p(\text{urn 1} \rightarrow \text{urn 2}) \Delta S(\text{urn 1} \rightarrow \text{urn 2}) + p(\text{urn 2} \rightarrow \text{urn 1}) \Delta S(\text{urn 2} \rightarrow \text{urn 1}). \quad (5)$$

The angled brackets,  $\langle \dots \rangle$ , denote an average. The probability of choosing to move a marble from an urn is equal to the number of marbles in that urn divided by the total number of marbles, *e.g.*,  $p(\text{urn 1} \rightarrow \text{urn 2}) = n_1/N$ . Expanding Eq. (4) in terms of  $n_1$  and substituting into Eq. (5), an accurate expression for the average change in the entropy between successive spins of the wheel can be derived,

$$\langle \Delta S \rangle = k \frac{n_1 - n_2}{N} \ln \left( \frac{n_1}{n_2} \right) \geq 0. \quad (6)$$

This average entropy change is positive when the occupation numbers differ and approaches zero as the occupations of each urn approach one another. As shown below, however, this expression does not preclude fleeting, instantaneous, entropy decreases due to random fluctuations in the urn occupational state about the equilibrium average.

Starting with  $n_1 = N = 100$  marbles in urn 1, Figure 2 (next page) shows the outcomes for two independent, random lotteries simulated using MATLAB®. As the game plays out, the number of marbles in urn 1 decreases for the first ~150 spins of the lottery wheel, and then fluctuates about the 50/50 occupational state (Figure 2a). The entropy concurrently increases as the marbles become more evenly distributed between the urns (Figure 2b). The occupational fluctuations about the 50/50 marble distribution are a result of the stochastic nature of Ehrenfest's lottery. The relative magnitude of these occupational fluctuations decreases as  $N^{-1/2}$  in accordance with the central



**Figure 1.** Schematic illustration of the two-urn lottery with 10 marbles.

limit theorem, so that on a per-marble basis excursions from the average diminish as the number of marbles increases (Figure 3). For a macroscopic number of molecules/marbles these fluctuations would appear insignificant, although they are manifested experimentally in measurable quantities like the heat capacity and isothermal compressibility.<sup>[14]</sup> While the occupation fluctuations are above and below the equilibrium 50/50 state, these deviations are manifested as spontaneous decreases in the entropy below the maximum value (Figure 2b). These downward fluctuations away from the maximal entropy point to the statistical nature of the Second Law of Thermodynamics. In particular, the Second Law of Thermodynamics is more appropriately thought of as a statement about the equilibrium distribution rather than a property of a single snapshot of molecular positions.<sup>[15]</sup>

The average urn occupancy can be solved analytically from a master equation for the discrete lottery spin dynamics. Given an average of  $\langle n_1(s) \rangle$  marbles are in urn 1 for spin  $s$ , the probability a marble in urn 1 is chosen to be moved into urn 2 is the number of marbles in urn 1 divided by the total number of marbles. Similarly, given  $\langle n_2(s) \rangle$  marbles are in urn 2, the probability a marble in urn 2 is chosen to be moved into urn 1 is  $\langle n_2(s) \rangle / N$ . The change in the average occupancy of urn 1 between spin  $s$  and  $s+1$  is the probability a marble is added to urn 1 less the probability one is taken away,

$$\langle n_1(s+1) \rangle - \langle n_1(s) \rangle = \frac{\langle n_2(s) \rangle}{N} - \frac{\langle n_1(s) \rangle}{N} = 1 - 2 \frac{\langle n_1(s) \rangle}{N} \quad (7)$$

The long time equilibrium state for which the average occupancy does not change between successive spins,  $\langle n_1(s+1) \rangle - \langle n_1(s) \rangle = 0$ , is

$$\langle n_1(s) \rangle = \frac{N}{2}, \quad (8)$$

as expected for a fair lottery. Conservation of the number of marbles dictates the average occupation of urn 2. For an initial occupation of  $0 \leq n_1(0) \leq N$  in urn 1, the solution of Eq. (7) yields

$$\langle n_1(s) \rangle = \frac{N}{2} + \left( n_1(0) - \frac{N}{2} \right) \left( 1 - \frac{2}{N} \right)^s \quad (9)$$

It is straightforward to verify that Eq. (9) satisfies Eq. (7) by back substitution. The occupation dynamics and entropy evolution described by Eq. (9) are compared to the simulated example discussed in Figure 2. The agreement between the random lotteries and master equation results is excellent, although the fluctuations are suppressed by the master equation since it only describes the mean behavior.

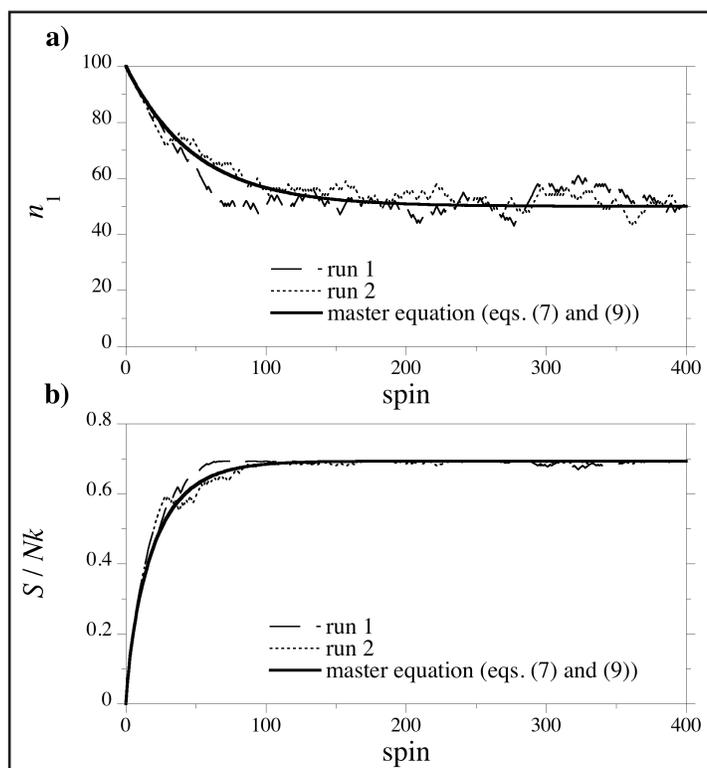
## APPLICATION TO MULTIPLE URNS – A MODEL FOR DIFFUSION

Ehrenfest's lottery can be extended to an arbitrary number of urns numbered from 1 to  $i_{\max}$ . In difference to the two-urn lottery, the marbles are moved following the spins of two lottery wheels. The first spin chooses the marble to be moved as in the two-urn game. The second wheel chooses whether the marble is moved to the urn above or below the starting urn in the sequence, *i.e.*, from urn  $i$  to either urn  $i+1$  or  $i-1$ . When a marble is chosen to move to an urn outside the sequence, *i.e.*, from urn 1 to urn 0 or from urn  $i_{\max}$  to urn  $i_{\max}+1$ , the marble is returned to its starting urn.

The combinatorial counting of states described by Eq. (3) can be extended by replacing the denominator with the product of factorials of the occupancy of each urn. The entropy in this case is

$$S = k \ln \frac{N!}{\prod_{i=1}^{i_{\max}} n_i!} \approx -k \sum_{i=1}^{i_{\max}} n_i \ln \frac{n_i}{N}, \quad (10)$$

where Stirling's approximation has again been used to simplify the factorials. It is worthwhile to consider the limits of Eq. (10) to assure ourselves the entropy follows intuitive expectations for the marble distribution as the lottery is played out. When all the marbles sit in urn  $j$ , substituting  $n_j = N$  and  $n_{i \neq j} = 0$  into Eq. (10) there is only one way to achieve this distribution and the entropy is zero. In the other extreme, the entropy is maximized when the occupancies



**Figure 2.** Outcomes of two random simulations of the two-urn lottery with 100 marbles and the master equation description of the mean behavior. Plots a and b show the occupation of urn 1 and the entropy, respectively.

of each urn are the same and equal to  $N/i_{\max}^{[16]}$ . The entropy maximum in this case is  $S_{\max} = kN \ln i_{\max}$ , which is a generalization of the entropy maximum obtained for the two-urn lottery where  $i_{\max} = 2$ .

While a derivation of the mean change in the entropy,  $\langle \Delta S \rangle$ , following each spin is more involved for the multi-urn lottery, each spin of the lottery wheel results in an exchange between only two urns. The mean entropy change is then expected to follow an equation comparable to Eq. (6). The entropy of the multi-urn lottery should therefore increase as the game is played out following the same logic as for the two-urn lottery.

Figure 4 shows the outcome of a multi-urn game with  $i_{\max} = 10$  urns and  $N = 100$  marbles all initially placed in the first urn. The occupancy of the first urn decreases as the lottery is played out, and the marbles disperse among the remaining urns (Figure 4a). After approximately 10,000 spins, the distribution of marbles is essentially uniform and equilibrium is attained within the statistical fluctuations. As in the two-urn game, the relative fluctuations about the occupation averages decrease as the number of marbles in the game increases. The entropy of the lottery increases as the game is played, and appears to asymptotically approach the equilibrium value of  $S_{\max}/kN = \ln 10 = 2.3$  (Figure 4c).

