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chemical engineering education

SUMMER 1968

featuring

CHEMICAL PROCESS PRINCIPLES TODAY

CHEMICAL ENGINEERING DIVISION OF AMERICAN SOCIETY FOR ENGINEERING EDUCATION

THERMODYNAMICS · KINETICS · STOICHIOMETRY

Sliepcevich & Hashemi

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Olaf Hougen : PIONEERING EDUCATOR

CREATOR OF TEACHERS · INSPIRER OF RESEARCHERS



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PROCESS

ENGINEERING

CONTROL

Mack Tyner and Frank P. May,
both University of Florida

An introduction to linear control theory for college students and practicing engineers. Emphasis is on the universality of the control problem in process engineering through mathematical equations that apply equally to components from all technologies. Linearization of non-linear forms and its limitations are discussed early in the book. Both the root locus method and the frequency response method are stressed as means of control system analysis, and Nyquist diagrams, Bode plots, and Nichols charts, which serve as useful analytical techniques, are demonstrated in many of the illustrative examples. Attention is directed to the use of both digital and analog computers. An Instructor's Supplement is available. 1968. 472 pages. \$14.00

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from the READERS

Editor:

Please refer to the article on the common thermodynamics course by Manning and Canjar in your winter issue, page 11.

Why should the chemical engineering staff at Carnegie have to put up with (a) a compromise, (b) conferences to make the compromise work?

I advise the staff to scream loudly and try to get out of the bed of Procrustes.

Ernest W. Thiele
University of Notre Dame

Editor:

The ASEE might render a real service to our country if it could get pages 78 and 79 Spring CEE into the hands of every senator and congressman in the country, with a forceful letter of transmittal calling attention to the analogy of General Hershey and Adolph Hitler as implied in "The Rise and Fall of the Third Reich" and alluded to in the last paragraph on page 78.

John E. Kiker, Jr.
University of Florida

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from the EDITOR

Since we wanted our first issues of **CHEMICAL ENGINEERING EDUCATION** to have as broad an appeal as possible, we included articles in a number of areas of modern chemical engineering. But in this issue, we are using a different approach: we are emphasizing the areas of thermodynamics, kinetics, and stoichiometry—the subjects that were joined together many years ago in a three-volume work called “Chemical Process Principles.” As our “ChE Educator” we are featuring one of the brilliant authors of that work, Professor Hougen, and, as our “ChE Department” his Alma Mater, the University of Washington.

Olaf Hougen might well be called the inspirational and intellectual father of modern chemical engineering: he is the inspirer of many prominent chemical engineers who were his students; he developed the areas of chemical engineering thermodynamics and kinetics; and he played an important role in the development of transport phenomena when he brought Professor Bird back to Wisconsin and charged him with the responsibility of placing the engineering computation of heat, mass, and momentum transfer on a sound theoretical and scientific basis.*

In this day of continued debate on the merits of the so-called “chemical engineering science” approach, there are lessons to be learned from the example of this great man. The first and most important lesson is that we cannot expect to know what is at the end of the research path before we get there; i.e., no one could know *a priori* what applications would arise from the first course in mass transport which Professor Bird began to teach back in 1954; nor could Professors Hougen and Watson initially know the extent to which the theoretical subject of chemical kinetics could be extended and applied to the flow, batch, and fluidized reactors of chemical engineering practice; nor could the profession know many decades ago that chemical plants would be designed on the basis of the thermodynamic properties of substances that were predicted by the theoretical methods developed by these same two men. Although talk about the “practicality” of thermody-

*Professor Bird recognized the inspiration and incentive placed before him by Professor Hougen in the preface of his text on “Transport Phenomena” with the coded acronym: “This book is dedicated to Olaf Hougen.”

namics persisted throughout the 1950’s, today not even the Neanderthals of the profession question the importance of thermodynamic information on enthalpies, free energies, heats of reaction and P-V-T data to modern industry. The lesson we must again learn is that chemical engineers—and particularly young teachers and graduate students—must be provided an opportunity to delve into those areas of science that are unexplored even if applications are not clearly visible. (An important area of this type today is the entire field of bioengineering and biomedical engineering). It is certainly destructive to stifle the curiosity and dull the initiative of our young scholars by harassing them with demands that they show the immediate application of their work. These men need instead the same kind of encouragement Professor Hougen provided Professor Bird and others.

But another lesson that can be learned from Professor Hougen’s career is one that must be learned by many of these same young scholars; namely, that the work of the engineering scholar should ultimately be placed—by himself or by others—in a form that is usable to the practicing engineer. For the real utility of the work of Hougen and Watson lies in the fact that these authors prepared numerous charts that could be easily used by the engineer in practice (e.g. to find the final conditions in a Joule-Thompson expansion or to predict enthalpy or PVT changes in a process.) Without such a step, the important work of the scholar may long go unheeded by engineers in industry who do not have the time or academic background to use it.

The AIChE Research Committee is currently studying the problem of the industry-academic gap. President Max Peters has often spoken of it and it was forthrightly discussed in the last issue of **CEE** by Bob Lenz. Perhaps one answer lies in our thinking again about the work of Olaf Hougen in not only developing the Chemical Process Principles but also in further making them applicable to real engineering problems. **CHEMICAL ENGINEERING EDUCATION** in this issue is proud to present articles on the “Chemical Process Principles Today” and to acknowledge the debts of the profession to a pioneering educator and a very warm and sensitive human being.

R. W. F.

This article was contributed
by an anonymous associate
of Professor Hougen.

Olaf Andreas Hougen, Emeritus Professor of Chemical Engineering at the University of Wisconsin, has pursued a distinguished career in the field of chemical engineering education. He has been one of the leaders in bringing the profession from a state of empirical practice to a state where it is firmly based upon sound basic principles of chemistry, physics, and mathematics.

He was born in Manitowoc, Wisconsin, on October 4, 1893, the son of a prominent pastor, who was a pioneer in the development of the Norwegian Evangelical Lutheran Church of America. When Olaf was four years old, his father was assigned a pastorate in Decorah, Iowa, and it was there that Olaf received his elementary grade school education. While the material resources of the Hougen family were limited—one of Olaf's daily chores was to take the family's cow to pasture and back—it was a family rich in intellectual and social activities, with constant encouragement to the children to achieve high educational attainments. Proximity to Luther College and the fact that he had several attractive sisters made the Hougen home in Decorah the center of much lively social activity. The family later moved to the State of Washington, where Olaf graduated from Tacoma High School. He then decided to enroll at the University of Washington in the Department of Chemical Engineering, which was headed by Dr. H. K. Benson, one of the early leaders in the development of chemical engineering as a separate educational discipline. At the University of Washington, Olaf established a distinguished career, both academically and in extracurricular activities. He received his BS degree in 1915, cum laude, and was a member of Tau Beta Pi, Phi Beta Kappa, and other honorary societies.

After graduation, he spent one year with the American Smelting and Refining Company, at their Tacoma plant. Then, with the encourage-

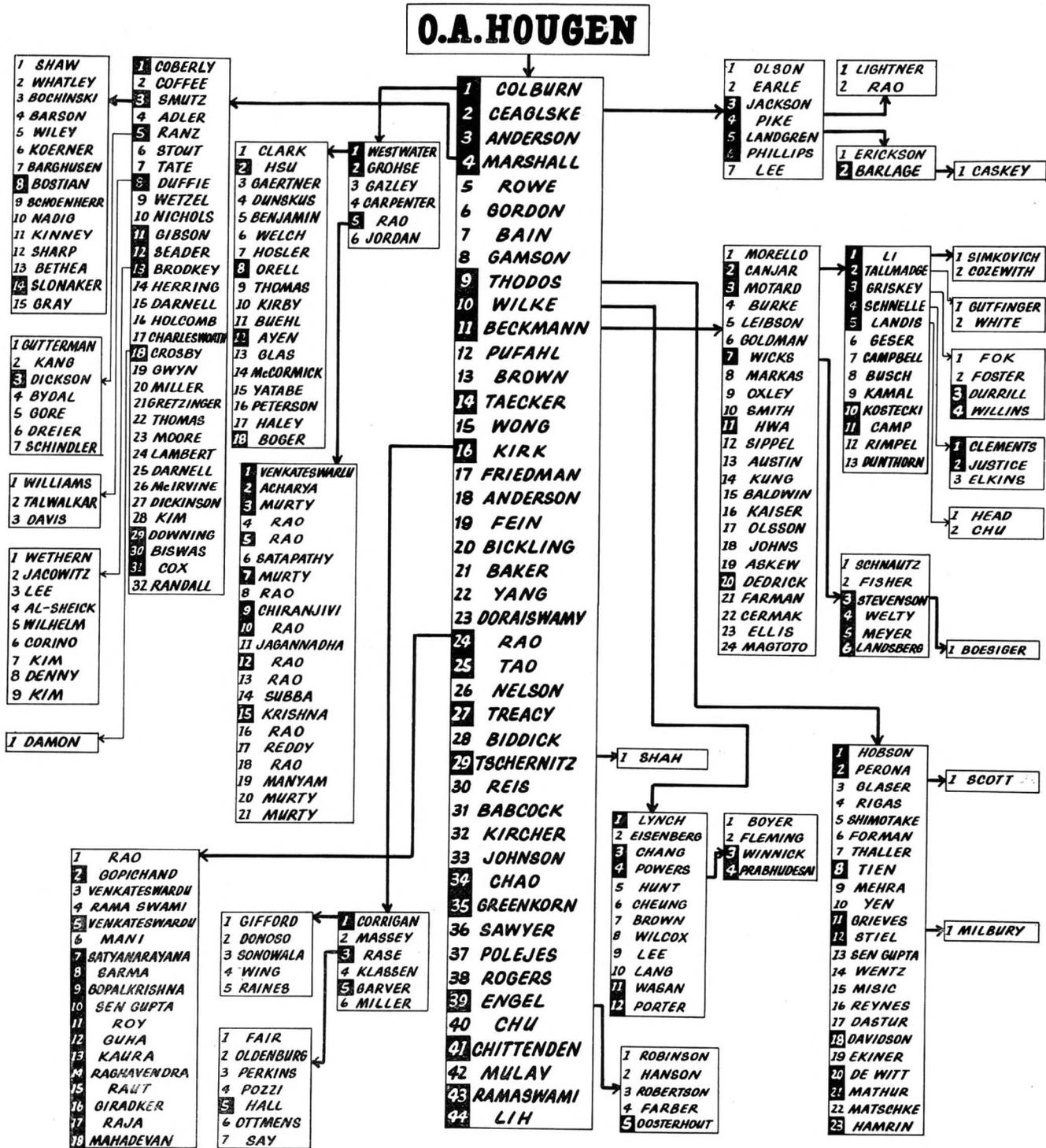
A GREAT TEACHER OLAF A. HOUGEN

ment of Dr. Benson, Olaf decided to take up graduate work in chemical engineering. He chose the University of Wisconsin because of the nationally recognized work of C. F. Burgess (founder of the Chemical Engineering Department and of the various Burgess companies, including the Burgess Battery Company), O. L. Kowalke (prominent in gas manufacture research; Chairman of the Chemical Engineering Department for 25 years), and O. P. Watts (leader in the field of applied electrochemistry). After two years at Wisconsin, first as a Graduate Fellow and then as a full time Instructor, he served in World War I, 1918-1919, in the Chemical Warfare Service, assigned to chemical engineering work at the Saltville, Virginia, plant. Following his discharge from the armed forces, he spent one year with the Carborundum Company, in their research laboratories at Niagara Falls, New York, where his work was largely focused upon the development of refractory materials.

The post war upsurge in student enrollment that was felt throughout the country resulted in an invitation being extended to Olaf to resume his Wisconsin connection. He accepted, and returned to Madison in the fall of 1920, as an Assistant Professor. Since that time until his retirement in 1964, he has been associated continuously with the University of Wisconsin, except for several leaves of absence. He rose through the various academic ranks, and served three terms as Chairman, totaling to 8 years. His first graduate degree, Chemical Engineer, was earned in 1918; his PhD was received in 1925, number 4 in a list that now includes over 200 names.

When Olaf Hougen started his career as a teacher, chemical engineering courses were largely qualitative in character; the pioneering texts of Walker, Lewis and MacAdams and of Badger and McCabe had not yet been published. Through-

The Academic "Family Tree" of a Great Teacher



The above academic family tree indicates those persons who have held university professorships by white numbers on a black background. Over the years Professor Hougén has been advisor for 44 Ph.D's of which nearly half are now in educational work.

Despite his many honors, Olaf remains a modest person, with a warm and outgoing personality; with a host of friends not only in University circles, but in the Madison community as well.

out his career at Wisconsin, Olaf was a leading force in bringing about a constant modernization and upgrading of the undergraduate curriculum, including the establishment of unit operations theory and laboratory courses, chemical engineering thermodynamics, and kinetics and reactor design. It was through his influence that Bird, Stewart, and Lightfoot wrote their text, *Transport Phenomena*, which has had such a widespread impact in chemical engineering education in recent years.

When Olaf started his teaching career at Wisconsin, graduate enrollment in chemical engineering was low, being generally limited to one or two graduate fellows and to the young members of the teaching staff working for their degrees. While some growth took place, it was greatly accelerated when Olaf, in recognition of his substantial research contributions with limited support, received a grant in 1941 of \$100,000 from the University Research Committee, using funds given by the Wisconsin Alumni Research Foundation. This grant enabled him to start a program of graduate research that not only resulted in a sharp increase in the number of graduate students, but also enabled him to initiate a program of staff additions. He was largely responsible for bringing in K. M. Watson (who later resigned), C. C. Watson, W. R. Marshall, E. N. Lightfoot, W. E. Stewart, and R. B. Bird, all of whom contributed greatly to making Wisconsin's Department of Chemical Engineering one of the leading ones in this country.

When Olaf Hougen joined the Wisconsin staff, his unusual talents as a classroom teacher became apparent at once. While his courses were demanding, his enthusiasm, his clarity of exposition, his excellent organization of subject matter, and his fresh approach to solving chemical engineering problems won him immediate acceptance by the students as being one of the outstanding teachers in the College of Engineering. Olaf has always treated his students with courtesy and respect, and has encouraged them to do original analytical thinking in solving difficult problems.

Olaf Hougen early recognized that the ideal teacher strikes an effective balance between classroom teaching and research, and he constantly

strove to match this ideal, with the high degree of success that his associates fully appreciate. Over the years, he has trained 44 PhD's, with somewhat less than half now being in educational work. The widely disseminated influence that Olaf has had in graduate education is illustrated by his academic "Family Tree," shown in the accompanying figure, which was prepared by R. B. Bird and presented to Olaf at a recognition dinner given in his honor on October 8, 1966. On this chart, the white numbers on a black background indicate those persons who have at sometime held university professorships. Olaf's publications cover a wide diversity of subjects in the field of chemical engineering, and total to over ninety.

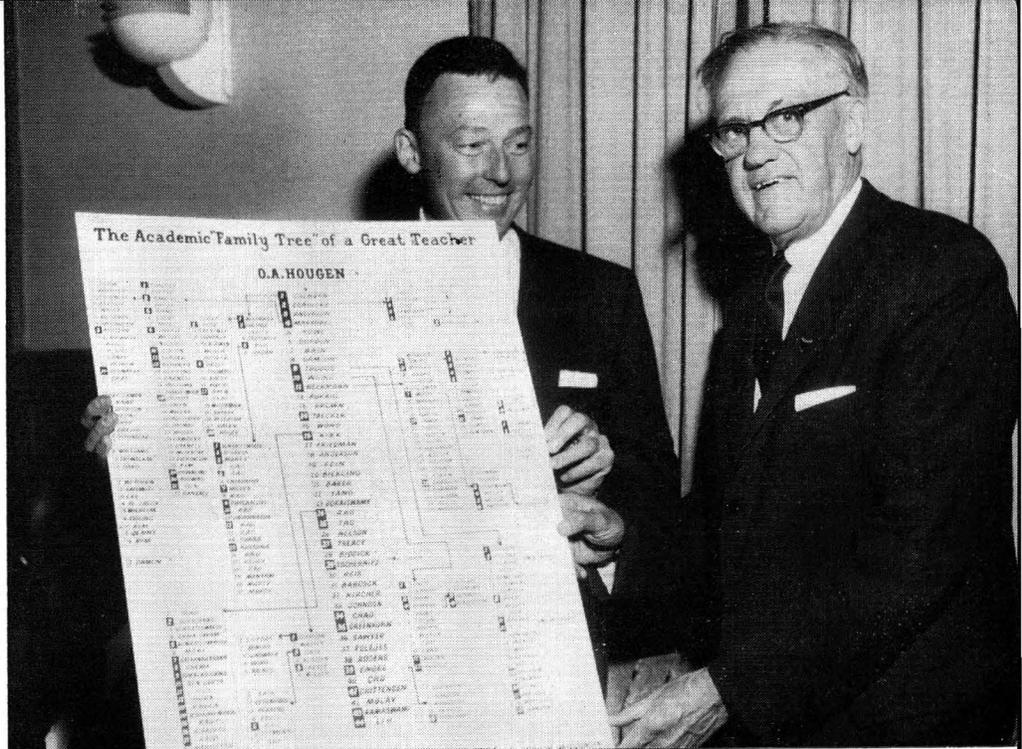
Olaf Hougen's influence in the field of chemical engineering education has been felt not only through his classroom teaching and his direction of graduate research, but also by the publication of a series of widely used text books. *Industrial Chemical Calculations*, published in 1931 with K. M. Watson as co-author, was later followed by the three volume series, *Chemical Process Principles* (Material and Energy Balances; Thermodynamics; Kinetics), again with K. M. Watson as co-author. These texts have been highly successful, and have been translated into Italian, Japanese, and Spanish.