As in the two-urn game, statistical fluctuations about the equilibrium occupational state where all urns have equal numbers of marbles results in downward fluctua-

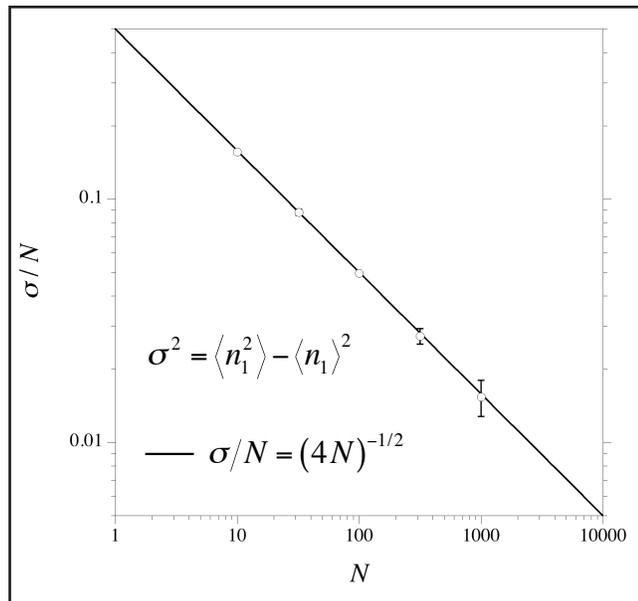
tions in the entropy. Indeed these fluctuations appear more prominent in the 10-urn lottery than in the two-urn lottery. For a fixed number of marbles (*e.g.*,  $N = 100$ ), the probability of observing the marbles to be evenly distributed between all the urns is lower for the multi-urn case than compared to the two-urn lottery, resulting in entropies below the maximum when each urn has equal numbers of marbles. Moreover, for a fixed number of marbles fluctuations about the mean occupational state have a larger relative effect on the fractional occupations used to calculate the entropy [Eq. (10)] as the number of urns increases. These spurious deviations from the monotonic increase in the entropy dictated by the Second Law diminish as the number of marbles increases, in agreement with the two-urn lottery.

A discrete master equation for the mean multi-urn occupation dynamics can be developed analogous to the two-urn equation [Eq. (7)]. In the present case, the change in the number of marbles in urn  $i$  as the result of a lottery spin is equal to the probability a marble from either urn  $i-1$  or  $i+1$  is chosen to be added to  $\left[ \langle n_{i+1}(s) \rangle + \langle n_{i-1}(s) \rangle \right] / 2N$ , less the probability a marble from urn  $i$  is removed,

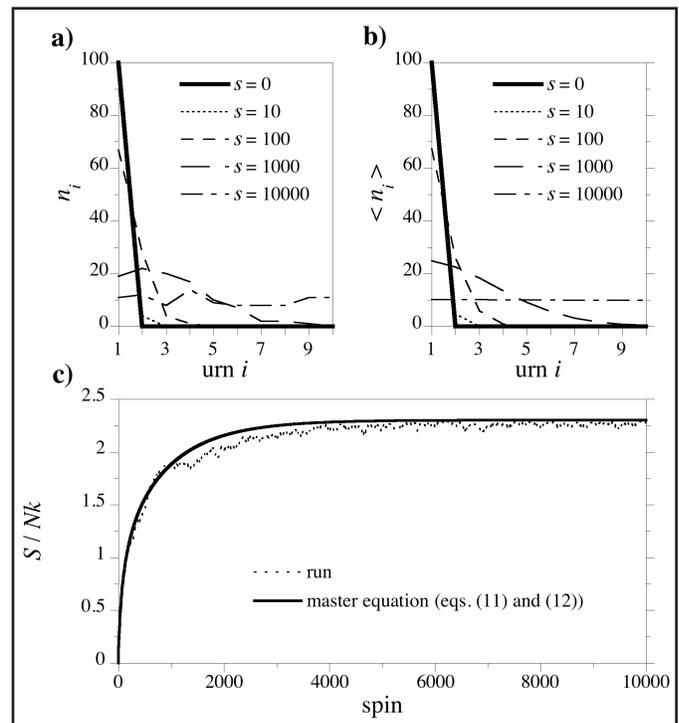
$$\langle n_i(s+1) \rangle - \langle n_i(s) \rangle = \frac{\left[ \langle n_{i+1}(s) \rangle + \langle n_{i-1}(s) \rangle \right]}{2N} - \frac{\langle n_i(s) \rangle}{N}. \quad (11)$$

When a marble is chosen to move to an urn outside the sequence, the marble return boundary condition applied to urns  $i = 1$  and  $i_{\max}$  reduces Eq. (11) to

$$\langle n_{i \text{ or } i_{\max}}(s+1) \rangle - \langle n_{i \text{ or } i_{\max}}(s) \rangle = \frac{\langle n_{2 \text{ or } (i_{\max}-1)}(s) \rangle}{2N} - \frac{\langle n_{i \text{ or } i_{\max}}(s) \rangle}{2N}. \quad (12)$$



**Figure 3 (above).** Relative fluctuation,  $\sigma / N$ , in the occupation number of urn 1 in the two-urn lottery as a function of the total number of marbles. **Figure 4 (right).** Results for a 10-urn lottery with all 100 marbles initially placed in the first urn. Occupational distributions after  $s$  spins for a random lottery and by numerical solution of the master equation description are plotted in a and b, respectively. The calculated entropies are plotted in c.



***By establishing entropy maximization in terms of familiar concepts, I hope to form a stronger foundation for explaining the connection between the Second Law of Thermodynamics and equilibrium, and show how this principle pervades problems outside the traditional thermodynamics curriculum.***

If the urns are considered as being evenly spaced apart from one another by  $\Delta x$ , this lottery can be thought of as a model for diffusion with no flux boundary conditions. Comparing Eq. (11) with Fick's Second Law in one dimension,  $\partial n/\partial t = D \partial^2 n/\partial x^2$ , the change in the average occupation of urn  $i$  after the spin on the left-hand side of the equals sign corresponds to a dimensionless time derivative, while the difference in mean urn occupations between neighboring urns on the right-hand side corresponds to a dimensionless spatial second derivative. The effective diffusion coefficient is

$$D = \frac{\Delta x^2}{2N\Delta t}. \quad (13)$$

It should be noted that the diffusion coefficient decreases as the number of marbles increases since the marbles are moved only one at a time, while molecules truly move simultaneously. Equilibrium is achieved for Eqs. (11) and (12) when the mean occupation of all the urns is the same, at which point the entropy [Eq. (10)] is maximized. This lottery can be readily generalized to multi-dimensional diffusion depending on the spatial arrangement of urns. The occupational distribution evolution predicted by Eqs. (11) and (12) and corresponding entropies are shown in Figure 4. The agreement with the random lottery is excellent.

### **A TECHNICAL ISSUE REGARDING THE CONVERGENCE OF THE TWO-URN LOTTERY**

It was recently pointed out that Ehrenfest's two-urn lottery technically does not converge to the binomial distribution in the limit of an infinite number of spins, but rather oscillates between two distributions whose average is the binomial distribution.<sup>[17]</sup> Perhaps the simplest demonstration of this non-convergence is if we consider a two-urn lottery with a single marble placed in urn 1. After the first spin the marble

will be moved to urn 2, and subsequently relocated to urn 1 after the second spin. As the lottery progresses, the marble will oscillate back and forth between the urns, occupying urn 1 after even numbers of spins and urn 2 after odd numbers of spins. After an even number of spins then, the marble will occupy urn 1 with a probability of one and urn 2 with a probability of zero. Similarly, after an odd number of spins the marble will occupy urns 1 and 2 with probabilities of zero and one, respectively. The occupational probability distribution then has not converged to a single distribution, but vacillates between two distinct distributions. If the even and odd spin probability distributions are averaged, however, we obtain a 50/50 probability distribution as dictated by the binomial distribution for a single marble.

The nonconvergence of the two-urn probability distribution can be alleviated by breaking the even/odd symmetry by introducing spin outcomes where no marbles are moved, thereby opening up the possibility of the marble in the example above of being found in urn 1 (2) after an odd (even) number of spins. The no-flux boundary condition for the multi-urn lottery breaks the even/odd symmetry of the two-urn lottery, allowing the occupational probability distribution to converge. The two-urn lottery could converge to a single distribution, rather than an average of even and odd distributions, by enforcing the no-flux boundary condition of the multi-urn lottery after performing a second move direction determining spin. In practice, however, the nonconvergence of the two-urn lottery does not have any practical consequences on the results presented in Figures 2 and 3, since they track the evolution of states of individual spin sequences.<sup>[17]</sup>

### **RELATIONSHIP TO THE IDEAL GAS LAW**

The long-time equilibrium of the multi-urn lottery provides an inroad for deriving the ideal gas law as an outcome of entropy maximization. From standard thermodynamic relationships, the equation of state follows from the derivative of the equilibrium entropy with respect to volume at constant internal energy and number of marbles (molecules), *i.e.*,  $P = T \left( \partial S_{\max} / \partial V \right)_{U,N}$ . As pointed out above, the equilibrium entropy of the multi-urn lottery is  $S_{\max} = kN \ln i_{\max}$ . Based on the lottery rules, the marbles do not interact and an infinite number of marbles could potentially be placed in an urn, making the energy effectively constant. If each urn has the same volume,  $v_{\text{urn}}$ , the total volume of the system is given by the product of the number of urns and their volumes  $V = i_{\max} v_{\text{urn}}$ . To this point I have not discussed the temperature,  $T$ , within the context of the lottery. Since the temperature is directly related to the average molecular velocity,  $\Delta x/N\Delta t$ , we can surmise the temperature is inversely related to the time between spins.