Many honors and awards have come to Olaf Hougen because of his distinguished career in engineering education and research. He has delivered many invited lectures at other universities, and before industrial groups. His major awards are as follows.

Awards Based on Contributions in Engineering Education

1. The Warren K. Lewis Award of the American Institute of Chemical Engineers, 1964. Second recipient of the award.
2. The Lamme Award of the American Society for Engineering Education, 1961. This is considered the major award of the ASEE.
3. Appointment to the Burgess Research Professorship at the University of Wisconsin, 1955-1961.
4. Benjamin Smith Reynolds Award for Excellence in Teaching Future Engineers, 1955. An award of \$1,000 given annually to an outstanding Wisconsin Faculty member. First recipient of the award.

Professor R. B. Bird presented the academic "family tree" to Professor Hougen at a dinner in his honor.



Awards From Professional Societies

1. American Chemical Society Award in Industrial and Engineering Chemistry, sponsored by the Esso Research and Engineering Company, 1961.
2. Founders Award, American Institute of Chemical Engineers, 1958.
3. Institute Lecturer, American Institute of Chemical Engineers, 1950. The second lecturer to receive this honor.
4. William H. Walker Award of the American Institute of Chemical Engineers, 1944.

International Recognition and Awards

1. Scientific Attaché, U. S. State Department. Assigned to American Embassy, Stockholm and covering Denmark, Finland, Iceland, Norway, and Sweden 1961-63.
2. Honorary Doctor of Science Degree from the Norwegian Institute of Technology, Trondheim, Norway, at 50th Anniversary Celebration, 1960.
3. Honorary member, Indian Institute of Chemical Engineers, 1958.
4. Fulbright Professorship
To Norwegian Institute of Technology, 1951
To Kyoto University, Japan, 1957-58.
5. Invited to give keynote address before the Deutsche Bunsen Gesellschaft, Duisberg, West Germany, 1953.

Despite his many honors, Olaf remains a modest person, with a warm and outgoing personality; with a host of friends not only in University circles, but in the Madison community as well.

Olaf Hougen was married in 1919 to Olga M. Berg, and one daughter, Esther, was born to them. Esther is married to F. G. Taylor, and has

3 children, in whom the Hougen grandparents take great pleasure. One of Olaf's brothers, Joel O. Hougen, is presently the Alcoa Professor of Chemical Engineering at the University of Texas. A nephew, Wendell T. Berg, is a chemical engineer with Union Oil Company. The nationally known CBS commentator, Eric Sevareid, is one of his nephews.

Because of his Norwegian ancestry, Olaf has taken a prominent role in Norwegian-American activities, as well as developing and maintaining strong ties with Norway. He is a member of Sons of Norway and of Ygdrasil Literary Society. Because of his activities in 1940-45 as Wisconsin Treasurer for American Relief for Norway, he received a citation from King Haakon of Norway. As a result of his father's influence, religion has been a strong and continuous force in his life. He has participated extensively in the activities of Luther Memorial Church, a large church located in the University area. Olaf is a long standing member of the Optimist Club, and has served as an officer. Golfing is his chief outdoor recreation, and keeps him in excellent physical condition.

Though Olaf retired in 1964, he is still actively interested in his department and in the chemical engineering profession. He frequently is at his office, and the members of the staff have the benefit of his counsel and advice. He truly is one of the revered elder statesmen of the chemical engineering profession.

UNIVERSITY OF WASHINGTON

R. W. MOULTON, *Head*

History (1900-1968)

In 1895 the University of Washington moved from downtown Seattle to its present location about 4 miles northeast of the city center. Denny Hall was the first structure built and in its basement there were facilities for what was known then as the Chemistry Department. Chemical Engineering at the University of Washington had its roots in the Chemistry Department. In 1904, Dr. Henry K. Benson joined the faculty of the University and while his educational background was in chemistry his interests were motivated strongly toward industrial chemistry.

Dr. Benson was interested in the application of chemistry to agriculture and he was a leader in the chemurgy movement in the Pacific Northwest. He was extremely conscious of the pulp and paper industry locally and throughout the world. He did much research during his lifetime in fields related to the production of pulp from wood and other forest products. In 1919, Dr. Benson was appointed executive officer of the Department of Chemistry and Chemical Engineering as it was known at that time. He served in that capacity until 1947.

In 1911, an organization called the Chemical Engineering Club was formed at the University of Washington. At that time leaders from chemical industry in the Pacific Northwest together with appropriate faculty members at the University of Washington established the first chemical engineering curriculum. This curriculum was somewhat weighted toward pulp and paper and also coal and gas technology. This curriculum was the precursor of the chemical engineering program as it is known today.

In 1922, Professor Warren L. Beuschlein joined the faculty of the department. Professor Beuschlein had received his Bachelor of Science in Chemical Engineering degree from the University of Washington and his Master of Science degree in Chemical Engineering from the California Institute of Technology. Professor Beu-

schlein became a dominant figure in the thinking of the faculty of the department during his tenure on the campus. He died suddenly in September 1944. Professor Beuschlein's research interests were quite broad. He made important contributions in the areas of the manufacture of charcoal from wood waste, the high pressure hydrogenation of coal, the fixation of nitrogen from air, and in the manufacture of pulp from forest products.

The first doctorate degree in Chemical Engineering on record was that awarded to Dr. Calvert D. Wright in 1931. Dr. Wright joined the faculty at Pennsylvania State University and was active in research dealing with the utilization of coal during his tenure there. During the 20's the department graduated a considerable number of individuals, some of whom obtained significant national prominence in their professional careers. Among these are Mr. Samuel G. Baker, Dr. Olaf A. Hougen, Mr. Victor Mills, and Dr. Waldo Semon. Mr. Baker had important responsibilities with the DuPont Company before his retirement. Dr. Hougen became a leading educator and spent most of his professional life at the University of Wisconsin. Mr. Mills was employed at the Procter and Gamble Company for most of his professional life and made significant contributions to their new product development. Dr. Waldo Semon was associated with the Goodrich Rubber Company and was their research director before retirement.

Accreditation of chemical engineering departments was initiated originally by the American Institute of Chemical Engineers in 1925. The University of Washington's department of Chemical Engineering became the first department accredited in the Pacific Northwest and this action took place in 1926. In the middle 30's accreditation was first carried out by AIChE for the new organization, the Engineers Council for Professional Development.

In 1930, Dr. Kenneth A. Kobe, a new PhD in Chemical Engineering from the University of Minnesota joined the faculty. Dr. Kobe was a very energetic, enthusiastic faculty member. Du-

**Many prominent
chemical engineers,
including Olaf Hougen
received their
education at the
University of Washington
in Seattle.**



ring his eleven years on the faculty he published well over 100 significant papers dealing with his area of research and related works. Dr. Kobe resigned from the department in 1941 to accept a position on the faculty of the Department of Chemical Engineering at the University of Texas.

Dr. Frank B. West joined the department in 1939. He left later during the war years. The author became affiliated with the department in 1941, as did Dr. Joseph L. McCarthy. Both Dr. McCarthy and the author are still active members of the Chemical Engineering faculty.

The post-war years have produced extensive changes in the department. There has been a dramatic increase in the number of faculty members, the size of the undergraduate classes, the size of the graduate program, and the amount and kind of facilities devoted to the department. These changes have created the department as it exists today.

Chemical Engineering Today

The faculty of the Department of Chemical Engineering now number fourteen individuals. Four of these men have joint appointments; two with Nuclear Engineering, and two with Forest Resources. The College of Forest Resources has developed within the last few years a Bachelor of Science degree program in Pulp and Paper Technology. Because of the long and deep interest of the Department of Chemical Engineering in the field of pulp and paper these two joint appointments were established and serve to maintain close and good working relationships in this area.

The Department of Chemical Engineering played a significant role in the formation of a Nuclear Engineering Department at the Uni-

versity of Washington. The first courses in nuclear engineering on this campus were given by the Department of Chemical Engineering. An early interest in the facilities at Richland, Washington dating back to about 1950 initiated some of this enthusiasm for the nuclear industry. Nuclear Engineering evolved into a group effort of five engineering departments and was eventually established as a separate department wholly at the graduate level. Dr. A. L. Babb, a member of the Chemical Engineering faculty, serves as its chairman. The joint appointments in Nuclear Engineering serve to emphasize the close tie of chemical engineering to nuclear engineering.

In 1953 the Department of Chemical Engineering was established as a separate department. Prior to 1953 there had been what was then called the Department of Chemistry and Chemical Engineering under one chairman who reported to the Dean of Arts and Sciences for Chemistry and the Dean of Engineering for Chemical Engineering. While this was a reasonably good arrangement it was decided in 1953 to formally separate the two departments. After separation the two departments occupied the same facilities and for all practical purposes continued in the same manner as before. The Department of Chemical Engineering owes much of its tradition and strength to the Department of Chemistry which has always been a strong department at the University of Washington.

After literally decades of effort in planning and study a new building for the Department of Chemical Engineering was authorized and completed in September 1966, in time for the 1966-67 school year. This new building increased the gross square feet allocated to the department from 30,000 square feet to 72,000 square feet.

The first courses in Nuclear Engineering were given by the Department of Chemical Engineering . . . Dr. Babb's involvement in the development of the artificial kidney has received international recognition.

Not only was there an increase in space but the space was now functionally suited for the needs of the department. Each faculty member now has his own office, and his own research areas. There are also many types of specialized research areas built into the building for the needs of the department. The philosophy followed in the design of the building was to provide for a maximum degree of flexibility. The building committee and the faculty as a whole felt that it was unwise to be highly precise about how space would be used five and ten years in the future.

The undergraduate program in the department has undergone a major revision in the last few years. The changes that have been made in the curriculum provide for more options in planning the students' programs. There is a core of required courses for the department (which is not common to all engineering departments). On top of this quota of required courses both in chemical engineering and related fields the students have the option of choosing technical electives amounting to 15 quarter credits and electives in the area of humanistic and social sciences amounting to 30 quarter credits. By judicious choosing of electives the student can plan his undergraduate program to be a foundation for graduate work or alternatively he can plan for direct employment in industry following graduation. Following this latter course he can specialize to some extent depending upon his interests. If he so chooses, he can take some courses in the field of pulp and paper technology, or he can enhance his background in fluid mechanics, heat transfer, or other selected chemical engineering areas.

The graduate program of the department is the one that has changed most significantly in the last twenty years. At the end of World War II there were from four to six graduate students. At the present time there are of the order of sixty graduate students in attendance. Current research activities of the faculty encompass the areas of reaction kinetics, transport phenomena, fluid mechanics, heat transfer, mass transfer, bio-engineering, interfacial phenomena, polymers,

cellulose and lignin, thermodynamics and phase equilibria, process dynamics and control, and applied mathematics. None of the faculty members exactly duplicate each other's interests, although there is some overlapping. The fourteen faculty members received their doctorate degrees almost entirely from different schools. **Schools represented are the University of Illinois, the University of California, Yale University, the University of Minnesota, Massachusetts Institute of Technology, Princeton University, the University of Wisconsin, McGill University, the University of Washington, the State University College of Forestry at New York, and the University of Michigan.** It is obvious from the spectrum of research interests and the backgrounds of the faculty that there is a considerable breadth built into the faculty of the department.

Future Trends

It is risky to predict the future with any degree of definiteness. Within the College of Engineering and within the Department of Chemical Engineering there is considerable interest today in various interdisciplinary areas. The most prominent of these at the present time is the cooperative programs being developed with the medical school. Fortunately, the University of Washington has on the same campus a very good medical school. This school has been developed since World War II. Many cooperative programs are already established. A prominent example of one of these is Dr. Babb's involvement with Dr. Scribner in the development of the artificial kidney. This work has received national and international recognition. Other research areas are being jointly prosecuted at the present time and it is certain that this work will expand in the future.

The area of marine sciences is another interdisciplinary area that is receiving a high degree of support on the campus at this time. The University has an outstanding department of oceanography and has recently received federal funding through a sea-grant award. A new division of marine science has been established with various segments of engineering being a part of this program.

Other areas of cooperation will certainly develop. About the only thing that can be stated with some conviction is that chemical engineering will be different in the future than it is today.



CHEMICAL ENGINEERING DIVISION ACTIVITIES

Scriven Delivers Annual Lecture

The 1968 ASEE Chemical Engineering Division Lecturer is Dr. L. E. Scriven of the University of Minnesota. The purpose of this award lecture is to recognize and encourage outstanding achievement in an important field of fundamental chemical engineering theory or practice. The 3M Company provides the financial support for this annual lecture award.

Bestowed annually upon a distinguished engineering educator who delivers the Annual Lecture of the Chemical Engineering Division, the award consists of \$1,000 and an engraved certificate. These were presented to this year's Lecturer, Dr. L. E. Scriven, at the Annual Chemical Engineering Division Banquet held June 19, 1968 at the University of California, Los Angeles, California. Dr. Scriven spoke on "Flow and Transfer at Fluid Interfaces." A paper based upon his lecture will be published in an early issue of CHEMICAL ENGINEERING EDUCATION.



PREVIOUS LECTURERS

- 1963, A. B. Metzner, University of Delaware, "Non-Newtonian fluids."
- 1964, C. R. Wilke, University of California, "Mass transfer in turbulent flow."
- 1965, Leon Lapidus, Princeton University, "Aspects of modern control theory and application."
- 1966, Octave Levenspiel, Illinois Institute of Technology, "Changing Attitudes to Reactor Design."
- 1967, Andreas Acrivos, Stanford University, "Matched Asymptotic Expansions."

BIOGRAPHIC SKETCH

L. E. Scriven was born in 1931 in Battle Creek, Michigan. He graduated from the University of California, Berkeley with honors in 1952, where he won the University Gold Medal for academic achievement and was elected to Tau Beta Pi and Phi Beta Kappa. He went on to do graduate work in chemical engineering at the University of Delaware and received the MChE and the PhD

degrees in 1954 and 1956 respectively. While there he was elected to Phi Eta Kappa and held NSF and Shell predoctoral fellowships.

After three years as a Research Engineer with the Shell Development Company, Emeryville, California, Dr. Scriven joined the faculty of the University of Minnesota where he is now Professor of Chemical Engineering. In 1963 he was Guest Investigator at the Rockefeller Institute and in 1967 Visiting Professor at the University of Pennsylvania. In 1960 he was corecipient (with C. V. Sternling) of the Colburn Award of the American Institute of Chemical Engineers for the outstanding paper published by the Institute. His teaching abilities were recognized in 1966 by the Distinguished Teaching Award of the University of Minnesota Institute of Technology.

In research and scholarly activities his interests have centered about fluid mechanics, some associated mathematical methods and the application of engineering to biology. He has published highly significant papers on continuum theory of transport and transformation processes, interface physics, interface transfer and dynamic instability and pattern. Dr. Scriven is Advisory Editor for the Prentice-Hall Series in the Chemical and Physical Engineering Sciences and is widely known for his editorship of **Theory of Energy and Mass Transfer** by A. V. Lykov and Y. A. Mikhaylov, translated in 1961 from the Russian by W. Begell. Many industrial firms have called upon him as a consultant or lecturer.

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IRREVERSIBLE THERMODYNAMICS*

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The macroscopic approach to irreversible thermodynamics originally proposed by Sliepcevic and Finn in 1963 is amplified to demonstrate that, of the four possible alternatives for obtaining the reciprocal relations, fluxes and forces for systems under the simultaneous influence of two potential differences, one alternative is identical to the results obtained by Onsager.

IN A PREVIOUS PAPER by Sliepcevic and Finn⁹ a macroscopic approach for deriving the linear laws, which relate the fluxes to the forces for irreversible processes under the simultaneous influence of two potential differences, was proposed. Subsequent to this publication a number of readers raised questions regarding the validity of this derivation and whether the fluxes and forces so derived had any physical significance. More recently Andrews¹ has published a negation of the macroscopic derivation as extended by Sliepcevic and Hashemi¹¹; however his paraphrasing of the macroscopic approach does not appear to be tenable.

In an attempt to amplify the macroscopic derivation, a simple example of a one-dimensional, one-component system under the influence of two potential differences will be used. Multi-component systems will not be considered since in these cases the definition of heat is at best ambiguous^{2, 5} and therefore, it is meaningless to relate the fluxes to physically significant quantities. Furthermore, systems under the influence of viscous dissipation forces or external fields (e.g., magnetic) pose some unresolved problems on their inclusion in the energy balance equations. An analysis of the complications introduced by the presence of electrical and magnetic fields has been presented by Martin.⁶

*Presented at the Annual Meeting of ASEE, June 19-22, 1967.

IN GENERAL, the literature of irreversible thermodynamics raises some profound questions as to its range of practical usefulness; an excellent review has been published by Wei.¹² In order to circumvent definitional dilemmas associated with more complex systems—which would serve no purpose other than to detract from the principal focus of this paper—attention will be given only to a simple process familiar to chemical engineers. Until agreement can be reached on the validity of the derivation for the simplified system treated herein, it would be folly to attempt to cover the more complex cases.

The system to be analyzed in this paper is a one-dimensional, one-component system in which the properties such as temperature T , pressure P , and chemical potential μ are assumed to be uniform throughout. Likewise, the properties of this same component which composes the surroundings are assumed to be uniform throughout and are denoted by the subscript i , viz. T_i , P_i , μ_i , which in general are different from the properties of the system. Obviously, then, discontinuities in the properties exist at the boundaries, and for this reason it has been called a discontinuous system.⁴ Neglecting kinetic and potential energy effects (without loss in generality) the following equations apply when a quantity of mass δM_i , having a specific enthalpy, h_i , and a quantity of heat δQ , are transferred simultaneously and irreversibly across the boundary of the system at T_i such that no work is done.

$$\text{Energy balance: } -h_i \delta M_i + \delta(uM) = \delta Q \quad (\text{a})$$

$$\text{Entropy balance: } \delta(sM) = \delta \left(-\frac{Q}{T_i} \right) + s_i \delta M_i + \frac{\delta l w}{T} \quad (\text{b})$$

$$\text{Mass balance: } \delta M = \delta M_i \quad (\text{c})$$

$$\text{Gibbs equation: } \delta u = T \delta s - P \delta v \quad (\text{d})$$

$$\text{Defining equation: } \mu = h - Ts = u + \frac{Pv}{T} - Ts \quad (e)$$

where u , s , v are the specific internal energy, entropy and volume, respectively, μ is the chemical potential, and lw is the lost work as defined in

Equation (b) so that $\frac{\delta lw}{T} = S_p =$ total entropy production. Combining these equations yields

$$\delta lw = \left[\delta \left(\frac{Q}{T_i} \right) + s_i \delta M \right] (T_i - T) + \delta M (\mu_i - \mu) \quad (f)$$

Replacing the potential differences by Δ 's, noting that $\Delta \mu_T = s_i \Delta T + \Delta \mu$ and converting to the differential form Equation (f) becomes

$$dlw = (\Delta T) d \frac{Q}{T_i} + (\Delta \mu_T) dM \quad (1)^*$$

Equation 1 is valid to the extent that Equations (a) through (e) hold, and no other restrictions are required. Although Equation 1 was derived for the discontinuous system the same form of the equation holds for steady state systems. However, in the latter case it is customary to replace the Δ 's in Equation 1 by the gradients, namely $-\text{grad } T$ and $-\text{grad } \mu$.

Another aspect of Equation 1, which is commonly overlooked, is that it is perfectly valid—subject to the aforementioned restrictions—irrespective of whether dlw is path dependent or path independent. In general, dlw for closed systems is regarded as path dependent because heat Q and work W are path dependent. However, if either Q or W is zero, then the non-zero quantity becomes path independent, as required by the first law energy balance, and in this case dlw becomes path independent. For open systems in which a transfer of mass occurs across the boundaries as well as a transfer of heat and work, then it is conceivable that the energy term associated with mass transfer is path dependent if the properties of the mass being transferred vary with the amount of mass transported. However, for discontinuous or steady state systems, the properties are invariant at the boundary so

$$\begin{aligned} * \text{Since } \frac{\partial \mu}{\partial T} = -s, \text{ then it follows that } s_i (T_i - T) + \\ (\mu_i - \mu) = (\mu_i)_{P_i, T} - (\mu_i)_{P_i, T} + (\mu_i)_{P_i, T_i} - (\mu)_{P, T} \\ = (\mu_i)_{P_i, T} - (\mu)_{P, T} \equiv \Delta \mu_T \end{aligned}$$

that the energy term associated with mass transfer is path independent. Therefore for the case of either discontinuous or steady state, open systems in which no work is done, dlw is an exact differential.**

In reality it is not essential to the objectives of this paper to argue further regarding the necessity and sufficiency of the conditions for which dlw can be treated as path independent or an exact differential. As will be seen in the following development, the subsequent restrictions to systems under the influence of very small potential differences or gradients (or fluxes) is equivalent to considering only those processes for which dlw is an exact differential; in other words the linear laws and the bilinear form of the entropy production or lost work equation are tantamount to the assumption that dlw is an exact differential. Therefore, it is permissible to express Equation 1 as

$$\begin{aligned} dlw = (\Delta T) d \frac{Q}{T_i} + (\Delta \mu_T) dM \equiv \\ \left(\frac{\partial lw}{\partial \frac{Q}{T_i}} \right) d \frac{Q}{T_i} + \left(\frac{\partial lw}{\partial M} \right) \frac{Q}{T_i} dM \quad (2) \end{aligned}$$

Once the conditions of exactness implied by Equation 2 are recognized, the remainder of the macroscopic derivation of the reciprocal relations is almost trivial.

FLUXES AS INDEPENDENT VARIABLES

EQUATION 1 CAN BE expressed in rate form:

$$\dot{lw} = \frac{\dot{Q}}{T_i} (\Delta T) + \dot{M} (\Delta \mu_T) \quad (3)$$

where the dot above the symbol denotes the time (θ) derivative.

From Equation 3 and well-established thermodynamic concepts, four postulates can be inferred:⁹

$$\text{I. } \dot{lw} = \dot{lw} \left(\frac{\dot{Q}}{T_i}, \dot{M} \right). \text{ Since both } \frac{\dot{Q}}{T_i}$$

and \dot{M} are continuous functions of ΔT and $\Delta \mu_T$,

**It is interesting to note that the form of Equation 1 is similar to the decrease in availability or maximum work which is an exact differential.⁸ Likewise, dlw is path independent for a process between two prescribed states in which no work is transferred. In other words the lost work, lw , can be no greater, nor less, than the maximum work that could have been transferred if each step of the process was carried out reversibly.

$\dot{l}w$ can be expressed as a function of two independent variables, namely $\left(\frac{\dot{Q}}{T_1}, \dot{M}\right)$, $(\Delta T,$

$\Delta\mu_T)$, $\left(\frac{\dot{Q}}{T_1}, \Delta\mu_T\right)$ or $(\dot{M}, \Delta T)$.

II. $\dot{l}w(0,0) = 0$. If $\frac{\dot{Q}}{T_1}$ and \dot{M} are each equal to zero, so is $\dot{l}w$.

III. $\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}}(0,0) = 0$ and $\frac{\partial \dot{l}w}{\partial \dot{M}}(0,0) = 0$.

Since $\dot{l}w$ is always positive and is a continuous, even function, with continuous derivatives,

$\dot{l}w\left(\frac{\dot{Q}}{T_1}\right) = \dot{l}w\left(-\frac{\dot{Q}}{T_1}\right)$ and $\dot{l}w(\dot{M}) = \dot{l}w(-\dot{M})$.

IV. $\frac{\partial^2 \dot{l}w}{\partial \frac{\dot{Q}}{T_1} \partial \dot{M}} = \frac{\partial^2 \dot{l}w}{\partial \dot{M} \partial \frac{\dot{Q}}{T_1}}$. The equivalence

of the cross partials follows immediately from the first postulate.

Referring to Equation 3 and recalling that according to Fourier's law, $Q \sim \Delta T$, and according to Fick's law, $\dot{M} \sim \Delta\mu_T$, it is postulated that $\dot{l}w$ is a homogeneous function of the second degree in

$\frac{\dot{Q}}{T_1}$ and \dot{M} (or in ΔT and $\Delta\mu_T$) at least to a first

approximation for small fluxes or forces. Thus Equation 3 can be expressed in general functional form for the case in which $\dot{l}w$ is time independent, such as for discontinuous or steady state systems,¹⁰

$$\dot{l}w = \dot{l}w\left(\frac{\dot{Q}}{T_1}, \dot{M}\right) \quad (4)$$

It is to be noted that Equation 4 implies that

$d\dot{l}w$ is an exact differential in $\frac{\dot{Q}}{T_1}$ and \dot{M} .

Applying Euler's theorem for homogeneous functions of the second degree to Equation 4:

$$\dot{l}w = \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}} \right) \frac{\dot{Q}}{T_1} + \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \dot{M}} \right) \dot{M} \quad (5)$$

Recalling the definition of the time derivative $d(z)/d\theta = \dot{z}$ so that $dz = \dot{z}d\theta$, Equation 5 becomes, after multiplying through by $d\theta$

$$d\dot{l}w = \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}} \right) d\frac{\dot{Q}}{T_1} + \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \dot{M}} \right) d\dot{M} \quad (6)$$

Since $d\dot{l}w$ is exact, the coefficients of the differentials of $\frac{\dot{Q}}{T_1}$ and \dot{M} in Equations 2 and 6 can be equated. Thus,

$$\Delta T = \left(\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}} \right) \frac{\dot{Q}}{T_1} = \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}} \right) \frac{\dot{Q}}{T_1} \quad (7)$$

$$\Delta\mu_T = \left(\frac{\partial \dot{l}w}{\partial \dot{M}} \right) \dot{M} = \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \dot{M}} \right) \dot{M} \quad (8)$$

The right-hand partial differentials of Equations 7 and 8 can be expanded in a MacLaurin series neglecting terms higher than second order.

$$\begin{aligned} \Delta T &= \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \frac{\dot{Q}}{T_1}} \right) \frac{\dot{Q}}{T_1} = \frac{1}{2} \left(\frac{\partial^2 \dot{l}w}{\partial \left(\frac{\dot{Q}}{T_1}\right)^2} \right) \frac{\dot{Q}}{T_1} \Bigg|_{0,0} \\ &+ \frac{1}{2} \left(\frac{\partial^2 \dot{l}w}{\partial \dot{M} \partial \frac{\dot{Q}}{T_1}} \right) \dot{M} \Bigg|_{0,0} \end{aligned} \quad (9a)$$

$$\Delta T = L_{11} \frac{\dot{Q}}{T_1} + L_{21} \dot{M} \quad (9b)$$

$$\Delta\mu_T = \frac{1}{2} \left(\frac{\partial \dot{l}w}{\partial \dot{M}} \right) \dot{M} = \frac{1}{2} \left(\frac{\partial^2 \dot{l}w}{\partial \dot{M}^2} \right) \dot{M} \Bigg|_{0,0}$$

$$+ \frac{1}{2} \left(\frac{\partial^2 \dot{l}w}{\partial \dot{M} \partial \frac{\dot{Q}}{T_1}} \right) \dot{M} \frac{\dot{Q}}{T_1} \Bigg|_{0,0} \quad (10a)$$

$$\Delta\mu_T = L_{21} \frac{\dot{Q}}{T_1} + L_{22} \dot{M} \quad (10b)$$

where the L 's are substituted for the second order, partial differential, constant coefficients. Note particularly that since the second order cross partials are equal, then $L_{12} \equiv L_{21}$. Equations 9b and

10b can be solved for $\frac{\dot{Q}}{T_1}$ and \dot{M} without destroying the symmetry (equivalence of cross partials) to obtain

$$-\frac{\dot{Q}}{T_1} = L_{11} \Delta T + L_{12} \Delta\mu_T \quad (11)$$

$$\dot{M} = L_{21} \Delta T + L_{22} \Delta\mu_T \quad (12)$$

where the L 's denote the terms containing the L 's. It can be shown easily that $L_{12} \equiv L_{21}$, since $L_{12} \equiv L_{21}$.

The forces as defined by Equations 7 and 8 and the fluxes as given by Equations 11 and 12 are identical to those of Onsager.^{3, 7}

SELECTION OF OTHER INDEPENDENT VARIABLES

AS NOTED in Postulate I above, $l\dot{w}$ could just as well have been expressed in terms of other independent variables. For example, instead of Equation 4, one could have started with

$$l\dot{w} = l\dot{w}(\Delta T, \Delta\mu_T) \quad (13)$$

By utilizing the same procedures as above, it can be shown that Equations 11 and 12 will result. In this case the fluxes and forces are defined as

$$\text{Flux} = \frac{\dot{Q}}{T_1} = \frac{1}{2} \left(\frac{\partial l\dot{w}}{\partial \Delta T} \right) \dot{M} \quad \text{and Force} = \Delta T \quad (14)$$

$$\text{Flux} = \dot{M} = \frac{1}{2} \left(\frac{\partial l\dot{w}}{\partial \Delta\mu_T} \right) \frac{\dot{Q}}{T_1} \quad \text{and Force} = \Delta\mu_T \quad (15)$$

In the paper by Sliepcevich and Finn⁹ the fluxes and forces were defined in the above manner. It can also be shown that these definitions are equivalent to those of Onsager.***

Similarly, Equations 16 and 17 could have been used as starting points.

***In reality, the definitions of the fluxes and forces as given by Equations 14 and 15 are more consistent with the treatment of the Onsager coordinates in the bilinear form of the entropy equation as intensive, rather than extensive, variables.

$$l\dot{w} = l\dot{w} \left(\frac{\dot{Q}}{T_1}, \Delta\mu_T \right) \quad (16)$$

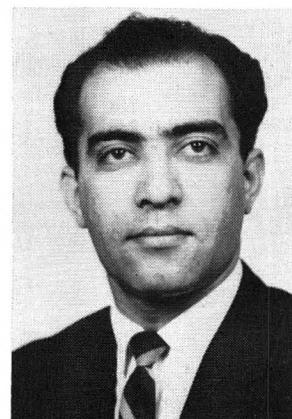
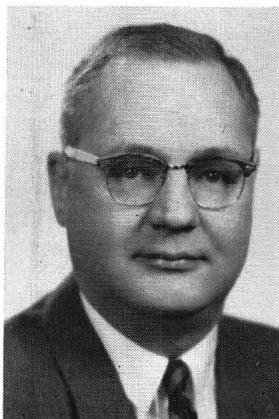
$$\text{or } l\dot{w} = l\dot{w}(\Delta T, \dot{M}) \quad (17)$$

to obtain Equations 11 and 12.

Of the four possibilities, Equations 4, 13, 16 and 17, Equation 17 would represent the most logical choice since ΔT and \dot{M} are the quantities that can be measured directly.

CONCLUSION

IT IS SUBMITTED that the foregoing macroscopic approach constitutes a valid derivation of the Onsager reciprocal relations without recourse to the theorem of microscopic reversibility. Recent experimental evidence has caused some physicists to question the validity of the time reversal invariance principle on which the theorem of microscopic reversibility is based. Notwithstanding, the assumptions and postulates for the macroscopic derivation presented herein are



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equally tenable to those involved in the microscopic derivation since both are consistent with empirical observations on related physical phenomena.

The principal result of the Onsager development is that the reciprocal relations, derived by application of the theorem of microscopic reversibility, permit a direct comparison of fluxes and forces with physically, identifiable quantities. On the other hand, the macroscopic derivation presented herein achieves the same result by virtue of the fact that $d\dot{w}$ and $d\dot{w}$ can be treated as exact differentials for the conditions under which the equations of irreversible thermodynamics hold and to the extent that the fundamental laws of classical macroscopic thermodynamics are valid. In other words, since the lost work is already known a priori to be path independent (when no work is done at any stage of the process) no new information is gained by resorting to the theorem of microscopic reversibility.

ACKNOWLEDGMENT

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SUMMER, 1968

APPROACHES TO STATISTICAL THERMODYNAMICS*

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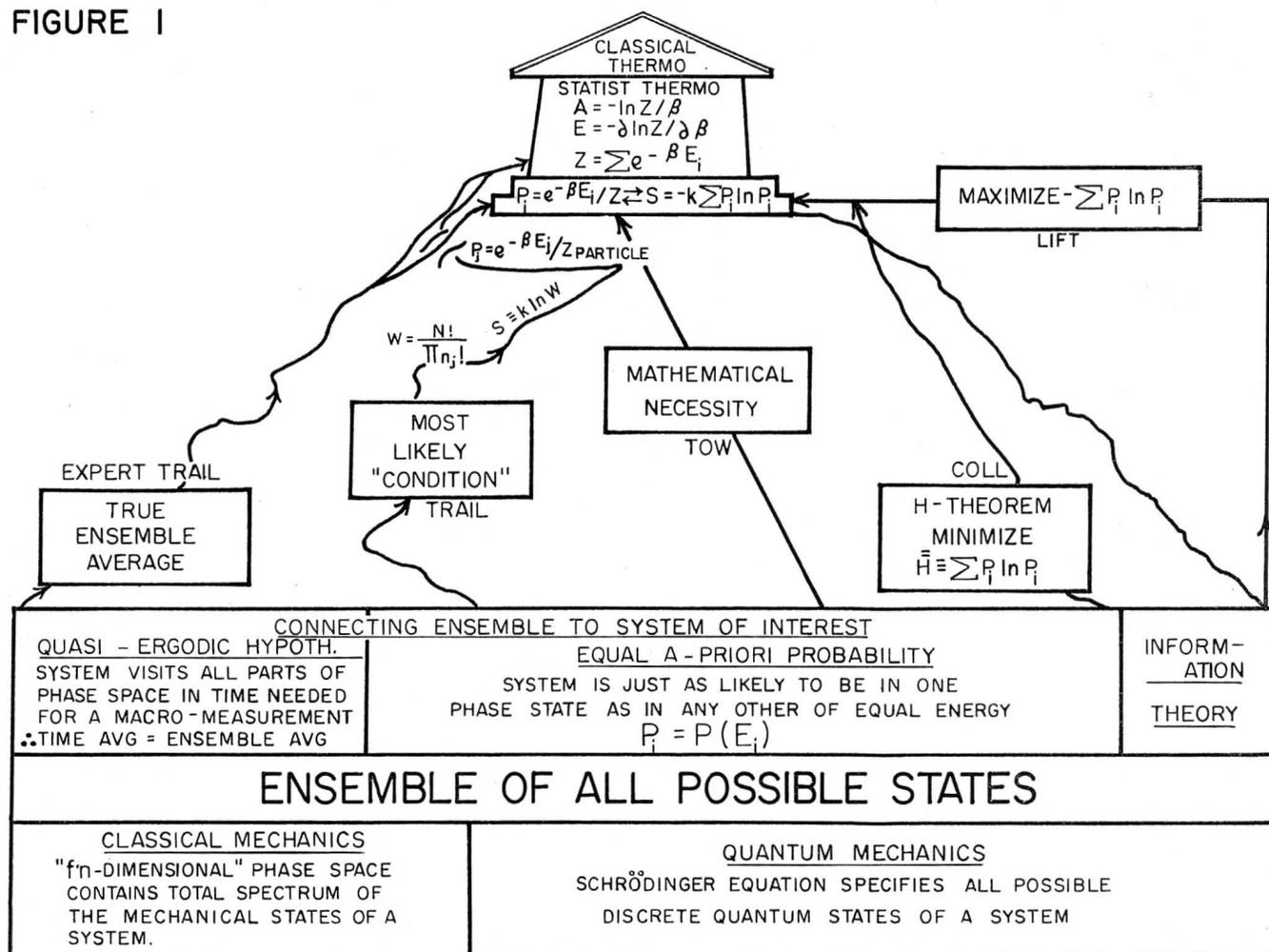
Statistical thermodynamics connects classical thermodynamics which describes the energetic interactions of macroscopic systems with the properties of the microscopic or molecular constituents of a system. The connection expands the application of thermodynamics to extreme temperature, solid state, thermo-electric, and other phenomena. It permits derivation of equations of state, and calculation of thermodynamic properties from spectroscopic data. It provides insights to many thermodynamic properties, particularly the entropy. Like many other worthwhile goals, statistical thermodynamics may be approached in a number of ways. The various approaches each have their strong proponents and detractors and the selection of an approach is often a subjective decision reflecting the user's mathematical sophistication, epistemological philosophy and teacher's prejudice.