Based on these considerations, the pressure is given by the increase in the equilibrium entropy associated with adding another urn (volume) increment to the lottery while keeping the number of marbles constant,

$$\begin{aligned}
P &\approx T \frac{\Delta S_{\max}}{\Delta V} = T \frac{S_{\max}(i_{\max} + 1) - S_{\max}(i_{\max})}{(i_{\max} + 1)v_{\text{urn}} - i_{\max}v_{\text{urn}}} = kNT \frac{\ln\left(\frac{V + v_{\text{urn}}}{v_{\text{urn}}}\right) - \ln\left(\frac{V}{v_{\text{urn}}}\right)}{v_{\text{urn}}} \\
&= kNT \frac{\ln\left(\frac{V + v_{\text{urn}}}{V}\right)}{v_{\text{urn}}} \approx \frac{kNT}{V} = \frac{nRT}{V}.
\end{aligned} \tag{14}$$

In the final equality,  $n = N/N_A$  is the number of marbles/molecules in mole units. Thus, the ideal gas law follows from the dispersal of marbles among a collection of urns. Non-ideal contributions to the equation-of-state arise from the introduction of energetic interactions between marbles, *e.g.*, excluded volume and dispersion interactions, which temper the urn occupancies.

## PROGRAM AVAILABILITY

The lottery results reported in Figures 2 – 4 were generated using a MATLAB® simulation. I have uploaded the MATLAB® program, sample input files, and run instructions to the MathWorks file exchange website for free distribution.<sup>[18]</sup> This program simulates the two- and multi-urn lotteries, solves the master equation spin dynamics, calculates entropies, and plots the results.

## DISCUSSION

Ehrenfest's Lottery can be used at multiple points throughout the thermodynamics curriculum to reinforce the role of the Second Law of Thermodynamics in determining equilibrium and to highlight the molecular nature of substances. In practice, I have used the two-urn lottery at the beginning of our discussions of the Second Law during the first semester thermodynamics class at Tulane University. The multi-urn lottery and the connection to the ideal gas law are introduced further along in the semester once thermodynamic partial derivative relationships have been discussed. I return to the multi-urn lottery in our second-semester thermodynamics class after our students have had transport phenomena to connect diffusion processes to the Second Law. This model can be readily extended to ideal mixing and the van der Waals equation of state by introducing additional rules into the game, like adding colors to the marbles (mixing) or finite marble volumes and attractive interactions between marbles in neighboring urns (van der Waals). An alternate formulation of this model, referred to as the Dog and Flea model, has also been developed to further explore transport phenomena for small systems and chemical reactions.<sup>[19]</sup> While not a panacea, Ehrenfest's lottery provides a simple model that, when used in conjunction with other illustrative examples like the Carnot cycle, can shore up student appreciation of the Second Law of Thermodynamics.

## REFERENCES

1. Avery, J., *Information Theory and Evolution*, World Scientific Publishing, River Edge, NJ (2003)
2. <<http://en.wikipedia.org/wiki/Entropy>>
3. <[http://en.wikipedia.org/wiki/Ludwig\\_Boltzmann](http://en.wikipedia.org/wiki/Ludwig_Boltzmann)>
4. Bent, H.A., *The Second Law: An Introduction to Classical and Statistical Thermodynamics*, Oxford University Press, New York, NY (1965)
5. Planck, M., *Scientific autobiography, and other papers*, Philosophical Library, New York, NY (1949); p 41-43
6. Styer, D.F., "Insight Into Entropy," *Am. J. Phys.*, **68**(12) 1090 (2000)
7. Laird, B.B., "Entropy, Disorder, and Freezing" *J. Chem. Ed.*, **76**(10) 1388 (1999)
8. Lambert, F.L., "Disorder—A Cracked Crutch for Supporting Entropy Discussions," *J. Chem. Ed.*, **79**(2) 187 (2002)
9. Ehrenfest, P., and T. Ehrenfest, *The Conceptual Foundations of the Statistical Approach in Mechanics*, Dover, New York, NY (1990)
10. Scalas, E., E. Martin, and G. Germano, "Ehrenfest Urn Revisited: Playing the Game on a Realistic Fluid Model," *Phys. Rev. E*, **76**(1) 011104 (2007)
11. Rastogi, S., "How a Clever Demon Nearly Blew Up the Second Law of Thermodynamics," *Chem. Eng. Ed.*, **26**(2) 78 (1992)
12. Jaynes, E.T., "The Gibbs Paradox" in *Maximum entropy and Bayesian Methods*, eds. Smith, C. R., G. J. Erickson, and P. O. Neudorfer, Kluwer Academic Publishers, Dordrecht, Netherlands (1992)
13. <[http://en.wikipedia.org/wiki/Stirling%27s\\_approximation](http://en.wikipedia.org/wiki/Stirling%27s_approximation)>
14. Callen, H.B., *Thermodynamics and an Introduction to Thermostatistics*, 2nd Ed., Wiley, New York, NY (1985)
15. Evans, D.J., and D.J. Searles, "The Fluctuation Theorem," *Adv. Phys.*, **51**(7), 1529 (2002)
16. Kinchin, A.I., *Mathematical Foundations of Information Theory*, Dover, New York, NY (1957)
17. MacCluer, C.R., "Nonconvergence of the Ehrenfest Thought Experiment," *Am. J. Phys.*, **77**(8), 695 (2009)
18. Ashbaugh, H.S., "Ehrenfest's Lottery," <<http://www.mathworks.com/matlabcentral/fileexchange/24626>> (2009)
19. Ghosh, K., K.A. Dill, M.M. Inamdar, E. Seitaridou, and R. Phillips, "Teaching the Principles of Statistical Dynamics," *Am. J. Phys.*, **74**(2), 123 (2006) □

# VAPOR-LIQUID EQUILIBRIA

## *Using the Gibbs Energy and the Common Tangent Plane Criterion*

MARÍA DEL MAR OLAYA, JUAN A. REYES-LABARTA, MARÍA DOLORES SERRANO, ANTONIO MARCILLA  
*University of Alicante • Apdo. 99, Alicante 03080, Spain*

Phase thermodynamics is often perceived as a difficult subject with which many students never become fully comfortable. It is our opinion that the Gibbsian geometrical framework, which can be easily represented in Excel spreadsheets, can help students to gain a better understanding of phase equilibria using only elementary concepts of high school geometry.

Phase equilibrium calculations are essential to the simulation and optimization of chemical processes. The task with these calculations is to accurately predict the correct number of phases at equilibrium present in the system and their compositions. Methods for these calculations can be divided into two main categories: the equation-solving approach (K-value method) and minimization of the Gibbs free energy. Isofugacity conditions and mass balances form the set of equations in the equation-solving approach. Although the equation-solving approach appears to be the most popular method of solution, it does not guarantee minimization of the global Gibbs energy, which is the thermodynamic requirement for equilibrium. This is because isofugacity criterion is only a necessary but not a sufficient equilibrium condition. Minimization of the global Gibbs free energy can be equivalently formulated as the stability test or the common tangent test.

The Gibbs stability condition is described and has been used extensively in many references.<sup>[1, 2]</sup> It has been more frequently applied in liquid-liquid equilibrium rather than vapor-liquid equilibrium calculations. Gibbs showed that a necessary and sufficient condition for the absolute stability of a binary mixture at a fixed temperature, pressure, and overall composition is that the Gibbs energy of mixing ( $g^M$ ) curve at no point be below the tangent line to the curve at the given

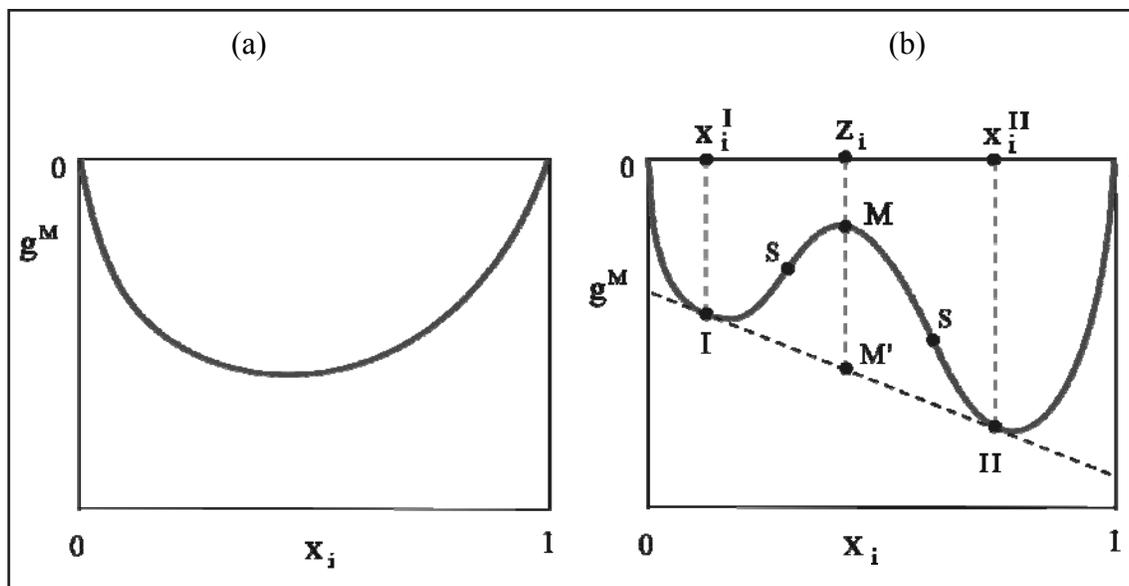
overall composition. This is the case with the binary system in Figure 1(a); it is homogeneous for all compositions. The  $g^M$  vs. composition curve is concave down, meaning that no split occurs in the global mixture composition to give two liquid phases. Geometrically, this implies that it is impossible to find two different points on the  $g^M$  curve sharing a common tangent line. In contrast, the change of curvature in the  $g^M$  function as shown in Figure 1(b) permits the existence of two conjugated points (I and II) that do share a common tangent line and which, in turn, lead to the formation of two equilibrium liquid phases (LL). Any initial mixture, as for example  $z_1$  in Figure 1(b), located between the inflection points  $s$  on the  $g^M$  curve, is *intrinsically unstable* ( $d^2g^M/dx_1^2 < 0$ ) and splits

**Antonio Marcilla** is a professor of chemical engineering at Alicante University. He has presented courses in Unit Operations, Phase Equilibria, and Chemical Reactor Laboratories. His research interests are pyrolysis, liquid-liquid extraction, polymers, and rheology. He is also currently involved with the study of polymer recycling via catalytic cracking and the problem of simultaneous correlation of fluid and condensed phase equilibria.