My purpose here is to outline the more common approaches to statistical thermodynamics, necessarily in qualitative terms and with more emphasis on the similarities than the differences. My point of view is summarized by the mountain-scape sketched in Fig. 1. In the brief time available I will run you over the various trails, passes and pathways which have been used to connect microscopic to macroscopic thermodynamic behavior.

*Presented at the Annual Meeting of ASEE, June 19-22, 1967.

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FIGURE 1



Statement of Basic Problem

All approaches to the problem start from the following common ground.

1. Recognition that every macroscopic system has a fantastically detailed microscopic structure, and that the existence of this micro structure makes possible an astronomically large number of different arrangements of the microscopic elements (quantum states) which are completely consistent with the macroscopic system's properties.
2. A realization that there is no way of knowing which arrangement or state actually represents the system and therefore, all (or a most representative portion of) the possible micro-states must be considered in determining the system's properties.

The basic problem of statistical thermodynamics is therefore the assignment of a weight (a probability) to each possible micro-state which reflects its contribution to the properties of the macroscopic system.

It is in the rationalization of the averaging technique, that is, in the derivation of the func-

tion (called a "distribution" function) assigning weight or probability to each micro state, that a variety of approaches are used. All approaches arrive at essentially the same result: For a closed constant-volume system in equilibrium with a heat bath the probability of the i'th micro-state is equal to

$$P_i = \frac{1}{Z} \exp - \beta E_i \tag{1}$$

where E_i is the energy of state i and β and Z are constants of the equilibrium system.

The sum of all the probabilities = 1, and therefore

$$\sum P_i = 1 = \sum_i \frac{1}{Z} \exp - \beta E_i$$

$$Z = \sum_i \exp - \beta E_i \tag{2}$$

Z is called the "partition function," or "sum over states."

β is shown to be $1/kT$. The expected energy of the macroscopic system is equal to:

$$\langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} \quad (3)$$

and the entropy of the system is equal to

$$S = - k \sum P_i \ln P_i \quad (4)$$

$$(\text{or } S = k \ln W) \quad (5)$$

From here the expressions of classical thermodynamics are obtained by straightforward, unsophisticated mathematical techniques.

Ensemble of States

Let us now explore the Fig. 1 mountain beginning at its base—the concept of an ensemble of all possible microscopic states of a macroscopic system. In quantum mechanics, the Schrödinger equation specifies the possible discrete macroscopic or quantum states of a system. The totality of these states is the quantum mechanical representation of the ensemble. An alternate and older view of the ensemble is provided by classical mechanics where a many dimensional hyperspace is used to chart the total spectrum of mechanical states of all the microscopic constituents of the system that are consistent with the macroscopic knowledge about the system. This hyperspace is called the “phase space” of the system.

Having set up the ensemble of all possible states in either quantum mechanical or classical mechanical terms, it becomes necessary to connect the ensemble to the macroscopic system of interest. The connection is made in the ways indicated in Fig. 1.

Quasi-Ergodic Hypothesis

The average properties of an ensemble are related to the properties of a given macroscopic system by making an assumption about the actual *mechanical* behavior of the macroscopic system, viz:

A property measurement (for example pressure) made on a macroscopic system is a time average property measurement rather than an instantaneous property measurement. The measurement time is long on a microscopic scale and within the measurement time interval the system visits (or comes arbitrarily close to) all points in the phase space of the ensemble. It therefore follows that a time average property of a macro-system is the same as an ensemble average property.

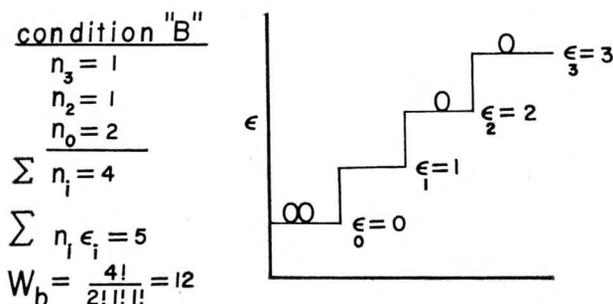
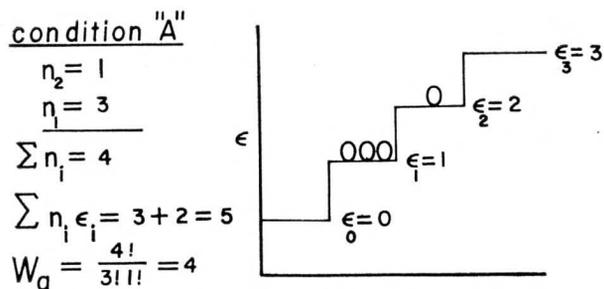


Figure 2.—Most likely “condition.” Condition “B” is more likely than condition “A” because $W_b > W_a$.

The validity of the ergodic hypothesis is questionable particularly because systems can be imagined where the hypothesis does not hold; for example, an ideal gas in a rigid parallel wall container whose particles are so arranged as to move perpendicular to the parallel faces of the container, and in such a manner that no collision occurs between the particles. This system would not visit all regions of phase space, that is go through all configurations of its particles’ positions and velocities consistent with the total energy of the system.

Equal A-Priori Probabilities

Another method of connecting the ensemble to the macro-system of interest is to assign equal statistical weight or probability to all equal micro-states of the ensemble. This is a reasonable assumption because knowing only the energy of the system, we have no basis for choosing one micro-state over any other micro-state having the same energy. The system has an equal likelihood of being in all such micro-states. Therefore, its *average* property is the average over all the equally likely states.

A corollary of this approach is that the probability of a micro-state is a function of the energy of that state only, that is,

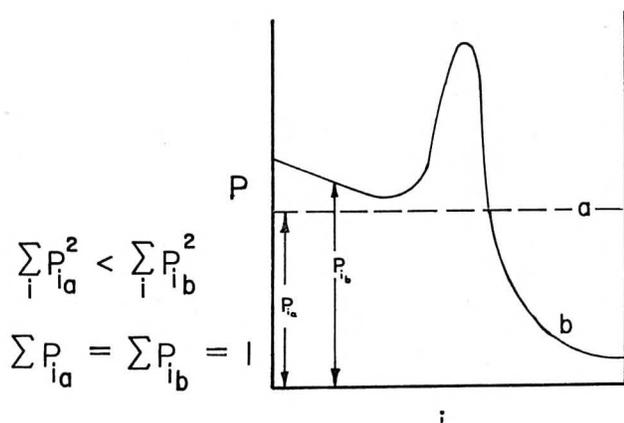


Figure 3.—Moment of a distribution.

$$P_i = f(\text{Energy of state } i) \quad (7)$$

The third way of connecting an ensemble to the system of interest indicated in Fig. 1 is the information theory approach which implicitly agrees with the equal probability assumption, although it does not make the assumption explicitly. More will be said about this later.

True Ensemble Average

We now turn to the trails ascending from our base camp to the "distribution function" (Fig. 1).

Given that ensemble average properties are the same as the macroscopic properties of a system, the system property (M) is found by integrating over phase space

$$M = \int \rho(p, q, t) M(p, q) dpdq \quad (8)$$

where p and q are the generalized coordinates of phase space; t is time and ρ is a density function which gives the probability of finding a state point in any unit volume of phase space. A mathematical theorem due to Liouville is then used to show that the density function is independent of time

$$d\rho/dt = 0$$

if ρ is a constant or a function of the energy of the entire system. (When this condition prevails the ensemble is said to be in statistical equilibrium). A suitable function is $\rho = \exp -(\lambda + \beta E)$ which leads to the conclusion that the probability of a state is proportional to exponential $(-\beta E_{\text{state}})$.

This is the route taken by the professional statistical mechanician. It requires considerable mathematical sophistication. It is thorough, elegant, rigorous, and generally unsuitable for presenting the useful concepts of statistical thermodynamics to undergraduates.

Most likely "Condition"

An alternate route to the "distribution function" I have called the "most likely condition." It is supposed to be a short cut since it attempts to evaluate the average property of an ensemble, not by covering all states in the ensemble, but only the most likely states, as represented by the most likely "condition." The "condition" of a system is the set of occupancy numbers (n_i) which designate the number of microscopic particles in each of the energy levels accessible to a system's particles. For example, Fig. 2 shows a system which has only four particles. The "a-condition" of that system is given by the set of occupancy numbers (n_i); $n_1 = 3$; $n_2 = 1$. The sum of the n_i is equal to the total number of particles in the system, in this case 4; and the energy of the system is equal to

$$E = \sum n_i \epsilon_i = (3 \times 1) + (1 \times 2) = 5 \text{ energy units}$$

Now, three 1-energy unit particles and one 2-energy unit particle can be permuted in $4!/3!1! = 4$ ways. (The general rule for the number of permutations of N total objects where N is equal to $\sum n_i$; is $W = N!/\pi n_i!$) Condition "b", given by $n_3 = 1$, $n_2 = 1$, $n_0 = 2$, allows for 12 accommodations or permutations. Therefore, if we were betting on condition "a" or "b" we would put our money on "b" as the more likely "condition."

Quite clearly, the most likely "condition" of any system is that set of n_i 's (consistent with the system's energy) which produces the maximum number of permutations. It can be shown that as the number of particles becomes very large the likelihood of any condition other than the most likely condition becomes very small. Therefore, the ensemble as a whole can be described with reasonable accuracy in terms of its most likely "condition" and the set of n_i 's that correspond to that most likely condition is simply found by maximizing the number of permutations W or $\ln W$ taking into account the fact that $\sum n_i = N$ and $\sum n_i \epsilon_i = E_i$. This technique if followed carefully, and if certain pitfalls are avoided, eventually leads to an expression for the partition function of a multiparticle system in

terms of the allowed energy levels of its constituent particles. The pitfalls and somewhat odd rationalizations* used to arrive at this final result offset the shortcut promised by averaging over the most likely condition rather than over the entire ensemble. In this approach $S \equiv k \ln W$.

Mathematical Necessity

Using the equal a-priori probability assumption, the probability of a state is a function only of its energy (see eq. 7). If we have two systems at equilibrium with a thermostatic bath whose size is such that fluctuations of the energy of one system will have no effect on the energy of the bath or the energy of the other system, then we can state

$$P_i = f(E_i) \quad (7)$$

$$P_j = f(E_j) \quad (9)$$

where E_i represents an allowed energy state of the first system and E_j represents an allowed energy state of the second system. Now, considering both systems together, the probability of the first system being at E_i and the second system at E_j must be

$$P_{i \text{ and } j} = f(E_i + E_j) = P_i P_j \quad (10)$$

$$\text{therefore } f(E_i + E_j) = f(E_i) f(E_j) \quad (11)$$

The only function satisfying (11) is an exponential

$$\text{Therefore } P_i = f(E_i) = \frac{1}{Z} \exp -\beta E_i \quad (1)$$

and we are again at the top of the mountain. A mathematical consequence of (1) and the classical definition of entropy is that S , can be shown to be equal to $S = -k \sum P_i \ln P_i$ (13) This is the approach taken by Denbigh,² Andrews,¹ and others. It is straightforward enough to be taught to undergraduates, requiring only acceptance of the fact of the existence of a multitude of quantum states and the assumption of the equal probability of equal energy quantum states. A maximization computation is avoided.

Information Theory Approach

The Information Theory approach, while using exactly the same mathematical forms established in the older statistical thermodynamic literature, has a somewhat different philosophical or logical orientation. It states that statistical

*Particles are assumed to be distinguishable. Also, Stirlings approximation, $\ln n! = n \ln n - n$, is used.

thermodynamics is not a physical theory whose validity depends either on the truth of additional basic assumptions, such as ergodic behavior or equal probability, or on experimental verification. It is instead a form of statistical inference; a technique for making the best estimates on the basis of incomplete information. If experimental verification is not obtained this is not a shortcoming of the statistical thermodynamics, but of the information supplied.

The relationship $S = -k \sum P_i \ln P_i$ (13) occupies the primal position in this approach. The equation is the basic equation of Shannon's "Mathematical Theory of Information" and is identified with thermodynamic entropy. Maximizing (13) subject to the constraints that

$\sum P_i = 1$, (The system must be in some state) and $\sum P_i E_i = E$; (The system has energy $\langle E \rangle$) leads immediately to

$$P_i = \frac{1}{Z} \exp -\beta E_i \quad (1)$$

It is the contention of the information theorists that maximizing $-\sum P \ln P$ subject to constraints produces the least biased distribution of probabilities; a distribution which is maximally non-committal with regard to missing information.

An identical technique using a different rationale was suggested by Pauli who showed that the distribution functions are obtained by minimizing the Boltzmann H- function

$$H \equiv \sum P_i \ln P_i$$

subject to constraints. The latter technique is discussed in detail by Tolman.³ Taking $\sum P \ln P$ to an extremum is not a new idea. The "information theorists" however give it new importance by insisting that it is the **most fundamental** approach to statistical mechanics, because evaluating the P_i is a problem in guessing (i.e., statistics) and not physics, and therefore there need be no further concern with Ergodicity or Equiprobability and their justification.

From an undergraduate teaching point of view, the information theory approach is almost as simple as the previously mentioned mathematical necessity approach. The student is asked to accept, without proof, the axiom that maximizing S subject to the known properties of a system produces a minimally biased set of P_i 's. The mathematics of maximization are reasonably straightforward. The trouble with the axiom is that it does not relate to much in the undergradu-

ate's experience whereas other thermodynamic and mathematical axioms usually have some intuitive acceptability.

Smoothing Function

A way of making the axiom more acceptable is to demonstrate qualitatively that maximizing $-\sum P_i \ln P_i$ or minimizing $+\sum P_i \ln P_i$ is a smoothing operation which tends to minimize the "moment" (lower the center of gravity) of a plot of P_i vs. i .

As qualitative example, assume that we have a system which is capable of existing in a great number of possible states, and we are asked to arbitrarily assign probabilities to each of these states. The states can be ordered in a sequence, and indexed by an integral subscript i . Assume that all we know about this system is that it must be in some state P_i . In Fig. 3, line b is an arbitrarily assigned distribution for this system which is constrained only by the fact that the sum of the ordinates equals unity, that is $\sum P_i = 1$. This is *not* an unbiased distribution because I have put maxima and minima in this distribution, that is, I have given some states more weight than others, without information that would justify so doing. The relative smoothness of the arbitrary curve in Fig. 3, can be represented by the mathematical index

$$\sum P_i^2 \quad (14)$$

which evaluates the "moment" of the distribution about the horizontal axis. The "moment" increases as the magnitude of the singularities or extrema in the system increase, and conversely, decreases as the center of gravity of the distribution drops, that is, as the curve becomes more uniformly *smooth*. In fact, it is a straightforward exercise in calculus of variation to show that the minimum "moment" corresponds to line "a," a constant value of P_i which is certainly the smoothest possible curve. If, in the smoothness index, (Eq. 14) we replace one P_i with a monotonic function of P_i , that is $-\ln P_i$, we should expect similar behavior. In other words, the effect of maximizing $-\sum P_i \ln P_i$ is to *smooth* out our distribution. The advantage of the logarithmic function is that it allows expressing S as a function of the probability of the microstates, and it prevents P_i from taking on negative values.

Allow me to end with a speculative aside. Maximizing entropy smooths a distribution. This

suggests to me that it might be possible to restate the principle in terms of geodesics. I say this because I would assume that a maximally smooth curve should have a minimum arc length.

I have tried using a criterion of "minimum arc length" to find a distribution function, harboring secret hopes that the criterion would lead to $-\sum P_i \ln P_i$ and even more general expressions for new entropies. I regret that I've not been successful. The geodesic idea (that an unbiased distribution has minimum arc length) nevertheless continues to intrigue me and I would welcome thoughts of others on how to work it into a selection formalism.

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The New Stoichiometry*

EDWARD M. ROSEN
Monsanto Company
St. Louis, Missouri

ERNEST J. HENLEY
University of Houston
Houston, Texas

In May of this year we sent a questionnaire to all AIChE accredited schools to determine the subject matter now included in stoichiometry or the equivalent first course in chemical engineering. The replies to this questionnaire indicate quite clearly that 1) the overwhelming majority of the courses are still in the mold cast by Hougen and Watson in the 1940's, and 2) there is a certain amount of experimentation, dealing mostly with the introduction of computer techniques into the curriculum.

This introduction of computing techniques into material and energy balance courses must ultimately give rise to what we call 'the new stoichiometry.' The new stoichiometry, in turn, will form the foundation for the computer aided design and simulation courses which we expect will find a place in all chemical engineering curriculums within a decade. It seems appropriate to examine first, therefore, the elements of a computer aided design system.

Table I is a partial listing of computer aided chemical design systems. Of the industry programs, the CHEOPS is considered by many to be the grandfather because of the wide publicity it received in the early 1960's. The CHEVRON program, which is oriented towards hydrocarbons, has been made operational at the University of California, Berkeley. The PEDLAN program is one of the first to be written in a problem oriented language and requires a Fortran pre-compiler.

The CHIPS, KELLOGG, PECOS, and UOS programs are available through service companies, as is PACER, which was originally developed at Purdue and Dartmouth. The CHESS program is in operation at the University of

*Presented at the Annual Meeting of ASEE, June 17-20, 1968.

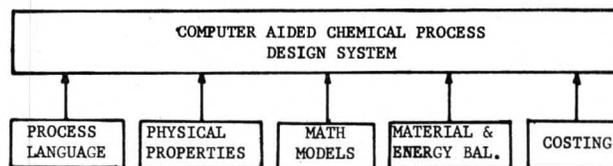


Fig. 1.—Elements in computer aided chemical process design systems.

Houston, and its capability is now being greatly extended with help of a Themis grant, ONR Contract N0014-68-A-0151. SLED, under development at Michigan, is analogous to PEDLAN in

Table I. Computer Aided Chemical Process Design Systems*

Industry

CHEOPS—Chemical Engineering Optimization System, Shell Oil
CHEVRON—General Heat and Material Balancing Program, CHEVRON Research Company
PEDLAN—Process Engineering Design Language, Mobil Oil Company

Service Companies

CHIPS—Chemical Engineering Information Processing System, IBM Service Bureau
KELLOGG Flexible Flowsheet—M. W. Kellogg
PECOS—Bechtel Company
UOS—Unit Operations Simulator, Bonner and Moore (Fluor Company)

Education Institutions

CHESS—Chemical Engineering System Simulator University of Houston
MAEBE—Material and Energy Balance Execution, University of Tennessee
PACER—Process and Case Evaluator Routine, Dartmouth
SLED—Simplified Language for Engineering Design, University of Michigan
SPEED-UP—Simulation Program for the Economic Evaluation and Design of Unsteady State Processes, Imperial College

that it utilizes a problem oriented language. MAEBE is a first generation material and energy balance program, and SPEED-UP is not fully implemented.

If a stoichiometry course is to serve as a precursor to a computer aided design course, we must analyze the design system in terms of its com-

*A complete tabulation and discussion of computer aided design systems is given by Evans, Stewart, and Sprague, CEP, Vol. 64, No. 4, 1968.

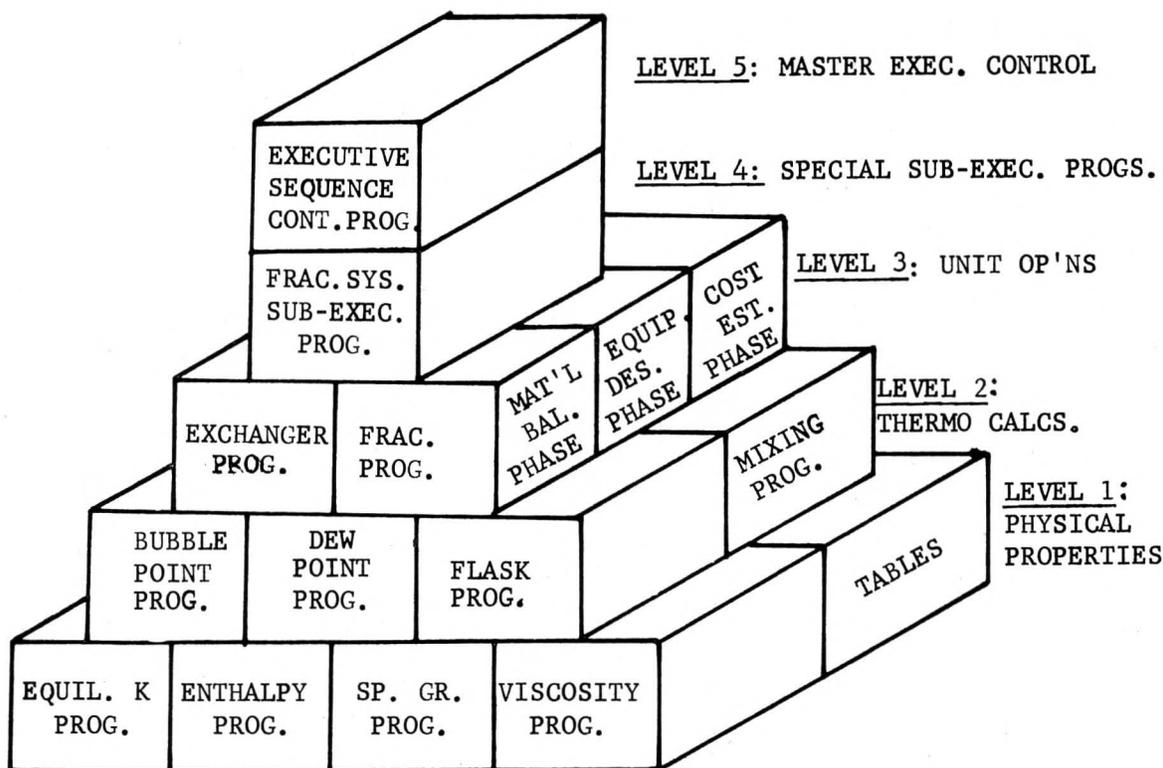


Fig. 2.—Building blocks in a preliminary design and capital cost system for fractionating columns.

ponent parts to see what fundamental principles are involved. Figure I shows the five component parts:

1. The process language which converts the language of the engineer to that of the computer
2. The physical property package which generates the necessary information regarding transport, P-v-T, and thermodynamic properties
3. The mathematical representation of the building blocks (transfer functions, if you will)
4. The material and energy balance 'executive program' which links the building blocks
5. Costing programs, which may include some sort of optimization program.

In Figure 2 we see a more detailed breakdown of the blocks in Figure 1 as they are used in the design of a fractionation column. On the lowest level we have the physical property tables or equations. These are really a part of a system which includes subroutines to produce enthalpy values, equilibrium constants, etc.

Next there is a second level of thermodynamic calculations which use the lower level physical property programs. Dew point, bubble point, and flash programs are the examples cited.

On the third tier we have the transfer functions for the building blocks; the mathematical

representation of the classic unit operations. The level four function ties together the block of programs comprising the fractionation system, and overseeing the whole conglomeration of subprograms which comprise the bottom four levels we have an executive control program which takes into consideration all input and output format and everything else that goes into a well formulated system.

If one of the objectives of the 'new stoichiometry' is to train a student to create and use computer aided design systems, it is necessary to define the topics which must be included. In Figure 3 we define the five building blocks for the new stoichiometry.

We have (1) thermodynamics and (2) classical stoichiometry; these two blocks together form the manual method block in the 'Hougen-Watson mold.' The other three elements, (3) linear algebra, (4) solution of equations, and (5) algorithm development, together with (1) and (2) are the required building blocks for machine method calculations. The remainder of this paper details the material in building blocks (3), (4), and (5). The examples used are from our forthcoming book "Material and Energy Balance Computation," John Wiley (June 1968).

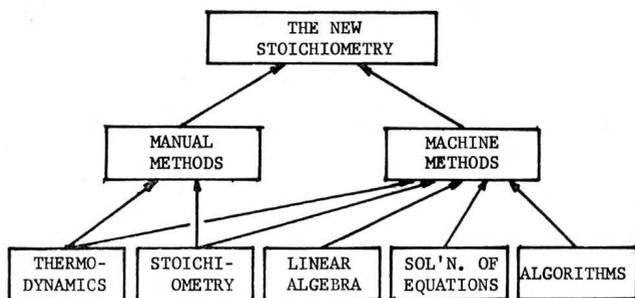


Fig. 3.—Elements of the new stoichiometry.

Linear algebra, in the words of Rutherford Aris, "is the proper language of stoichiometry." Indeed, linear algebra is the only type of algebra digital computers can do; they cannot handle nonlinear problems. Consider, for example, Gibb's Rule of Stoichiometry, Figure 4. It states that the maximum number of linearly independent chemical reactions in a set of reactions is equal to the number of chemical species known (from experiment) to be present, minus the rank of the atom matrix. The atom matrix for a five component mixture consisting of CO, H₂, CH₃OH, CO₂, and H₂O is shown in Figure 5, where the rows are the species and the columns the atoms. The determination of the rank of this matrix is an exercise in linear algebra. A classic technique for determining the rank of a matrix is the Gram-Schmidt method where we attempt to construct a set of *m* orthogonal vectors, Y₁, Y₂, . . . Y_M from X₁, X₂, . . . X_M. If the length of a Y vector is zero, then orthogonalization is impossible, and the X vector is parallel to one of the others. The procedure is shown in Figure 6: the rank of the atom matrix in Figure 5 is three. Thus, according to the Gibb's Rule of Stoichiometry, there are two independent reactions.

Taking the two reactions shown in Figure 7 as the independent reactions, we construct the reaction matrix in Figure 7. The rows are the species; the columns the stoichiometric coefficients for reactions (1) and (2). The matrix formulations of the material balance lead logically and simply to the elegant statement for the

$$\left(\begin{array}{c} \text{MAX. NUMBER OF} \\ \text{LINEARLY INDEPEN-} \\ \text{DENT REACTIONS} \end{array} \right) = \left(\begin{array}{c} \text{NUMBER} \\ \text{OF} \\ \text{SPECIES} \end{array} \right) - \left(\begin{array}{c} \text{RANK OF THE} \\ \text{ATOM} \\ \text{MATRIX} \end{array} \right)$$

$$M = N - R$$

Fig. 4.—Gibbs rule of stoichiometry.

conservation of atoms shown in Figure 8. The product of the transpose of the reaction matrix times the atom matrix must be zero. We hope that this example is a convincing demonstration of Aris' axiom.

Next we consider the nature and function of block four, the solution of nonlinear equations. In the isothermal flash vaporization shown in Figure 9, $f_H(\alpha)$ and $f_R(\alpha)$ are two valid and identical solutions of the material balances. In these equations $\alpha = L/V$ and $K_i = y_i/x_i$. Since z_i , the feed composition is known, and K is known,

SPECIE	ATOMS		
	C	O	H
CO	1	1	0
H ₂	0	0	2
CH ₃ OH	1	1	4
CO ₂	1	2	0
H ₂ O	0	1	2

Fig. 5.—Atom matrix for a five component system, example 1.

GIVEN: X₁, X₂, . . . X_M

$$Y_1 = X_1$$

$$Y_2 = X_2 - \left(\frac{Y_1 \cdot X_2}{Y_1 \cdot Y_1} \right) Y_1$$

⋮

$$Y_M = X_M - \left(\frac{Y_{M-1} \cdot X_M}{Y_{M-1} \cdot Y_{M-1}} \right) Y_{M-1} - \dots - \left(\frac{Y_1 \cdot X_M}{Y_1 \cdot Y_1} \right) Y_1$$

Fig. 6.—The Gram-Schmidt procedure for example 1. Rank, R = 3.

SPECIE	REACTION	
	1	2
CO	-1	1
H ₂	-2	-1
CH ₃ OH	1	
CO ₂		-1
H ₂ O		1

$$M = 5 - 3 = 2$$

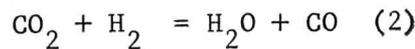
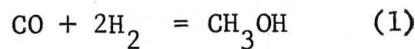


Fig. 7.—Reaction matrix for two linearly independent reactions.

these are simply non-linear equations in one unknown, α . They can be solved readily by any number of one-dimensional, non-linear root finding techniques.

In Figure 10 we have a plot of both $f_R(\alpha)$ and $f_H(\alpha)$ vs. α . The root, at $f_R(\alpha) = f_H(\alpha)$, has been successfully found and is, as it should be, identical for both equations. There are, however, major differences in the shape of the curves, and we see that the $f_H(\alpha)$ function gives us two roots,

REACTION MATRIX

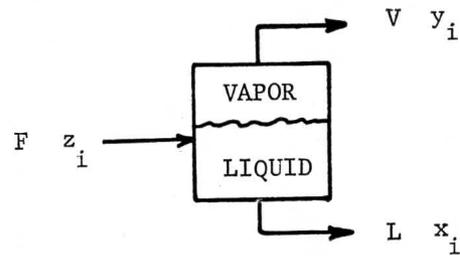
ATOM MATRIX

$$\begin{pmatrix} -1 & -2 & 1 & 0 & 0 \\ 1 & -1 & 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 2 \\ 1 & 1 & 4 \\ 1 & 2 & 0 \\ 0 & 1 & 2 \end{pmatrix} = 0$$

Fig. 8.—The conservation of atoms.

one of which is spurious. Clearly, if we are to avoid such pitfalls we can not blindly set up and solve material and energy balances and feed the resulting equations to a computer.

In this 'one-dimensional' example we had only one non-linear equation to deal with. Let us now examine the multi-dimensional set of equations



$$F z_i = V y_i + L x_i$$

BY REARRANGEMENT:

$$\sum_{i=1}^N y_i = \sum_{i=1}^N \frac{z_i K_i}{1 + \alpha(K_i - 1)} - 1 = f_H(\alpha)$$

$$\sum_{i=1}^N x_i - \sum_{i=1}^N y_i = \sum_{i=1}^N \frac{z_i(1 - K_i)}{1 + \alpha(K_i - 1)} = f_R(\alpha)$$

Fig. 9.—Isothermal flash equations, example 2.

which will arise from the flowsheet for the catalytic dehydrogenation of propane, Figure 11. We note immediately that there are two recycle streams, S12 and S2, which preclude a straight-through solution to the material and energy balances.

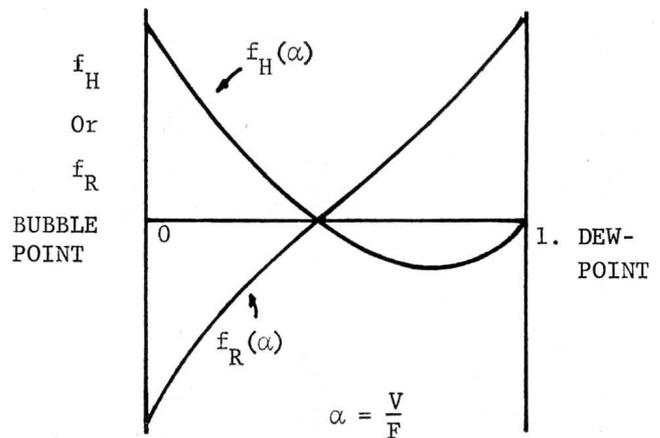


Fig. 10.—Plot of functions $f_H(\alpha)$ and $f_R(\alpha)$ for example 2.

One method of handling problems of this type is by 'tearing' the flowsheet and estimating a composition. If, for instance, we tear stream S13 (between the stripper and absorber) and guess at the composition for S7, we are able to calculate all of the remaining process streams, S1 - S13, in the sequence S8, S12, S10, S11, S2, S3,

S4, S5, S9, S6, S13. If we have guessed the composition S7 correctly, then S13 will equal S7. If not, we have to re-estimate S7 and try again.

This physical situation is given a mathematical formulation in Figure 12. We estimate the stream vector X , calculate the process vector $\phi(X)$ and if $\phi(X)$ equals X we are finished. If not we pass through a convergence block which, hopefully, will give us a new X which is a better approximation to $\phi(X)$. Since the X stands for all unknown parameters of temperature, pressure, compositions, and properties, it is apparent that the solution of problems of this type are primarily exercises in the solution of large sets of non-linear equations in many unknowns.

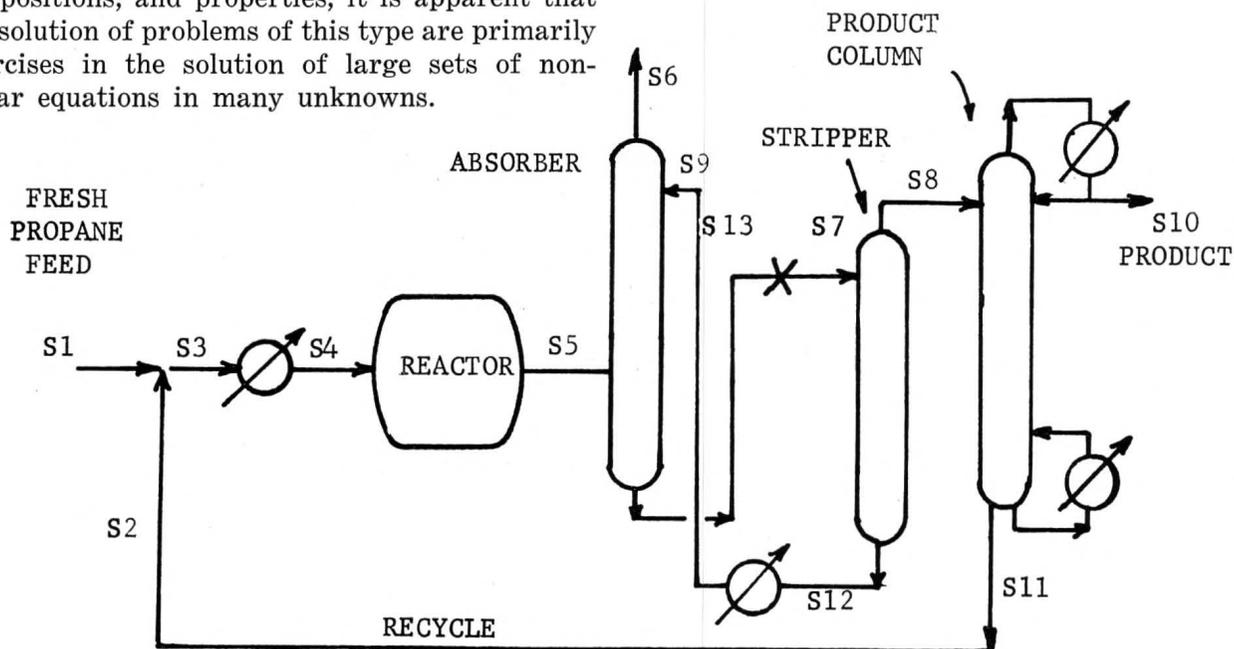
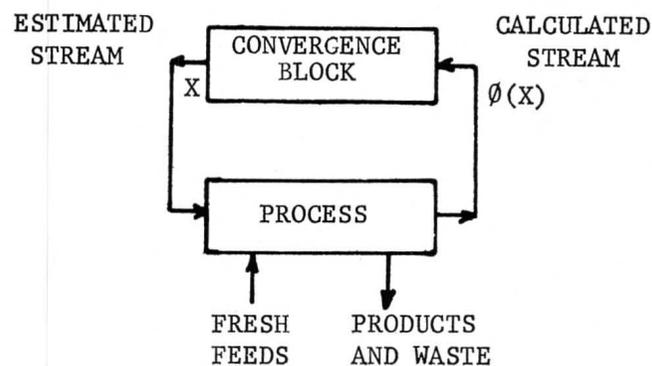


Fig. 11.—Flowsheet for catalytic dehydrogenation of propane to propylene, example 3.