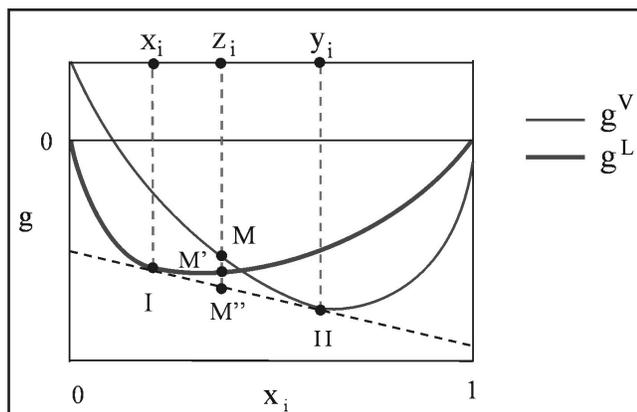
**María del Mar Olaya** completed her B.S. in chemistry in 1992 and Ph.D. in chemical engineering in 1996. She teaches a wide range of courses from freshman to senior level at the University of Alicante, Spain. Her research interests include phase equilibria calculations and polymer structure, properties, and processing.

**Juan A. Reyes-Labarta** received both his B.S. and Ph.D. in chemical engineering in 1993 and 1998, respectively, at the University of Alicante (Spain). After post-doctoral stays at Carnegie Mellon University (USA) and the Institute of Polymer Science and Technology-CSIC (Spain), he is now a full-time lecturer in Separation Processes and Molding Design.

**María Dolores Serrano** is a recent chemical engineering graduate of the University of Alicante. She is currently a post-graduate student, working on different aspects of phase equilibria.



**Figure 1.** Dimensionless Gibbs energy of mixing ( $g^M$ ) for a binary liquid mixture as a function of the molar fraction of component  $i$  ( $x_i$ ): (a) for a homogeneous system, and (b) for a heterogeneous system (LL).



**Figure 2.** Dimensionless Gibbs energy curves ( $g^V$ ,  $g^L$ ) for a binary mixture with a VLE region at constant  $T$  and  $P$  as a function of the molar fraction of component  $i$ .

into two liquid phases having compositions  $x_i^I$  and  $x_i^{II}$ , and a lower value for the overall Gibbs energy of mixing ( $M' < M$ ). Global mixtures located between points I and s or s and II are *metastable* or *locally stable* ( $d^2g^M/dx_i^2 > 0$ ). Therefore, the inflection points separate the metastable equilibrium region from the definitely unstable region.<sup>[3]</sup>

Of course, the Gibbs stability criteria can be extended to ternary or multicomponent systems, where the  $g^M$  curve is replaced by the  $g^M$  surface or  $g^M$  hyper-surface and the common tangent line by the common tangent plane or hyper-plane, respectively.

The analytical expression for the Gibbs energy in LLE calculations is the same for both phases (let it be denoted by  $g^L$ ). This is not the case for equilibria involving different aggregation state phases such as vapor-liquid equilibria (VLE), where different expressions for the Gibbs energy must be used for each phase, yielding two possible Gibbs energy curves:  $g^V$

and  $g^L$ . Obviously, a common reference state must be used for each of the components in the calculations, and for both of the phases involved (for example the pure component as liquid at the same  $P$  and  $T$ ). VLE exists at a given  $T$  and  $P$ , whenever any initial mixture, such as  $z_i$  in Figure 2, is thermodynamically unstable and splits into a vapor and liquid phases having compositions  $y_i$  and  $x_i$ , respectively, with a common tangent line to both  $g^V$  and  $g^L$  curves and a lower value for the overall Gibbs energy of mixing ( $M'' < M' < M$ ).

The geometrical perspective of the Gibbs energy minimization is not new and there are interesting papers dealing with this topic in depth. The paper of Jolls, et al.,<sup>[4]</sup> for instance, presents images of thermodynamic fundamental and state functions for pure binary and ternary systems. These authors discuss the relationship between the model geometry and stability criteria. This geometrical perspective, however, is not usually considered in practice when dealing with VLE using local composition models for the liquid phases, although it clearly illustrates the conditions for stable equilibrium vs. other possible unstable situations. The goal of the present paper is to show an example of the visualization of the VLE from a Gibbs perspective for teaching purposes.

## EDUCATIONAL ASPECTS

Our objective is to propose an exercise to analyze the VLE using the Gibbs common tangent plane criterion using Excel and Matlab. In the engineering education literature, a number of papers concerning the use of spreadsheets have been described.<sup>[5, 6]</sup> Excel spreadsheets are used mainly due to their simplicity and built-in graphics capabilities. Matlab software, which has more powerful graphical tools, can be used to represent 3-D diagrams that support the graphical interpretation of equilibrium since plots can be easily rotated and manipulated to facilitate their understanding.

This activity is framed in the subject of Principles of Separation Processes in Chemical Engineering in a fourth-year course of a five-year program of chemical engineering. This task takes place during the first part of the course and consists of:

- A lecture of the theoretical fundamentals of VLE, presentation and analysis of T-x,y diagrams and sketch of Gibbs stability criterion.
- A guided classroom solution of different VLE problems with increasing difficulty. Previous presentation of a simple non-azeotropic VLE binary system, and consequent solution of a binary homogenous azeotropic mixture, where students work on their own computers using Excel and Matlab.
- Development of a project in groups of students where an analogous analysis of VLE, but also of LLE, must be done for a heterogeneous azeotropic binary mixture.
- As optional projects, VLE for ternary or more complicated mixtures could also be considered, but the visualization becomes more complicated.

## THEORY

The equilibrium condition for component  $i$  being simultaneously present as a liquid and vapor equilibrium phase can be written as the isofugacity condition

$$f_i^v = f_i^L \quad (1)$$

$$\varphi_i^v \cdot P \cdot y_i = p_i^{OL} \cdot \varphi_i^{OL} \cdot \exp\left(\int_{p_i^0}^P \frac{v_i^c}{RT} dP\right) \cdot \gamma_i \cdot x_i \quad (2)$$

where  $\varphi_i^v$  is the fugacity coefficient for the vapor phase,  $P$  is the total pressure,  $y_i$  and  $x_i$  are the molar fractions of component  $i$  in the vapor and liquid phases, respectively,  $p_i^{OL}$  is the vapor pressure of component  $i$ ,  $\varphi_i^{OL}$  is the fugacity coefficient for the vapor phase at the point of saturation,  $\gamma_i$  is the activity coefficient, defined by the selected model, and  $v_i^c$  is the molar volume of the condensed phase as a function of pressure. The exponential correction is the *Poynting* factor which takes into account that the liquid is at a pressure  $P$  different from the liquid saturation pressure  $p_i^0$ .<sup>[7]</sup>

At moderate pressures,  $\varphi_i^v$ ,  $\varphi_i^{OL}$ , and the *Poynting* factor are near unity, and Eq. (2) can be rewritten as

$$P \cdot y_i = p_i^0 \cdot \gamma_i \cdot x_i \quad (3)$$

The constant pressure T-x,y diagram can be obtained by calculating the bubble temperatures ( $T_b$ ) of the various liquid mixture compositions ( $x_i$ ), and also by calculating the composition of the equilibrium vapor phase ( $y_i$ ). The calculation is to be carried out according to the flowchart in Figure 3.

On the other hand, the Gibbs energy of mixing (dimensionless) is the sum of two contributions, the ideal and excess Gibbs energies:

$$g^M = g^{id} + g^E \quad (4)$$

## Gibbs Energy for the Liquid Phase

For liquid mixtures the ideal Gibbs energy of mixing (dimensionless) is

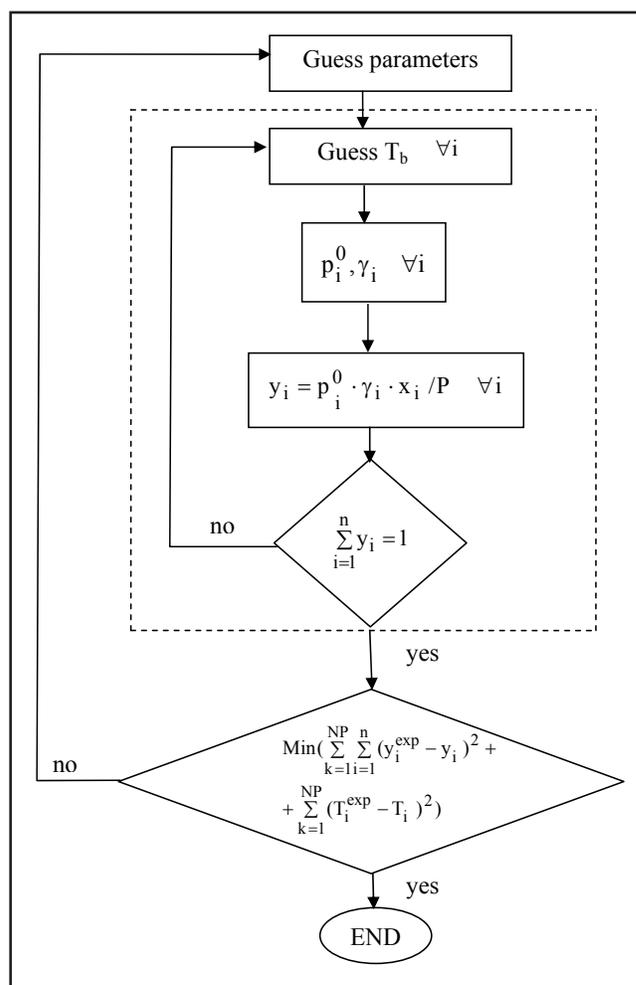
$$g^{id,L} = \sum_i x_i \cdot \ln x_i \quad (5)$$

where the reference state for each component  $i$  is the pure liquid at the temperature and pressure of the system.

Many equations have been proposed to model the excess Gibbs energy and can be found in the literature. For example, the van Laar equation for binary systems:

$$g^{E,L} = \frac{A_{12} \cdot A_{21} \cdot x_1 \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \quad (6)$$

where  $A_{12}$  and  $A_{21}$  are the binary interaction parameters of the model that must be obtained by equilibrium data correlation.



**Figure 3.** Flowchart for the calculation of the activity coefficient model parameters by equilibrium data regression. The discontinuous line represents the algorithm for the bubble point equilibrium calculations.

Substituting Eq. (5) and Eq. (6) into Eq. (4), and considering the selected reference state, the expression obtained for the Gibbs energy of the liquid phase at the temperature of the system T is:

$$g^L(T) = g^{M,L} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{A_{12} \cdot A_{21} \cdot x_1 \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \quad (7)$$

### Gibbs Energy for the Vapor Phase

The vapor phase is considered ideal and, therefore, the following equation is used for the Gibbs energy of mixing of the vapor phase:

$$g^{M,V} = g^{id,V} = y_1 \ln y_1 + y_2 \ln y_2 \quad (8)$$

To compare Gibbs energy curves for liquid and vapor phases both must be obtained from a common reference state. For VLE calculations at constant T and P a convenient reference state is the pure component as liquid at the same T and P of the system. In this case, the Gibbs energy of pure component i in the vapor and liquid phases are  $g_i^{o,V} \neq 0$  and  $g_i^{o,L} = 0$ , respectively. The difference in the Gibbs energy between a pure vapor and a pure liquid can be approximated using the following equation:

$$g_i^{o,V} - g_i^{o,L} = \ln \frac{P}{p_i^o} \quad (9)$$

Consequently the following equation is used for the Gibbs energy of the vapor phase, referred to the liquid aggregation state at the temperature of the system T:

$$g^V(T) = y_1 \cdot g_1^{o,V} + y_2 \cdot g_2^{o,V} + y_1 \ln y_1 + y_2 \ln y_2 \quad (10)$$

According to Eq. (9), the sign of  $g_i^{o,V}$  may be positive or negative; depending on the ratio between the total pressure of the system and the vapor pressure of component i, which, in turn, depends on the temperature:

$$\text{—If } P > p_i^o \rightarrow g_i^{o,V} - g_i^{o,L} > 0 \rightarrow g_i^{o,V} \text{ is positive}$$

$$\text{—If } P < p_i^o \rightarrow g_i^{o,V} - g_i^{o,L} < 0 \rightarrow g_i^{o,V} \text{ is negative}$$

After both the  $g^V$  and  $g^L$  isotherm curves have been calculated and represented, the Gibbs stability or common tangent plane test can be easily applied to them to ascertain which phases are most stable and what the equilibrium compositions are.

The reference state is defined to be arbitrary and for a system at constant T and P can be selected to be the liquid state at the temperature of the system for both components in both phases. If Gibbs energy surfaces for both p phases are generated to analyze the equilibrium as a function of temperature T, however, a reference state must be used in the calculations at a unique temperature  $T_0$ .

$$g^p(T_0) = g^p(T) - \frac{1}{RT} \int_{T_0}^T S \cdot dT + \frac{1}{RT} \int_{p_0}^P V \cdot dP \quad (11)$$

For non-isothermal VLE, however, the Gibbs energy for both p phases (V and L) must be calculated as a function of temperature T using a reference state (*i.e.*, the pure liquid) at a unique reference temperature  $T_0$   $g^p(T_0)$ . In this case, the Gibbs energy for both vapor and liquid phases includes an entropic term from  $T_0$  to T.

For isobaric conditions, Eq. (11) becomes:

$$g^p(T_0) = g^p(T) - \frac{1}{RT} \int_{T_0}^T \int_{T_0}^T \frac{C_{pL}}{T} \cdot dT dT \quad (12)$$

where  $C_{pL}$  is the heat capacity of the liquid. In the above expression  $g^p(T)$  is calculated with Eq. (7) for p=L or with Eq. (10) for p=V.

### PROBLEM STATEMENT

For the binary homogeneous azeotropic system ethanol (1) + benzene (2) at P=1 atm:

- Calculate the parameters for the selected thermodynamic model regressing T-x,y experimental data.
- Build the temperature vs. composition (T-x,y) diagram with an Excel spreadsheet.
- Represent graphically in a 3-D diagram (for example, using Matlab) the g (vapor and liquid) vs. composition and temperature surfaces for this system.
- For a more precise analysis of the above 3-D figure, plot g curves in Excel for the vapor and liquid mixtures of the following isotherms: 90.0 °C, 79.0 °C, 72.0 °C, temperature of the calculated azeotrope, and 60.0 °C. The number of phases present and their compositions must be deduced using the Gibbs common tangent test.
- Show that the results obtained using the Gibbs stability criteria are consistent with those obtained using the T-x,y diagram.

The Van Laar equation can be used to represent the excess Gibbs energy ( $g^E$ ) and the activity coefficient ( $\gamma_i$ ) of the liquid mixtures. The vapor phase can be considered as ideal.

### SOLUTION

The  $A_{ij}$  parameters for the Van Laar model [Eq. (6)] calculated for the ethanol (1) + benzene (2) binary system have been calculated by fitting VLE data<sup>[8-10]</sup> according to the flow diagram shown in Figure 3. Figure 4 (next page) shows an example of the possible spreadsheet distribution to obtain the model parameter values and the T-x,y diagram by successive bubble temperature calculations with Solver function in Excel using various liquid mixture compositions ( $x_i$ ) and calculating the equilibrium vapor phase composition. The parameter values obtained are  $A_{12}=1.965$  and  $A_{21}=1.335$  (dimensionless). As can be seen in Figure 4, a homogeneous azeotropic point occurs for this system at a minimum boiling temperature.

**Figure 4 (right).** Spreadsheet example of the Van Laar parameters calculation regressing T-x,y experimental data for the ethanol (1) + benzene (2) binary system at P=760 mmHg.

	A	B	C	D	E	F	G	H	I
27	Guess A <sub>12</sub>	Guess A <sub>21</sub>							
28	1.9649	1.3348							
29	T exp (°C)	x <sub>1</sub> exp	y <sub>1</sub> exp	Guess Tb	P* <sub>1</sub> (mmHg)	P* <sub>2</sub> (mmHg)	x <sub>2</sub>	y <sub>1</sub> (van Laar)	y <sub>2</sub> (van Laar)
30	80.09	0	0	80.05	815.82	760.94	1.000	7.1340	10.000
31	70.61	0.086	0.296	70.95	564.75	570.01	0.914	4.5534	10.200
32	68.52	0.258	0.392	68.41	507.43	523.97	0.742	2.3623	1.1653
33	68.26	0.325	0.41	68.18	502.52	519.98	0.675	1.9600	1.2581
34	68.24	0.448	0.448	68.06	500.03	517.95	0.552	1.5037	1.4852
35	68.06	0.438	0.446	68.03	499.39	517.43	0.562	1.5314	1.4638
36	68.61	0.64	0.515	68.56	510.67	526.61	0.360	1.1621	2.0112
37	70.17	0.788	0.608	70.23	547.89	556.58	0.212	1.0480	2.5965
38	73.87	0.917	0.778	73.91	638.02	627.38	0.083	1.0066	3.2695
39	78.29	1	1	78.27	760.39	720.07	0.000	1.0000	3.7992
40	g <sub>1</sub> calc (eq. 3)	g <sub>2</sub> calc (eq. 3)	g <sub>1</sub> cal-g <sub>2</sub> cal	(Σg <sub>1</sub> cal-l) <sup>2</sup>	(T cal-T exp) <sup>2</sup>	Σ(g <sub>1</sub> cal-g <sub>1</sub> exp) <sup>2</sup>	Σ(Σg <sub>1</sub> cal-l) <sup>2</sup>	Σ(T cal-T exp) <sup>2</sup>	Σ(Σg <sub>1</sub> cal-g <sub>1</sub> exp) <sup>2</sup>
41	0.000	1.001	1.0012	1.51E-06	0.00144	0.00E-00	1.23E-04	1.82E-01	8.27E-04
42	0.291	0.699	0.9902	9.66E-05	0.11844	2.51E-05			
43	0.407	0.596	1.0031	9.38E-06	0.01300	2.23E-04			
44	0.421	0.581	1.0022	4.96E-06	0.00694	1.25E-04			
45	0.443	0.559	1.0019	3.74E-06	0.03295	2.29E-05			
46	0.441	0.560	1.0008	6.87E-07	0.00093	2.77E-05			
47	0.500	0.502	1.0014	2.02E-06	0.00286	2.33E-04			
48	0.595	0.403	0.9985	2.31E-06	0.00339	1.60E-04			
49	0.775	0.224	0.9989	1.16E-06	0.00175	9.56E-06			
50	1.001	0.000	1.0005	2.64E-07	0.00042	2.64E-07			
51	azeotrope calculation								
52	Guess x <sub>1</sub>	g <sub>1</sub> exp	Guess Tb	P* <sub>1</sub> (mmHg)	P* <sub>2</sub> (mmHg)				
53	0.4409	0.4480	68.0075	498.8214	517.0483				
54	x <sub>2</sub>	y <sub>1</sub> (van Laar)	y <sub>2</sub> (van Laar)	g <sub>1</sub> calc (eq. 3)	g <sub>2</sub> calc (eq. 3)				
55	0.5591	1.5233	1.4699	0.4409	0.5591				
56	g <sub>1</sub> cal-g <sub>2</sub> cal	(Σg <sub>1</sub> cal-l) <sup>2</sup>	(x <sub>1</sub> -y <sub>1</sub> ) <sup>2</sup> +(x <sub>2</sub> -y <sub>2</sub> ) <sup>2</sup>						
57	1.0000	1.45E-12	7.23E-13						

**Figure 5 (below).** Gibbs energy surfaces for vapor g<sup>v</sup> (ideal) and liquid g<sup>l</sup> (Van Laar) mixtures as a function of the temperature and composition for the ethanol (1) + benzene (2) binary system at P=1 atm.