The next block in our 'new stoichiometry' is a not-so-new subject, thermodynamics. The rigorous formulation of material and energy balances requires a deeper background in thermodynamics than is now attempted in the majority of material and energy balance courses. For example, if a chemical reaction takes place thermodynamics tells us that at equilibrium the stoichiometric coefficient times the chemical potential equals zero (Figure 13).

In terms of the reaction extent, e , the number of moles of component i present at any time is $n_i = n_{i0} + \alpha_i e$, where n_{i0} is the initial number of moles. The final equation from which we calculate the composition of the reaction mix given free energy data and the initial number of moles is a non-linear function in one unknown, $\phi(e) = 0$. To obtain this equation we needed thermodynamics.

The methods of the new stoichiometry provide the tools for the development of useful algorithms, which is building block five for the machine methods. By useful algorithms we mean a well defined set of statements that lead to the solution of a problem. In order to obtain the output of any building block as a function of the input to the block, and hence to set up our design system, we must have algorithms. Let us now see how we would use our knowledge of thermodynamics and non-linear equation solving techniques to develop



$$F(X) = \phi(X) - X = 0; \quad X \geq 0$$

Fig. 12.—The convergence block as an equation solver.

an algorithm to calculate the composition of a mixture in physical and chemical equilibrium.

CONDITION OF EQUILIBRIUM AT T AND P IS

$$\sum_{i=1}^N \alpha_i \mu_i = 0$$

FOR IDEAL CONDITIONS

$$\mu_i = \mu_i^{\circ} + RT \ln P_i$$

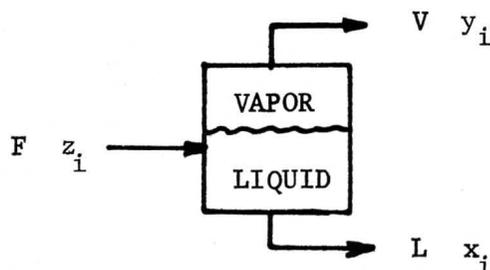
$$RT \sum_{i=1}^N \alpha_i \ln P_i = - \sum_{i=1}^N \alpha_i \mu_i^{\circ}$$

FOR: $n_i = n_{i0} + \alpha_i e$

SOLVE: $\phi(e) = 0$

Fig. 13.—Use of thermodynamics, example 4.

In Figure 14 we have a simple system in which we have a flash vaporization plus a series of M chemical reactions ($j = 1$ to $j = M$). There are N components ($i = 1$ to $i = N$). The component balances as well as the overall balance are shown in Figure 14 and our final equation is shown in Figure 15 in terms of K_i which, as before, is y_i/x_i .



COMPONENT BALANCE

$$F z_i = V y_i + L x_i - \sum_{j=1}^M \alpha_{ij} e_j$$

OVERALL BALANCE

$$F = V + L - \sum_{i=1}^N \sum_{j=1}^M \alpha_{ij} e_j$$

Fig. 14.—Model of process.

If the temperature and pressure and the feed composition z_i are fixed, $f(\alpha)$ is one equation in two unknowns, α and e . To solve the equation we propose the algorithm shown in Figure 15. We (1) estimate the e reaction extents, (2) solve for α , (3) calculate the material balances, (4) check to see if the equilibrium constant has been satisfied. If it is not, we make a new estimate of e and start again. The new estimate is usually made using a Wegstein or similar convergence-forcing routine.

What we have tried to demonstrate in this paper are (1) the techniques now being used by industry in the formulation of computer aided design and simulation systems and (2) how these may be incorporated into existing stoichiometry courses to produce the 'new stoichiometry.'

BY REARRANGEMENT

$$\sum_{i=1}^N \frac{\left(z_i + \frac{\sum_{j=1}^M \alpha_{ij} e_j}{F} \right) (1 - K_i)}{\left(1 - \alpha + \sum_{i=1}^N \sum_{j=1}^M \alpha_{ij} e_j \right) + K_i \alpha} = f(\alpha)$$

1. ESTIMATE $e_1, e_2 \dots e_M$
2. SOLVE FOR α
3. CALCULATE x_i AND y_i FROM RESULTS OF STEP 2
4. EVALUATE

$$\left[\frac{\Delta G_T^{\circ}}{RT} \right]_j = -\ln K_j = \phi(y_i) \quad j = 1, 2, \dots M$$

Fig. 15.—Suggested algorithm.

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*Kinetics**

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The background of the current extent of chemical engineering kinetics laboratory work is briefly discussed along with some observations on laboratory operation. The statistical results of a survey on this topic are presented and indicate that although many departments have laboratory work, there are a number that do not. As an aid to the introduction of more experiments, a list of successfully used reactions is given. Finally, a detailed example of an experiment used at the University of Texas is discussed.

It is realized that some type of formal chemical engineering kinetics course is a vital part of chemical engineering education. Utilizing the aspects of applied chemistry through reactor design is a unique feature which differentiates chemical engineers from other engineers.

In the 1940's Hougen and Watson began to systematically treat chemical reactor design, which resulted in their well-known textbook. Even then, it was felt that this was essentially graduate level material. It was not until the late 1950's that many chemical engineering departments had undergraduate courses dealing with reactor design. During the last decade this seems to have changed in that now most departments have some sort of undergraduate lecture course in this area. Although the trend had started, the Dynamic Objectives Report¹ of AIChE, with its recommendation that more emphasis be placed upon the chemical content of the curriculum, undoubtedly also had an effect.

In recent years with the introduction of courses on transport phenomena, process dynamics and control optimization, along with ki-

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netics into the curriculum, the time available for extensive laboratories has been steadily decreasing.

The major aims of this paper will be to first discuss what is currently done in the chemical engineering departments of the U.S. and Canada concerning chemical engineering kinetics laboratories and to list some examples of chemical reactions which could be used by other departments to introduce kinetics experiments into their curriculum. The final part of the paper will describe in detail an experiment used with success at the University of Texas.

Survey of Chemical Engineering Kinetics Laboratory Work

A survey of the North American departments was conducted to obtain data on the extent of chemical engineering kinetics laboratories. Re-

TABLE I
Extent of Kinetics Laboratory Work*

Topic	Number of Departments
Separate chemical engineering kinetics laboratory course and/or taught in conjunction with chemical engineering kinetics lecture course.	8
Experiments in other chemical engineering laboratory courses.	41
No chemical engineering kinetics experiments.	28

* Note: 76/145 replies were received.

TABLE II.
Type of Chemical Reaction

Type	Number of Departments
Homogeneous	38
Heterogeneous, non-catalytic	6
Catalytic	20
Reaction engineering/design study	16

plies were received from 76 of 145 surveys mailed. The results are shown in Table I from which it is seen that very few departments have either a separate kinetics laboratory course or have one taught in conjunction with the chemical engineering kinetics lecture courses. These two categories from the survey have been lumped together, since there is not a clear distinction between them. Most of the present work is designed as a part of other existing laboratory courses. In other words, the term "unit operations laboratory" quite often seems to be something of a misnomer since things other than this topic are studied. Thus, about half of the replies indicated that they had some work dealing with kinetics and, in fact, several departments had more than one experiment of this type.

Perhaps the most interesting figure in Table I is the fact that 28 departments indicated that they had essentially no work at all. This seemingly large lack does need some qualifications, since most students do get some exposure to kinetics in physical chemistry. However, it does seem that chemical engineering kinetics laboratory experience is lacking in a substantial fraction of chemical engineering departments. Several departments are presently in the process of adding kinetics experiments, but many are not.

Table II indicates various types of reactions that have been used for the laboratories. It can be seen that the major emphasis has been with homogeneous reactions, probably because they are the easiest to perform and obtain consistent results. Heterogeneous catalytic reactions are also fairly extensively used, probably because of their great practical interest. Very few non-catalytic heterogeneous reactions were reported. The final category of reaction engineering design study seems to have a relatively small amount of work, but this may be somewhat ambiguous. Many of the homogeneous and heterogeneous reactions are run for "engineering" purposes and could pos-

TABLE III.
Examples of Reactions Used for Kinetics Experiments

Homogeneous	
1.	Ethyl acetate saponification
2.	Acetic anhydride hydrolysis
3.	Methyl acetate hydrolysis
4.	Ethyl acetate hydrolysis
5.	Acetone bromination
6.	Isopropanol oxidation to acetone
7.	Acetic acid + ethanol esterification
8.	Benzaldehyde oxidation to benzoic acid
9.	Permanganate reduction with dissolved hydrogen
10.	Crystal violet hydrolysis
11.	Methyl acetate saponification
12.	Phthalic anhydride + butanol esterification (pilot plant scale)
13.	Ethylene glycol + periodate
14.	Hydrogen peroxide + iodide (iodine clock reaction)
15.	Ethylene-propylene polymerization
16.	Formaldehyde + methanol esterification
17.	N.N-dimethylaniline + ethyl iodide (by DTA)
Heterogeneous, non-catalytic	
1.	Coke oxidation on cracking catalyst
2.	Corrosion kinetics
3.	Cyclohexane hydrogenation
4.	Cu ⁺⁺ -H ⁺ ion exchange
5.	Cottonseed oil hydrogenation
6.	Pyrolysis of plastics
Catalytic	
1.	Ammonia decomposition, iron oxide
2.	Cumene cracking, silica-alumina
3.	Ammonia oxidation, platinum gauze
4.	Toluene hydrogenation, Raney nickel
5.	Isopropanol (liq.) dehydrogenation, nickel
6.	Propylene oxidation, copper oxide
7.	Acetaldehyde decomposition, copper gauze
8.	Benzene alkylation, acid catalyst
9.	Propylene disproportionation to ethylene + 2-butene, cobalt oxide-molybdena-alumina
10.	Sulfur dioxide oxidation
11.	n-Propanol dehydrogenation
12.	Cumene hydrogenation
13.	Styrene hydrogenation
14.	1-Hexanol dehydration
15.	Catalytic cracking
16.	Permanganate reduction with dissolved hydrogen, Ag ⁺

sibly be included here also. Many of the departments out of the 16 indicated that an important part of this topic was the use of analog or digital computers to simulate chemical reactor operation. Also, the various reactions were run in a variety of reactors such as tubular, stirred tank, as well as batch.

Table III presents a list of the actual chemical reactions used, which might serve as an aid to those who are trying to find proven reactions for their own laboratories. The saponification of ethyl acetate is the most popular reaction in use,

probably because of its good kinetic characteristics, the ease of measuring the results, and the experiment devised by Kendall.²

Detailed Example

An example of a chemical engineering reaction kinetics experiment that has worked well in our laboratories at the University of Texas is ethyl acetate saponification in a tubular reactor. Kendall² has given a very complete discussion of the system he developed to study the effects of different flow patterns in the reactor. Our system has many features in common with his but the emphasis is somewhat different. A major aspect of our system is to measure and interpret the effects of non-plug flow in the liquid phase tubular reactor and to interpret these results quantitatively in terms of mathematical models.

The fact that the ethyl acetate saponification is a very "clean" second order reaction with no side reactions is given to the student as basic data. The reaction is run in a Tygon tube of 0.615 cm diameter and 810 cm (35 feet) long, looped through baffles in a section of glass pipe which serves as a constant temperature water bath. Gravity feed lines from bottles of ethyl acetate and sodium hydroxide are run through the constant temperature water feed tank to attain reaction temperature and joined in a Y section at the reactor tube entrance. Analysis of product samples is by a simple titration method similar to that described by Kendall. Electrical conductivity methods were tried but did not work any better and were somewhat more complicated than simple titration.

In order to have high conversions of 50-90% the reactor is run at a temperature of 100°F, where the rate constant is 0.22 liter/gm mole-second, and with the feed concentrations of both reactants $C_0 = 0.2$ gm mole/liter. Since non-plug flow is most pronounced under laminar conditions, the flow rates range between Reynolds numbers of 100 to 3000. A comparison of the experimental data with theoretical predictions from the axial dispersion model (see Levenspiel³) is required, using the established correlations of the axial dispersion coefficients.

Results of some of the recent student data are shown in Figure 1. At the turbulent end of the range, the plug flow equations give good agreement with the experimental data. At the lower flow rates, although there is quite a bit of

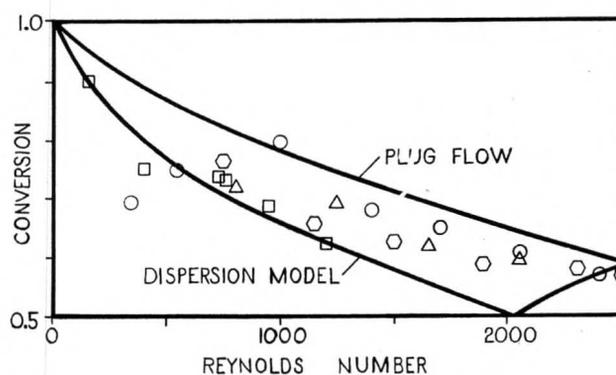


Figure 1.—Student data for ethyl acetate saponification in a tubular reactor.

scatter, it is seen that the plug flow predictions are not very good and the data approach the axial dispersion model line. The data actually fall mostly between the two predictions, but this may be caused by the looped Tygon tube which would lead to less effective axial dispersion than that predicted by the correlations for straight tubes. In any event, the experiment not only gives an example of tubular plug flow reactor results but also illustrates quantitatively the effects of non-plug flow.

Conclusions

The survey of chemical engineering kinetics experiments indicated that many departments do have some work in this area, but there are a large number that do not. Very few departments have separate kinetics laboratory or one taught in conjunction with a lecture course.

In addition to the statistical information, the survey produced a rather large selection of chemical reactions that apparently have been successfully used. These have been tabulated to help instructors find experiments that might develop their own laboratories. Finally, an example of an experiment used at the University of Texas was discussed in some detail and the types of results that can be obtained in a student laboratory were indicated.

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The Student
The Teacher
The Psychologist

View Programmed Instruction*

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The potential of programmed instruction as an educational device is demonstrated by its present use in the classroom, industrial training programs, the continuing education program of the medical profession, and by the recent interest of several large corporations who have entered the education business with systems based on programmed instruction. This paper describes a set of thermodynamics programs developed at Purdue University and examines their potential from the viewpoint of the student who used them, the teacher, and the psychologist. Various aspects of the design of these programs are examined including linear versus branched style, step size, concrete illustrations of abstract concepts and perceptual organizers. The programs and the textbook are compared in terms of their ability to transmit information to the student. The program is described as psychologically superior because it shapes behavior from the simple to the complex and guides the student so he avoids misconceptions which must be unlearned. Finally, the value of the programs in freeing class time for more valuable activities is described.

If you asked Harvard psychologist B. F. Skinner¹ what programmed instruction can do for education he would reply, "What is now taught by teacher, textbook, lecture, or film can be taught in half the time . . . by a teaching machine" using programmed instruction. Before you dismiss Skinner's claim you should carefully consider the fact that RCA, IBM, GE, Westinghouse and several other large corporations have recently

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staked a claim in the education business with systems that involve programmed instruction materials. In addition, many industrial firms already use programmed instruction to teach basic skills to their employees. And the medical profession is using programmed instruction in a program of continuing education. While Skinner's claim of a 50% gain may be a little unrealistic, it should be clear that programmed instruction has definite potential as an educational device. In the discussion that follows I will examine this potential from three view points: that of the educational psychologist who applies the theories of psychology to the classroom; my own viewpoint as a teacher who has written, experimented with and used programs in my teaching over a period of five years; and the viewpoint of the student who has studied from my programs.

WHAT IS PROGRAMMED INSTRUCTION?

The concept of programmed instruction was introduced by Skinner in 1954. Since that time three methods of presentation and two different styles have been developed. The three methods are:

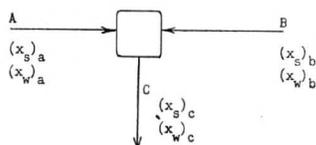
1. Computer assisted instruction: the student operates a typewriter linked to the computer which contains the programmed material.
2. Teaching machines, any device which mechanically controls the presentation of the program to the student.
3. Programmed texts, which place the material in the hands of the student.

Each method has its advantages, but the programmed text is basic to the other two. Therefore, this discussion will be limited to that method.

The two program styles are called linear and branched. Table I shows an example of a simple linear program, a series of questions and answers. To use this program the student covers the answer with a sheet of paper, reads the question and thinks or writes his answer. He then uncovers the program answer and checks his work. Table II shows a branched program. In this case the student reads the question, selects one of the given answers, and then checks his choice against the answer given in the program. When he selects the correct answer he proceeds to the next question.

Table I. Simple Linear Program.

Consider the open system, steady state process shown below, mixing operation with salt and water.



5Q. How many flow rate unknowns are there?

5A. Three flow rate unknowns: A, B, C.

6Q. How many composition unknowns?

6A. Six composition unknowns, two in each stream. The total number of flow rate and composition unknowns is 9.

7Q. What is the total number of material balance equations that can be written?

7A. Three material balance equations can be written:
salt balance
water balance
stream balance

8Q. How many of these material balance equations are independent?

8A. Two material balance equations are independent.

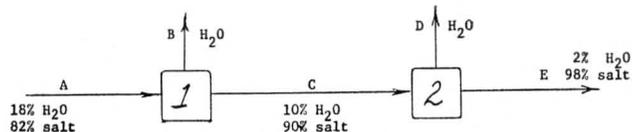
Program Versus Text

If you have had no previous personal contact with programs your first question will probably be, why a program instead of a text? The answer to this question is provided by the psychologist Ausubel² who identifies the most crucial condition affecting the acquisition and transfer of knowl-

TABLE II. Physical Material Balance Calculations

Two or more process units may be included in the system chosen for a material balance calculation. For example, Figure 8 shows two driers used in series to remove water from salt. In this problem it is possible to write material balances not only for each unit but also for the pair of units combined

Figure 8



Section 1

Q. 1220 lbs/hr of wet salt (A) are supplied to the two-stage drier system shown in Figure 8. Assume steady state operation. How many unknown flow rates are there in this system:

Your A.

5 unknowns	See section 4
4	7
8	9

Section 2

A. 6 equations. No. You counted material balances around unit 1 and unit 2. What about balances around both units?
Go to section 7.

Section 3

A. 4 independent equations. Correct. All the other equations are dependent, they can be derived by adding or subtracting the four independent equations. Is it possible to solve a salt and a stream balance around unit one, a stream balance around unit two, and a stream balance around both units?

Your A.

Yes	See section 6
No	11

Section 4

A. 5 unknowns. Check the problem again, you probably counted the flow rate of stream A as an unknown. The flow rate of this stream is given and should be used as the "basis" for your calculations.

Section 5

A. 9 equations. Correct. You can write a stream, salt, and water balance around each unit and around both units combined. Now, how many of these equations are independent?

Your A.

4 equations	See section 3
6	8

Table II. (Continued)

Section 6

A. Your answer is yes. The correct answer is no. It is impossible to get an answer if you use three equations of the same kind (i.e., stream balances). Try it if you have doubts.
Go to section 3.

Section 7

A. 4 unknowns. Correct. The unknowns are stream flow rates B, C, D, and E. Streams B and D are pure water so there are no composition unknowns in this problem.

Next, what is the total number of equations that relate these 4 unknown variables?

Your A.

4 equations	See section 10
6	2
9	5

Section 8

A. 6 independent equations. No. You have correctly reasoned that not all three equations in one set (i.e., unit one) may be used. But it is also impossible to use all three equations of one kind (i.e., salt balances).
Go to section 5.

Section 9

A. 8 unknowns. No. You have counted 4 composition unknowns for the water streams which are pure water.
Go to section 1.

Section 10

A. 4 equations. No. You didn't read the question carefully. What is the total number of equations you can write for this system that involve the stream flow rate unknowns?
Go to section 7.

edge as the internal logic and the organization of the material. The usual text is logically sound but psychologically incongruous because it segregates material by topic, does not clarify the relationship between topics, and presents material at a uniform level of abstraction instead of building from the simple to complex. As a result the student treats meaningful material as if it were rote in character. He memorizes formulas, learns type problems, performs mechanical manipulations and both learning and retention are reduced.

By contrast, Ausubel identifies the program as a psychologically correct device because it is constructed around the basic organizing concepts of

the discipline and ideas are arranged sequentially to build the hierarchical structure that matches the way in which psychologists believe knowledge is organized and stored in the human nervous system. The method used to construct a program illustrates Ausubel's point. First, the basic concepts of the course must be identified and organized into a logical pattern. Second, a detailed set of performance objectives such as those shown in Table III are prepared for each concept. Then the teacher begins the final step, the writing of the questions and answers that will lead the student from the objectives he learned in the previous program to the objectives of the new program. It is the combination of all these steps that gives the program its great strength.

Table III. First Law of Thermodynamics—Summary*

A. State Properties (Q 1-3)

1. Define a state property: a property that depends only on a point's location, not on the path used to get there.
2. Name 5 state properties: P,T,V,U,H.

B. Path Properties (Q 4-12)

1. Define a path property: A property that depends on the path used. Q and W are path properties.
2. Use a P-V diagram to prove that W depends on the path used.

C. First Law of Thermodynamics for a Closed System (Q 13-32)

1. State the first law of thermodynamics for a closed system:

$$Q - W_c = U_2 - U_1 = \Delta U$$

2. Define internal energy

a. $Q - W = \Delta U$ for any closed system, any material.

b. $\Delta U = C_v(T_2 - T_1)$ for any ideal gas process and for an isometric process for any material which has a constant C_v .

c. Units, BTU/lb mole or BTU/lb

d. Zero point, arbitrary

3. Apply the First Law to a Closed System

Ideal Gas	Real Material
------------------	----------------------

a. Closed Isothermal Process

$$Q - W_c = U_2 - U_1 \qquad Q - W_c = U_2 - U_1$$

$$= C_v(T_2 - T_1)$$

$$Q - W_c = 0 \qquad U = \phi(P,T)$$

$$Q = W_c$$

b. Closed Adiabatic Process

$$Q - W_c = \Delta U = C_v \Delta T \qquad Q - W_c = \Delta U$$

$$-W_c = C_v \Delta T, \text{ for } Q = 0.$$

$$+W_c = \frac{R}{\gamma - 1} (T_1 - T_2) \qquad U = \phi(P,T)$$

$$+W_c = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

*Part of the Performance Objectives for the program on the first law.

By its Socratic form the program provides the student with many of the best features of fine tutorial instruction. The program *shapes* the student's understanding by establishing simple behaviors which are gradually combined and modified until they lead to the final performance objectives which include both abstract concepts and concrete applications.

Programs were the primary vehicle for transmitting information in the thermodynamics course I taught at Purdue last semester. The students also had the regular text and they were told which sections of the text they should study. At the end of the semester they were given a questionnaire which asked, "If you had to choose between good programs or a good text as the basis for study in a class, which would prefer? Some of their anonymous replies were:

"The program, you can understand it rather than memorize it."

"In a program a person can usually tell which points he did not understand, whereas in a text he may not understand the whole material."

"The program, it forces you to stop and think and not just read, I tend to read over things in a text."

As you can see, the students identified many of the factors predicted by the psychologists. In all, twenty-five students preferred the program while three preferred the text. One of those who picked the text gave the following reason. "I would probably choose a good text because that is more familiar, but I never read a text that left me with as clear an understanding of the subject as the programs did." Because the material in the programs is not exactly the same as that in the text I asked the students the additional question, "Would you have preferred to have the material in the programs written in text form without the questions and answers?" Twenty-six replied no; two were undecided.

Linear or Branched Programs

As he creates the program, the teacher must make many decisions. First he must choose the style of the program, either linear or branched. The linear style was chosen for my thermodynamics material because it provides the most direct control of the shaping process. In addition, the linear program makes the student a more active learner. To answer each question he must reformulate the material in terms of his own vocabulary, background and structure of ideas. Ac-

Table IV. First Law of Thermodynamics—Self Quiz*

-
7. The flow work terms do not appear in the equation $Q - W_o = \Delta H$, the first law of thermodynamics for an open system. Does one of the terms in this equation include the flow work energy? If so which one?
- Q
 - W_o
 - ΔH
 - none of the above
-
- 7a. The term Q accounts for the energy transferred to or from the system as heat. Flow work is not included in this term. Return to question No. 7.
-
- 7b. The term W_o accounts for the energy transferred to or from the system as shaft work. Flow work occurs when a stream crosses the boundary of a system. Some of the flow work energy may be converted to shaft work in a given process but the two types of work energy are not directly related. Reread the program from just after A31 to Q33, then return to question No. 7.
-
- 7c. This answer is correct. The flow work is accounted for by the enthalpy $H = U + PV$. The terms U and PV are added because U represents the energy carried by a stream that enters (or leaves) and PV represents the flow work done at the boundary when that stream enters (or leaves) the system.
-
- 7d. This answer is not correct. In an open system, flow work occurs whenever a stream enters or leaves the system. One of the terms in the first law must account for this energy. Reread the program from just after A31 to Q33, then return to question No. 7.
-

*Sample Self-Quiz question for the program on the first law.

cording to the psychologists these acts are crucial to the learning process. In a sense the linear program is an experience in guided discovery. The student participates in the development of the first law and in the application of the law to different reversible and irreversible processes. The students find this participation stimulating. In response to the question, "What is the greatest strength of the programs? they replied: "Having the student answer the questions to work out the principles for himself." "I got into the act of actually developing equations."

In a branched program the student does not construct answers to the questions. Instead, he demonstrates that he has learned something by choosing the correct answer from a set of given answers. This behavior is most appropriate for a testing situation and that is exactly how the branched program has been used here. Table IV

is part of the branched program used as the Self-Quiz at the end of the program on the first law. A branched program requires that each question have one correct answer and two or three reasonable alternates or distractors. Since each incorrect answer must provide some feedback information to the student, more effort is required to construct a branched program. In some types of material there are no logical alternates and the branched program cannot be used. However, when these alternates exist, the branched program can be very effective in teaching the student to discriminate between similar ideas.

Step Size

The second decision the teacher must make is one of step size. Skinner's original concept of a linear program involved a short, one or two sentence question properly cued or prompted to insure the correct answer would be forthcoming. Recently, several, psychologists have questioned the wisdom of the small step. For example, Resnick³ has said "good students become bored with too many small steps and come to resent the time spent on such programs." Ausubel² also supports this conclusion with the thought that small steps often artificially and unnecessarily "fragment ideas so that their interrelationships are obscured and their logical structure destroyed." By a trial and error process I came to the same conclusion, the small step does not suit the ability of the engineering student. Using feedback from my students I finally evolved the program style shown in Table V. These programs involve relatively large steps, meaningful, unprompted questions combined with uninterrupted sections of explanatory material. This style integrates the best features of a textbook, the lecture that fills in the gaps left by the text, and the recitation or discussion that supplements both.

Guiding the Student

Some of you may question the idea of carefully guiding the student through derivations, proofs and sample problems. In fact you may prefer the incomplete ideas presented in textbooks because you want the student to provide the necessary clarification for himself. I agree that the student should learn to think for himself but I would argue that this struggle should not take place when the student is learning basic concepts. This reasoning is supported by Ausubel who says, "Excessively difficult material makes for an un-

Table V.—Sample Page from the first law programs

Since we can always use a path such as (1-a-2) between any two points, this equation can be used to evaluate ΔH for any ideal gas process. This is an important characteristic of a state property, any path between two points can be used to evaluate the change in a state property.

37Q. An ideal gas is compressed adiabatically in an open system process, can the work for this process be evaluated with the following equation?

$$-W_o = \Delta H = \int C_p dT = C_p(T_o - T_i)$$

37A. Yes, the ΔH of an ideal gas always equals $C_p(T_o - T_i)$.

38Q. If a real material is compressed adiabatically in an open system process, can the work for this process be evaluated with the equation

$$-W_o = \Delta H = \int C_p dT$$

38A. No. The equation $-W_o = \Delta H$ is valid for any material, but $\Delta H = \int C_p dT$ is valid only for an isobaric process for all real materials.

The enthalpy of an ideal gas is a function of only the temperature. The definition $\Delta H = C_p(T_o - T_i)$ proves that when $T_o = T_i$, $\Delta H = 0$. Pressure has no effect on the enthalpy of an ideal gas. We can reach the same conclusion by noting that both U and the (PV) product (note $PV = RT$) are functions of only the temperature. Since $H = U + PV = U + RT$ the enthalpy of an ideal gas must also be a function of only the temperature.

2. Isothermal Process

39Q. Write the first law for an open system, combine it with the definition of ΔH for an ideal gas and prove that $Q = W_o$ for an isothermal process involving an ideal gas.

$$\begin{aligned} 39A. \quad Q - W_o &= H_o - H_i = C_p(T_o - T_i) \\ \text{Since } T_o &= T_i \\ Q - W_o &= 0 \\ Q &= W_o \end{aligned}$$

desirably large number of initial errors and misconceptions that have to be unlearned." This interferes with further learning, it lowers the student's self confidence and motivation, and promotes task avoidance. It is not that the student doesn't want to learn on his own, but rather that he lacks the necessary self-critical ability. The student usually finds it easy enough to manipulate words so as to create an appearance of knowledge and thereby to delude himself and others that he really understands. Does that sound like some

of your students? By contrast, consider the following reactions of my students to the programs: "They don't let you get a misconception."

"We could go back over a question to clarify points."

"Being able to correct ideas before going on to new material."

"You can't go on unless what came before is understood."

Other Factors

We have considered several of the factors the psychologist considers crucial to effective learning. They are: organization around the broadest principles, systematic sequential organization which shapes the students behavior, and an active learner who reformulates ideas in his own words. There are two additional factors to be considered.

First the psychologists say that new, abstract subject matter should include concrete—empirical illustrations and analogies to clarify meanings. For this reason, my programs include both theory and example problems. The student's reaction to this combination is very positive. Their response to the question, "What is the greatest strength of the programs?," was:

"Working with the material as it is introduced."

"Seeing how each concept can be related to a problem right after the concept is presented."

The second factor to be considered is what the psychologist would call an integrative perceptual organizer, a device which helps the student relate similar concepts and discriminate between overlapping ideas. In my thermodynamics programs this organization is accomplished by relating each concept and calculation to an appropriate phase diagram. As each subject is introduced it is related to a process line on a projection of the three dimensional surface for an ideal gas. For example, the concept of reversible shaft work is related to the area under a process curve drawn on a P-V diagram. The concept of reversible heat transfer is related to the area under a process curve drawn on a T-S diagram. When real materials are introduced the appropriate three-dimensional models and projections of the models are used to relate the process conditions to the change in a state property. The students response to the question, "Did you find the emphasis on the graphical representation of each process helpful in understanding the material?" varied from

"definitely"; and "very helpful"; to "yes, I can picture what is happening"; "yes, it was something basic to refer to"; and "yes, I need a physical feeling for something to really understand it." In all, twenty-six students found this graphical approach helpful, two others liked the approach but were confused by the great number of graphs presented.

Programs Free the Teacher

Designed as carefully as they are, you would expect programs to teach a subject and teach it well. The response of my students to the question "Do you think the programs helped you learn more than you usually do?," bears this out. The students' reply was a unanimous yes.

When asked if the programs helped them understand more than usual, twenty-seven students said yes; one was undecided. Part of the students' reactions can probably be attributed to the Hawthorne effect, but I'm not willing to admit that this is a major factor. I don't think engineering students are that naive. The fact that graduate students ask me for copies of my programs to study for their qualifying exams is further support for the value of the programs.

Hopefully, by now I have convinced you that programs can be of significant value in an engineering course. If not, let me tempt you with one final attribute of programmed instruction. During the past semester I taught an entire course in thermodynamics using the set of programs I have developed. Each program and its accompanying problem set were assigned as homework. There were no lectures in this course, class time was completely free for other activities. In a typical class meeting I spent from five to twenty minutes answering the students' questions about the material in the program and discussing the homework problems. During the rest of the period we did a variety of things; we probed the concept to greater depth, we extended the concept to new situations and we applied the concept to industrial type problems. Those of you who would like to find time to put some engineering in the engineering curriculum should be especially eager to try programs. By increasing the efficiency of the transmission of knowledge, the programs can give you the time you need for other activities.

This, I might point out, is exactly the role the psychologists predict for programmed instruction. Ernest Hilgard, a former chemical engineer, head of the Department of Psychology and

dean of the Graduate Division at Stanford put it this way⁴. “. . . the program does not replace the teacher but can hopefully free the teacher from routine exposition, and give time for doing the things that only the teacher can do,” teaching students to think for themselves.

Programmed instruction can help you give your students a better education; I hope the information I have presented here will encourage you to try programs in your classroom.

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Dr. Charles E. Wales is an associate professor of engineering and the President's assistant for educational research and development at Wright State University. His

present assignment includes organizing and presenting a series of seminars on effective teaching techniques for the Wright State faculty. He was educated at Wayne State (BSChE), University of Michigan (MSChE), and Purdue University (PhD).

Professor Wales has written programmed instruction material in the areas of material balance calculations and basic thermodynamics. His programs have been or are being used on an experimental basis at Purdue, Kansas State, West Virginia, Ohio, and Wright State universities, at the Universities of Texas and Missouri (Columbia), and at Ohio College of Applied Science.



ChE book reviews

Engineering Thermodynamics

M. W. Zemansky and H. C. Van Ness,
McGraw-Hill (1966).

Professors Zemansky and Van Ness have written a text on thermodynamics with the “common core” course in mind. As such, the text represents a combination of and selection from the material offered in the conventional beginning courses in thermodynamics in the chemical and mechanical engineering curricula. In following this path, the authors had to judge that certain topics included in these portions of the typical chemical engineering program would either be deleted, or discussed in other courses. A similar statement, but with different topics in mind, applies equally well to the typical mechanical engineering program.