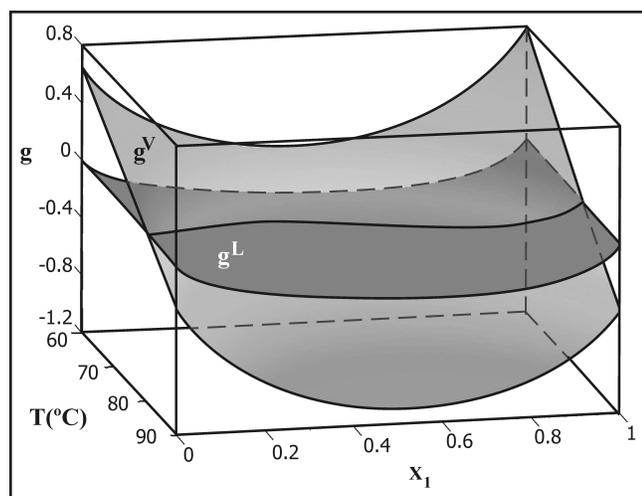


Figure 5 shows the 3-D graph used to represent the Gibbs energy surfaces of the liquid ( $g^l$ ) and vapor phases ( $g^v$ ) as a function of temperature and composition. The selected reference state for each one of the components is the liquid state at the azeotrope boiling point ( $T_0$ ). The Gibbs energy surfaces for L and V have been calculated using Eq. (12) where  $g^p(T)$  when  $p$ =liquid is calculated with Eq. (7) and when  $p$ =vapor is calculated with Eq. (10). The values for  $g_i^{o,v}$  are calculated with Eq. (9), where the vapor pressures for ethanol and benzene have been obtained using the Antoine equation, with the constants given in Table 1.<sup>[11]</sup> The entropy changes of Eq. (12) are calculated with  $C_{p,L}(T)$  given in Table 2.<sup>[12]</sup>

As can be seen in Figure 5, the  $g$  surfaces cross each other so that the vapor phase is the stable phase at high temperatures

( $g^v$  lower than  $g^l$ ) and the liquid phase the stable aggregation state at lower temperatures ( $g^l$  lower than  $g^v$ ). For a more detailed analysis of this figure some sectional planes have been selected, corresponding to the following isotherms: 90 °C, 79 °C, 72 °C, 68.01 °C (calculated azeotrope), and 60 °C.

Figure 6 shows the Gibbs energy curves plotted for the vapor and the homogeneous liquid mixtures at each one of these temperatures. After students have completed these representations, an analysis of Figure 6 is done, taking into account the Gibbs stability criteria:

- For  $T=90$  °C,  $P_2^o < P=1\text{atm} < P_1^o$ ; therefore, taking into account Eq. (9),  $g_i^{o,v} < g_i^{o,l}$  for  $i=1, 2$ , and the entire  $g^v$  vs. composition curve is lower than  $g^l$  [Figure 6(a)], showing that the vapor phase is the stable aggregation state over the entire composition space at this temperature.
- For  $T=79$  °C,  $P_2^o < P=1\text{atm} < P_1^o$ ; therefore, for the ethanol component,  $g_1^{o,v} < g_1^{o,l}$ , but for benzene,  $g_2^{o,v} > g_2^{o,l}$ . The  $g^v$  and  $g^l$  curves have two points sharing a common tangent line, corresponding to the VL equilibrium  $y_1=0.0355$  and  $x_1=0.00497$ . At molar fractions below  $x_1=0.00497$  the liquid is the stable aggregation state, and at values higher than  $x_1=0.0355$  the vapor is the stable phase [Figure 6(b)]. Any global mixture between those values will split in the VLE.
- For  $T=72$  °C,  $P_2^o < P_1^o < P=1\text{atm}$ ; therefore,  $g_2^{o,v} > g_2^{o,l}$  for both ethanol and benzene components. Two regions of the  $g^v$  and  $g^l$  curves each contain one point of VL equilibrium:  $[y_1=0.269, x_1=0.0708]$  and  $[y_1'=0.681, x_1'=0.861]$  having common tangent lines that connect

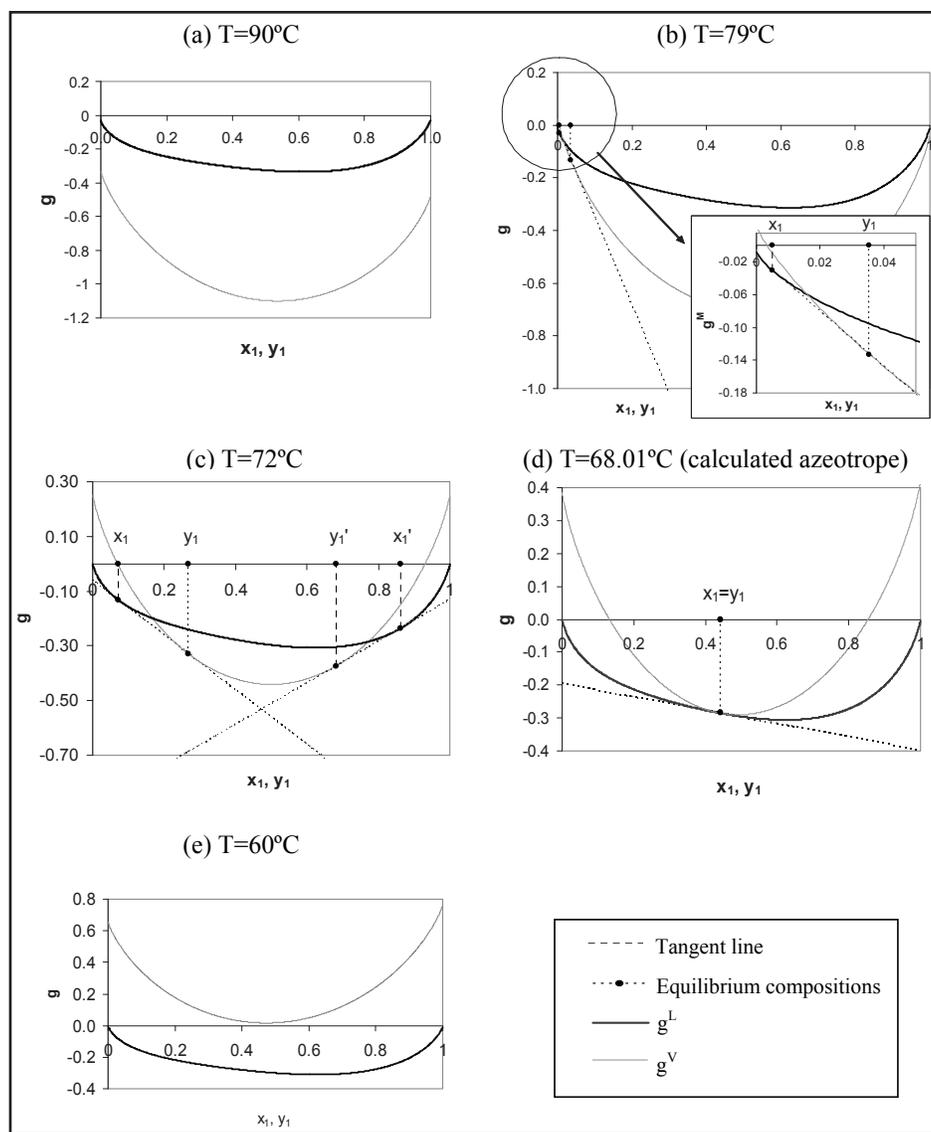
the conjugated y-x equilibrium compositions, as can be seen in Figure 6(c). The vapor is the stable aggregation state at intermediate concentrations and the liquid is the stable phase near each pure component.

- The  $g^V$  curve rises as the temperature decreases until the azeotropic temperature (68.01 °C) is reached. Here, both  $g^V$  and  $g^L$  curves are tangent in one point [Figure 6(d)]. This point corresponds to the homogeneous azeotrope, for which the vapor and liquid phases in equilibrium have identical compositions ( $y_1 = x_1 = 0.441$ ).
- For  $T = 60$  °C, the  $g^L$  curve lies below the  $g^V$  curve over the entire composition space, demonstrating that a homogeneous liquid phase is the most stable aggregation state for any global mixture composition [Figure 6(e)].

It must be highlighted that all of the above, deduced from the Gibbs energy curves, is obviously consistent with the T-x,y diagram shown in Figure 4. Treatment of the VLE calculation using the Gibbs common tangent plane criteria provides students with a deeper understanding of the problem, however, because the insight into the reasons for the V or L phase stability or the VLE splitting is much more evident than with using the isofugacity condition. Although solving the isofugacity condition together with the mass balance equations (K-value method) constitutes the most popular method of calculation, our experience has shown that the Gibbsian geometrical framework is a very useful tool for educational purposes. Students state that the geometric analysis of chemical equilibrium, with an available and easy to use program such as Excel, permits a clear understanding of the VLE splitting in terms of Gibbs energy minimization.

## EXTENSION TO HETEROGENEOUS AZEOTROPIC MIXTURES

An extension of this exercise is proposed where the VLE is studied for a heterogeneous instead of a homogeneous azeotropic system. The binary system



**Figure 6.** Analysis of the Gibbs energy curves for vapor ( $g^V$ ) and liquid ( $g^L$ ) mixtures at different temperatures for the ethanol (1) + benzene (2) binary system at  $P=1$  atm showing the common tangent equilibrium condition.

**TABLE 1**  
Antoine Equation Constants for Ethanol and Benzene<sup>[10]</sup>

	$\log(p^\circ) = A - B/(T+C)$ ( $p^\circ$ in bar, $T$ in °C)		
	A	B	C
Ethanol	5.33675	1648.220	230.918
Benzene	3.98523	1184.240	217.572

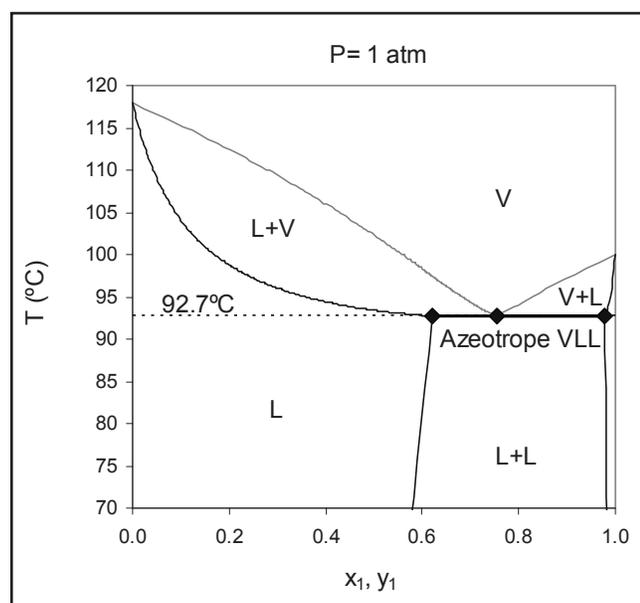
**TABLE 2**  
Heat Capacity Constants of Liquid for Ethanol and Benzene<sup>[12]</sup>

	$C_{p,l} = A + BT + CT^2 + DT^3$ (J/mol/K, $T$ in K)			
	A	B	C	D
Ethanol	59.342	0.36358	-0.0012164	1.803·10 <sup>-6</sup>
Benzene	-31.662	1.3043	-0.0036078	3.8243·10 <sup>-6</sup>

water-n-butanol at  $P = 1$  atm is an example of a heterogeneous azeotrope. The vapor phase can be considered ideal as in the previous example. The NRTL equation can be used to represent the excess Gibbs energy ( $g^E$ ) and the activity coefficient ( $\gamma_i$ ) of the liquid mixtures. The equation parameters can be obtained by fitting the VLE and VLLE data at 1 atm<sup>[10,13,14]</sup> following the same calculation algorithm shown in the previous section. The values obtained for these binary NRTL interaction parameters are:  $A_{12} = 1256.9$  K,  $A_{21} = 374.86$  K, and  $\alpha_{12} = 0.476$ .

Figure 7 shows the T-x,y diagram of the system under consideration. Figure 8 shows the 3-D graph used to represent the Gibbs energy surfaces for the vapor and liquid phases, as functions of the temperature and composition. The selected reference state for each one of the components is the liquid state at the boiling point of the azeotrope ( $T_0$ ). The  $g$  surfaces cross each other, as in the previous example shown in Figure 5, but the existence of a heterogeneous azeotrope implies that one vapor and two different liquid phases must coexist in equilibrium at a unique temperature. The isotherm of the azeotrope ( $T = 92.7$  °C) has been included in Figure 8. To provide a better understanding of this 3-D graph, some sectional planes corresponding to the following isotherms—91 °C, 94 °C, and 92.7 °C (calculated azeotrope)—have been shown in Figure 9:

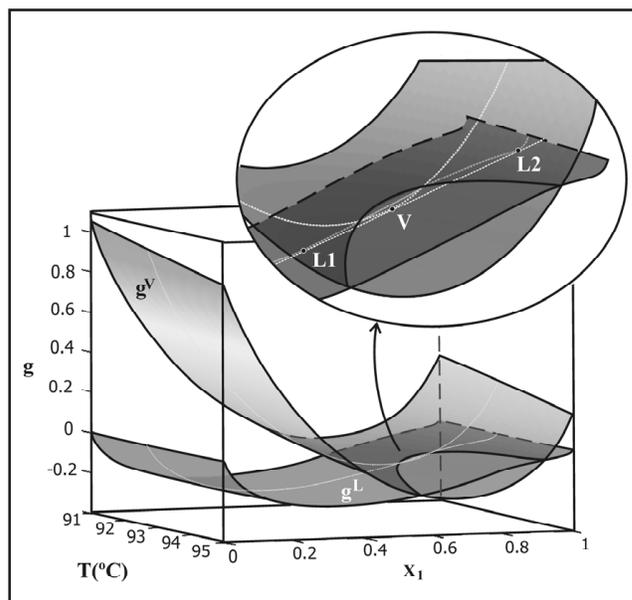
- For all temperatures below the azeotrope,  $g^L$  is lower than  $g^V$  over the entire composition space. According to the Phase Rule constraint, for  $n=2$  components and  $p=2$  phases, there are two degrees of freedom:  $f=n+2-p=2$ . Consequently, when the pressure is fixed, a temperature



**Figure 7.** Temperature versus liquid ( $x$ ) and vapor ( $y$ ) molar fractions for the binary system water (1) + n-butanol (2) at  $P=1$  atm, including the azeotropic isotherm line.

must be specified to calculate the LL equilibrium compositions. Figure 9(a) shows the isotherm corresponding to  $T=91$  °C where two points of the  $g^L$  curve ( $x_1^{L1} = 0.623$ ,  $x_1^{L2} = 0.978$ ) have a common tangent line, demonstrating that a liquid phase splitting is the most stable situation for any global mixture composition  $z$  comprised between them,  $x_1^{L1} < z_1 < x_1^{L2}$ .

- For temperatures above the azeotrope, the  $g^V$  curve intersects the  $g^L$  curve twice giving two regions of VL equilibrium since there are two common tangent lines. When the pressure is fixed, a temperature must be specified to calculate the corresponding equilibrium compositions in the two VL regions. Figure 9(b) shows the isotherm  $T=94$  °C where there are two common tangents to the  $g^V$  and  $g^L$  curves, each one defining a VL equilibrium:  $[y_1 = 0.710, x_1 = 0.435]$  and  $[y_1 = 0.795, x_1 = 0.986]$ . The vapor is the stable aggregation state at intermediate concentrations and the liquid is the stable phase near each pure component.
- It is obvious that between the above situations, there must be a temperature, which is the azeotrope temperature, where the  $g^V$  and  $g^L$  curves have a unique common tangent line. According to the Phase Rule, for  $n=2$  components and  $p=3$  phases, there is only one degree of freedom:  $f=n+2-p=1$ . Consequently, when the pressure is fixed, only the azeotrope temperature describes the VLL equilibrium. Figure 9(c) shows the  $T=92.7$  °C isothermal section where one point on the  $g^V$  curve ( $y_1 = 0.756$ ) and two points on the  $g^L$  curve ( $x_1^{L1} = 0.622$ ,  $x_1^{L2} = 0.978$ )



**Figure 8.** Gibbs energy surfaces for vapor ( $g^V$ ) and liquid ( $g^L$ ) mixtures as a function of the temperature and composition for the water (1) + n-butanol (2) binary system at  $P=1$  atm. The isotherm curves ( $T=92.7$  °C) of the azeotrope have also been included on the surfaces.

have a common tangent line. The existence of this VLL equilibrium is consistent with the T-x,y representation of this system (Figure 7).

With this example, the students demonstrate the reason for the VLL splitting in terms of stability or the minimum Gibbs energy of the system.

## CONCLUSIONS

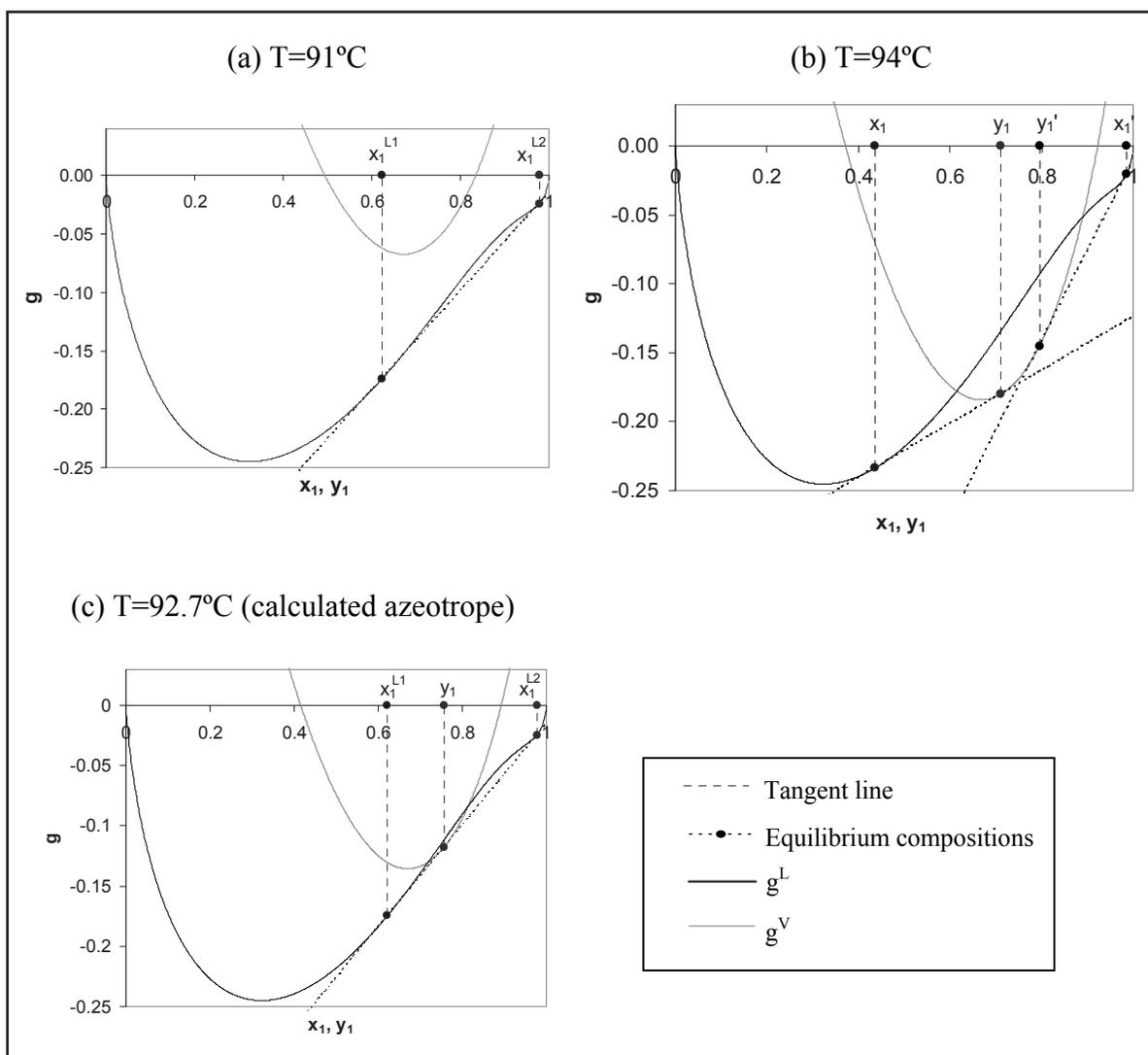
Dealing with the VLE calculation in terms of the Gibbs common tangent criteria provides students with a deeper understanding of the problem than using the isofugacity condition.

An exercise of application of the Gibbs common tangent criteria to VLE has been proposed for a homogeneous azeotropic binary system at a constant pressure using simple tools such as Excel spreadsheets and Matlab graphics. The Gibbs energy surface and curves at different temperatures have been analyzed to compare distinct situations that are consistent with

the T-x,y diagrams. This graphical analysis proves that the vapor is the stable phase at high temperatures, the liquid phase is the stable aggregation state for lower temperatures, and that the azeotrope (VLE) corresponds to a temperature where both liquid and vapor Gibbs energy curves are tangent in one point. Students use this previous spreadsheet to develop an extension to consider the VLLE of a heterogeneous azeotropic system, which is tackled as a project in groups. Their reports of results show that the reasons for the V or L phase stability or the VLE and VLLE splitting is much more evident with the Gibbsian framework than using the isofugacity condition.

## NOMENCLATURE

- $f_i^F$  Fugacity of component i in phase F
- P Pressure
- p phase
- f Degrees of freedom (Phase Rule)



**Figure 9.** Analysis of the Gibbs energy curves for vapor ( $g^V$ ) and liquid ( $g^L$ ) mixtures at different temperatures for the water (1) + n-butanol (2) binary system at  $P=1$  atm, showing the common tangent equilibrium condition.

$T_b$	Boiling temperature
$n$	Number of components
$\varphi_i^V$	Fugacity coefficient for the vapor phase
$\varphi_i^{o,L}$	Fugacity coefficient for the liquid phase at $p_i^o$
$V_i^c$	Molar volume of the condensed phase as a function of pressure
$p_i^o$	Vapor pressure of component $i$
$y_i$	Molar fraction of component $i$ in the vapor phase
$x_i$	Molar fraction of component $i$ in the liquid phase
$\gamma_i$	Activity coefficient of component $i$ in the liquid phase
$A_{ij}$	Binary interaction parameter between species $i$ and $j$ (van Laar or NRTL equation)
$\alpha_{ij}$	Non-randomness factor (NRTL equation)
$g^{id}$	Ideal Gibbs energy of mixing (dimensionless)
$g^E$	Excess Gibbs energy (dimensionless)
$g^M$	Gibbs energy of mixing (dimensionless)
$g$	Gibbs energy (dimensionless)
$g^V, g^L$	Gibbs energy (dimensionless) of the vapor and liquid phase, respectively.
$g_i^{o,V}, g_i^{o,L}$	Gibbs energy of pure component $i$ (dimensionless) in the vapor and liquid phase, respectively.

### Superscripts

id	Ideal
E	Excess
M	Mixture
L, L1, L2	Liquid phase, Liquid phase 1, Liquid phase 2
V	Vapor phase

### ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Vicepresidency of Research (University of Alicante) and Generalitat Valenciana (GV/2007/125).

### REFERENCES

1. Wasylkiewicz, S.K., S.N. Sridhar, M.F. Doherty, and M.F. Malone, "Global Stability Analysis and Calculation of Liquid-Liquid Equilibrium in Multicomponent Mixtures," *Ind. Eng. Chem. Res.*, **35**, 1395-1408 (1996)
2. Baker, L.E., A.C. Pierce, and K.D. Luks, "Gibbs Energy Analysis of Phase Equilibria," *Soc. Petrol. Eng. AIME.*, **22**, 731-742 (1982)
3. Sandler, S.I., *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York (1994)
4. Jolls, K.R., and D.C. Coy, "Visualizing the Gibbs Models," *Ind. Eng. Chem. Res.*, **47**, 4973-4987 (2008)
5. Castier, M., "XSEOS—an Open Software for Chemical Engineering Thermodynamics," *Chem. Eng. Ed.*, **42**(2) 74 (2008)
6. Lwin, Y., "Chemical Equilibrium by Gibbs Energy Minimization on Spreadsheets," *Int. J. Eng. Ed.*, **16**(4) 335-339 (2000)
7. Prausnitz, J.M., R.N. Lichtenthaler, and E. Gomes De Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Ed., Prentice Hall PTR, Upper Saddle River (1999)
8. Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection. Alcohols, Ethanol and 1, 2-Ethandiol, Supplement 6*, Chemistry Data Series, DECHEMA (2006)
9. Wisniak, J., "Azeotrope Behaviour and Vapor-Liquid Equilibrium Calculation," *AICHE M.I. Series D. Thermodynamics*, V.3, AIChE, 17-23 (1982)
10. Lide, D.R., *CRC Handbook of Chemistry and Physics 2006-2007: A Ready-Reference Book Of Chemical and Physical Data*, CRC Press (2006)
11. Poling, B.E., J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, McGraw Hill (2001)
12. Yaws, C.L., *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health-Related Properties for Organic and Inorganic Chemicals*, McGraw-Hill (1999)
13. Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection. Aqueous System*, Supplement 3. Vol. I, part 1c. Chemistry Data Series, DECHEMA, (2003)
14. Iwakabe, K., and H. Kosuge, "A Correlation Method For Isobaric Vapor-liquid and Vapor-liquid-liquid Equilibria Data of Binary Systems," *Fluid Phase Equilib.*, **192**, 171- 186 (2001) □

## *Heat Transfer*

by Gregory Nellis and Sanford Klein

Cambridge (2009) \$155.00

---

### Reviewed by

Kemal Tuzla

Lehigh University, Bethlehem, PA 18015

This book is different from most existing heat transfer books in two ways. First, it incorporates computational tools into each chapter, so that students can learn theory and computational solution methods together. This approach allowed the authors to include more complicated problems into the book. Second, the book also contains advanced material definitely beyond the requirements of a first-level undergraduate heat transfer course.

Today, integration of computations with the lectures is an essential part of engineering education. Some of the faculty require use of computational tools to solve homework problems and submit homework electronically. Although many heat transfer books suggest using computational methods for solution of some problems, they mostly assume that student knows how to use the software. This book goes much beyond and provides examples/guidance in use of computational methods together with the theory. Some specific commands and output associated with these software packages are presented as the theory is developed. The book introduces computations progressively, starting with simple applications in the beginning chapters and moves to advanced features in later chapters. There are many example problems, in which the authors describe the computational solutions and, when

possible, they compare the results with analytical ones. This gradual introduction of programming and detailed examples should encourage students to learn and speed up their use of computational tools. It is my impression that the presence of computational subjects will not slow down the rate or reduce the contents of the course. The descriptions of computational methods and related examples in this book will be a good resource and help. Popular software packages Maple, Matlab, EES, and FEHT are integrated into the computations used in the book. Educational versions of these software packages are provided at the Web site of the book.

On the analytical side, the book presents much more material than classical contents of a first-level undergraduate heat transfer book. Conduction, convection, radiation, and heat exchanger chapters contain a good amount more additional materials than standard first-level books. There is also a boiling and condensation section. These additional materials include detailed applications of mathematical solution methods using Bessel functions, Laplace transforms, separation of variables, Duhamel's theorem, and Monte Carlo methods. These additional materials definitely will be useful for practicing engineers as well as some of the undergraduates who are taking the first-level course. Furthermore, there is enough material to compose a second-level course for advanced undergraduates and graduate students.

For the future edition of the book, the authors may want to consider adding a section for gas radiation, and use more examples from bioengineering applications.

In conclusion, this is a very good heat transfer book with a lot of emphasis on use of computational methods. The authors did a very good job incorporating computations side-by-side with the theory. This is a suitable textbook for first- and second-level courses, where the instructor wants to use computational tools, as well as a reference book for practicing engineers. □

**Visit  
us  
on the  
Web  
at**

---

**<http://cee.che.ufl.edu/index.html>**

---