Viewed against the background of the typical chemical engineering program, there are certain features which make this book different. First, there are a number of applications discussed in the text which are not presently included in this part, if indeed in any part, of the chemical engineering program. In this category are such topics as “bars in tension and compression” (chap. 2), “work in straining a bar” (chap. 3), “work

in changing the polarization of a dielectric in a parallel plate capacitor” (chap. 3) “work in changing the magnetization of a magnetic solid” (chap. 3) and some of those discussed in “applications” (chap. 14).

Secondly, a number of the classical experiments are discussed. This includes the determination of “J” factor mechanical equivalent of heat (chap. 4), determination of $(\partial U/\partial P)_T$ of a gas (chap. 5), reversible change of volume of a gas (chap. 7), and the measurement of latent heat of vaporization (chap. 11) to cite a few. By the discussion of experimental methods and the inclusion of experimental data in some figures, I believe the authors are attempting to impress on the student the physical significance of the quantities which are later used in the solution of problems. This is a part of education which is apparently being phased out in the fundamental sciences and mathematics.

Looking at the other side of the coin, the missing material, the chemical engineer will note that “fugacity” is not mentioned. The theorem of correspondence states is introduced and used only in one problem—11.1. Also, only mixtures of ideal gases are considered. Nothing is included on heats of solution, or properties of real mixtures, and very little on thermochemistry. Also, the development and use of the humidity



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chart and calculation of dewpoints and bubblepoints using Raoult's law—topics common to practically all initial chemical engineering courses—are not considered.

Undoubtedly, many mechanical engineers reviewing this book would find that some of their favorite topics have been omitted or treated with brevity and, conversely, some topics have been covered more extensively than is usually the case.

The book is well written and the level of mathematics—some partial differential equations are used—such that the second year, or certainly the first semester third year, student should have no trouble. If a student cannot learn the the principles of thermodynamics from this book, it should certainly not be due to the mathematics used. Each chapter is concluded with a number of problems which appear to offer the user a reasonable choice; i.e. some difficult ones and some not so difficult. Apparently, the problems were selected so a slide rule is the only type of computer necessary.

The usage of this book by chemical engineers depends upon how our programs develop over the next few years. If we move to more common core courses—and thermodynamics is one of the prime areas where such movement is possible—this book "Engineering Thermodynamics," should be seriously considered for use.

James H. Weber
University of Nebraska

ChE problems for teachers

The following solutions to thermodynamics problems published in CEE Spring quarter, pp. 95-96, 1968, were prepared by Professors R. K. Irey and J. H. Pohl at the University of Florida. We continue to solicit questions on subjects of general engineering or scientific interest to be presented in this department.

1. (a) Consider u as $u(s, x_i)$,

$$du = \left(\frac{\partial u}{\partial s}\right)_{\vec{x}_i} ds + \sum_{j=1}^N \left(\frac{\partial u}{\partial \vec{x}_j}\right)_{s, \vec{x}_i} \cdot d\vec{x}_j$$

By analogy with

$$du = Tds - \sum_{j=1}^N \vec{F}_j \cdot d\vec{x}_j$$

$$\left(\frac{\partial u}{\partial s}\right)_{\vec{x}_i} = T \quad \text{and} \quad \left(\frac{\partial u}{\partial \vec{x}_j}\right)_{s, \vec{x}_i} = -\vec{F}_j, \quad (N+1 \text{ eqs.})$$

- (b) The Maxwell relations are

$$\left(\frac{\partial T}{\partial \vec{x}_j}\right)_{s, \vec{x}_i} = -\left(\frac{\partial \vec{F}_j}{\partial s}\right)_{\vec{x}_i, \vec{x}_i}$$

$$\left(\frac{\partial \vec{F}_j}{\partial \vec{x}_i}\right)_{s, \vec{x}_i} = \left(\frac{\partial \vec{F}_i}{\partial \vec{x}_j}\right)_{s, \vec{x}_j}$$

- (c) i) $N+1$, for a total of $4(N+1)$ eqs.
ii) $\frac{3N(N+1)}{2}$, for a total of $2N(N+1)$ eqs.
iii) Take the derivative of Ψ_q and substitute du into the equation

$$d\Psi_q = -sdT - \sum_{j=1}^N \vec{F}_j \cdot d\vec{x}_j$$

Consider the total derivative of $\Psi_q = \Psi_q(T, \vec{x}_i)$, $i=1, \dots, N$.

$$d\Psi_q = \left(\frac{\partial \Psi_q}{\partial T}\right)_{\vec{x}_i} dT + \sum_{j=1}^N \left(\frac{\partial \Psi_q}{\partial \vec{x}_j}\right)_{T, \vec{x}_i} \cdot d\vec{x}_j$$

$$\text{thus, } \left(\frac{\partial \Psi_q}{\partial T}\right)_{\vec{x}_i} = -s \quad \text{and} \quad \left(\frac{\partial \Psi_q}{\partial \vec{x}_j}\right)_{T, \vec{x}_i} = -\vec{F}_j$$

$$\text{Since } \frac{\partial^2 \Psi_q}{\partial T \partial \vec{x}_j} = \frac{\partial^2 \Psi_q}{\partial \vec{x}_j \partial T}$$

$$\text{we have } \left(\frac{\partial \vec{F}_j}{\partial T}\right)_{\vec{x}_i, \vec{x}_i} = \left(\frac{\partial s}{\partial \vec{x}_j}\right)_{T, \vec{x}_i}$$

2. (a) Consider $s = s(T, \vec{x}_i)$ and $s = s(T, \vec{F}_i)$.

Then

$$ds = \left(\frac{\partial s}{\partial T}\right)_{\vec{x}_i} dT + \sum_{j=1}^N \left(\frac{\partial s}{\partial \vec{x}_j}\right)_{T, \vec{x}_i} \cdot d\vec{x}_j \quad (i)$$

and

$$ds = \left(\frac{\partial s}{\partial T}\right)_{\vec{F}_i} dT + \sum_{j=1}^N \left(\frac{\partial s}{\partial \vec{F}_j}\right)_{T, \vec{F}_i} \cdot d\vec{F}_j \quad (ii)$$

$$C_{\vec{F}_i} = \left(\frac{\partial \Psi_q}{\partial T}\right)_{\vec{F}_i} = T \left(\frac{\partial s}{\partial T}\right)_{\vec{F}_i} \quad \text{and}$$

$$C_{\vec{x}_i} = \left(\frac{\partial u}{\partial T}\right)_{\vec{x}_i} = T \left(\frac{\partial s}{\partial T}\right)_{\vec{x}_i} \quad (iii)$$

Use the Maxwell relations,

$$\left(\frac{\partial s}{\partial \vec{x}_j}\right)_{\vec{x}_i, \vec{x}_j} = \left(\frac{\partial \vec{F}_j}{\partial T}\right)_{\vec{x}_i, \vec{x}_j} \quad \text{AND} \quad \left(\frac{\partial s}{\partial \vec{F}_j}\right)_{T, \vec{F}_i} = -\left(\frac{\partial \vec{x}_j}{\partial T}\right)_{\vec{F}_i, \vec{F}_j}$$

and the relations (iii) in (i) and (ii). Then set the right of (ii) equal to the right of (i).

$$C_{\vec{F}_i} - C_{\vec{x}_i} = T \left\{ \sum_{j=1}^N \left(\frac{\partial \vec{F}_j}{\partial T}\right)_{\vec{x}_i, \vec{x}_j} \cdot \frac{d\vec{x}_j}{dT} + \sum_{j=1}^N \left(\frac{\partial \vec{x}_j}{\partial T}\right)_{\vec{F}_i, \vec{F}_j} \cdot \frac{d\vec{F}_j}{dT} \right\}$$

If \vec{F}_j is constant,

$$C_{\vec{F}_i} - C_{\vec{x}_i} = T \sum_{j=1}^N \left(\frac{\partial \vec{F}_j}{\partial T}\right)_{\vec{x}_i, \vec{x}_j} \cdot \left(\frac{\partial \vec{x}_j}{\partial T}\right)_{\vec{F}_i, \vec{F}_j}$$

If \vec{x}_j is constant, the result is the same.

- (b) From (i) above

$$ds = \left(\frac{C_{\vec{x}_i}}{T}\right) dT + \sum_{j=1}^N \left(\frac{\partial \vec{F}_j}{\partial T}\right)_{\vec{x}_i, \vec{x}_j} \cdot d\vec{x}_j$$

From the exactness of this equation

$$\left(\frac{\partial C_{\vec{x}_i}}{\partial \vec{x}_j}\right)_{T, \vec{x}_i} = T \left(\frac{\partial^2 \vec{F}_j}{\partial T^2}\right)_{\vec{x}_i, \vec{x}_j}$$

Hold T constant in this equation and integrate with respect to all \vec{x}_j . The lower limit is a reference value, $C_{\vec{x}_i}^*$. The upper limit is variable.

$$C_{\vec{x}_j} - C_{\vec{x}_i}^* = T \sum_{j=1}^N \int_{\vec{x}_i^*}^{\vec{x}_j} \left(\frac{\partial^2 \vec{F}_j}{\partial T^2}\right)_{\vec{x}_i, \vec{x}_j} \cdot d\vec{x}_j$$

would you like to write “The Formation of Perhydrophenalenes and Polyalkyladamantanes by Isomerization of Tricyclic Perhydroaromatics?”



How's that again? Well, never mind —Bob Warren, Ed Janoski, and Abe Schneider already wrote it. They're chemists in Sun Oil Company's Research and Development Department. Their paper is just one of many resulting from imaginative and original basic research conducted at Sun Oil.

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CHEMICAL ENGINEERING EDUCATION

THERMODYNAMICS: DEATH AND TRANSFIGURATION

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In a recent article¹ I criticized vehemently present approaches to the teaching of thermodynamics. In particular, I argued that thermodynamics at present is based on mysticism and magic when dealing with the fundamental concepts such as temperature, energy, and entropy. I argued that what was needed was a rational approach to the development of concepts and their application to chemical engineering and that, for the non-thermodynamicist, in particular, thermodynamics *should* be viewed as a handmaiden to the major chemical engineering areas such as kinetics, process design and control, and transport mechanics.

In this paper, then, I offer a program which attempts to prepare the graduate engineer for a career in which thermodynamics plays an important, *but not dominant*, role. While this program also has limitation, I should hasten to point out that it has been used successfully at Ohio University on a first-semester graduate level for some time.

Statistical or Mechanical Approach?

As I pointed out in the earlier paper, I consider that the fundamental concepts of thermodynamics are three in number:

1. The concept of temperature
2. The concept of energy
3. The concept of entropy

Traditionally, there are two major ways of introducing these concepts:

1. The intuitive approach, sometimes referred to as a phenomenological approach, in which, for example, the concept of temperature is regarded as a primitive concept, like force and displacement, and therefore, **not** requiring definition, merely illustration.

2. The statistical approach, in which it is necessary to identify a constraint in the system of describing equations

*A biography of Dr. Throne is available in CEE 2, 92, 1968.

with one of the concepts. The describing equations may deal with energy in kinetic form (classical approach), or quantum form, or even level of information form (Tribus).

As I stated earlier, probably the only time the statistical approach is applied in traditional graduate level chemical engineering first courses is in shoring up otherwise weak and faltering developments of the concept of entropy. It is apparent that if the proper approach to the development of the concept of entropy is employed, no shoring up is needed and, hence introduction of statistical concepts into a first course is not needed!

Traditionally, the intuitive approach to chemical engineering thermodynamics has been "moleculeless mechanical thermodynamics," with emphasis on steady-state operations of system containing continua of material. To say that this approach represents a crazy-quilt of sterile applications of sound principles of mathematics and classical physics and empirical rules-of-thumb so typical of chemical engineering in the thirties would undoubtedly insult many so-called chemical engineering thermodynamicists. In this program, I attempt to establish a firm, rational basis for the determination of a working program (no pun intended). I emphasize establishment of rigorous axioms on which we can evaluate the empirical concepts presently in vogue in the literature.² Undoubtedly, I cannot hope to prescribe a single remedy that will cure the multiple ills plaguing authors of articles and textbooks in one, introductory course. It is my primary goal to make the average graduate student *aware* of the maladies, so that he can intelligently evaluate work in his chosen field of endeavor.

Our Program: Goals and Gaols*

We begin the course by reviewing the fundamental laws of thermodynamics as primitive concepts, requiring no definition. We then construct concepts total and path differentiation from a mathematical viewpoint. Concepts such as work

*The texts we have been using, along with the supporting reference material, are listed in Table 1.

introduced *in metric form* as being the result of relationships between generalized forces and differential displacements.** The close relationship between fluid mechanical systems and thermodynamic systems is then discussed, and the generalized concepts of enthalpy and heat capacities (in terms of generalized forces and displacements) are developed, with specific examples in linear extension, surface extension, and pressure-volume. The theorems of Caratheodory, Pfaff, inaccessible states, and mathematical development of constitutive equations for entropy, reversible heat and temperature are developed. Shaw's method of Jacobian of Transformation⁵ and the development of Maxwell's equations are presented, with extension of Shaw's method to multi-component systems. These equations are then applied to the generation of equation such as the Gibbs-Duhem Equation.

Partial molar properties, multicomponent systems, and the natural appearance of the chemical potential are presented. With special emphasis on gases, rules for the development and evaluation of constitutive equations are presented, along with fugacity and perfect mixtures of perfect and nonideal gases. It is emphasized that fugacity *is* the true thermodynamic pressure. The role and limitation of chemical potential, the phase rule, and degrees of freedom are then developed.

We then consider first and higher order phase transitions, developments of Clapeyron and Ehrenfest equations from direct integration of Maxwell's equations and from L'Hopital's rule, and their physical implications in single component and multicomponent systems.

We then expend considerable effort in applying the Gibbs-Duhem equation to the selection of constitutive relationships between partial pressure, composition and temperature, emphasizing Raoult's law of ideal systems, Henry's law of equations. It is important to note here that we emphasize the approximate empirical nature of these constitutive equations; we *do not* let these equations live by themselves, as it were.

Application of constitutive equations to engineering systems such as heat of mixing and volume change, depression of freezing point, os-

**It is important to note that standard approaches to work utilize affine coordinates. While developments of concepts in affine coordinates are satisfactory for explicit problem-solving, development of general concepts, particularly when thermodynamics is used in transport mechanics, must be made in metric coordinates.^{3,4}

TABLE I.

Books Used in First Course in Graduate Thermodynamics

Required Texts:

1. Denbigh, K. G. The Principles of Chemical Equilibrium, 2nd Ed., Cambridge 1966.
2. Tribus, M., Thermostatistics and Thermodynamics, D. Van Nostrand, Co., 1961.

Recommended Reading Reference:

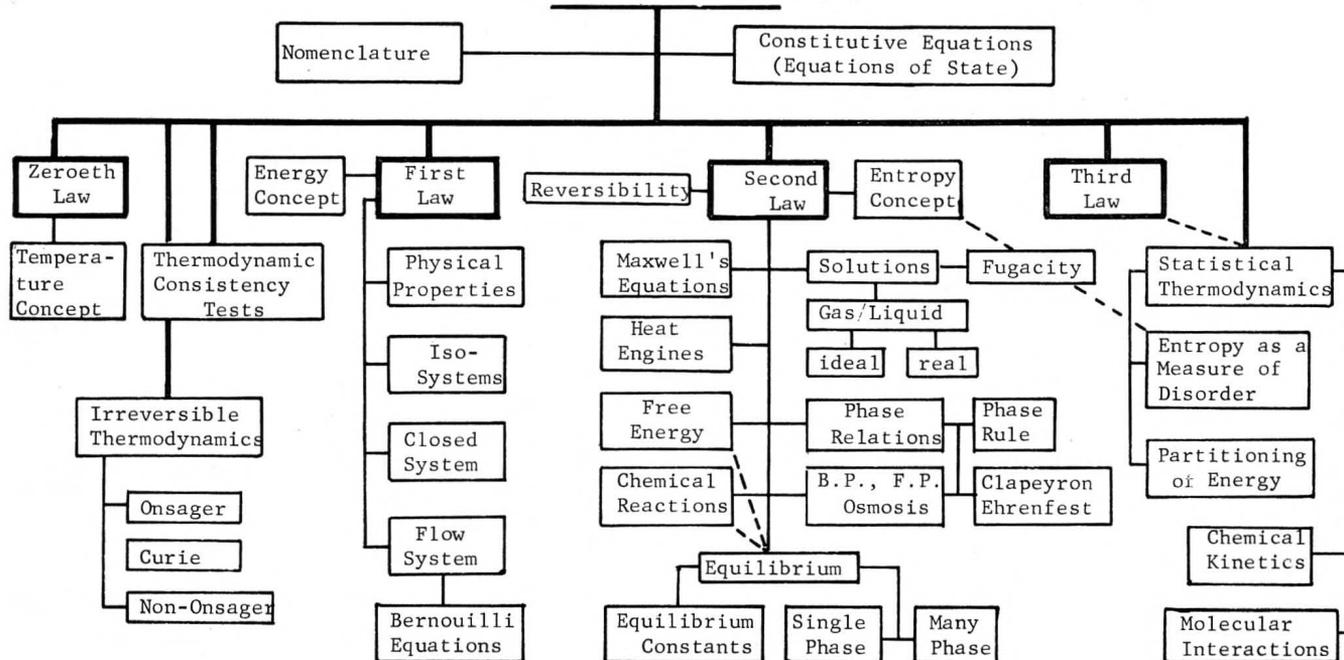
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otic pressure, and such, follow. Thermodynamic consistency tests and their relative reliability are stressed.

Finally, we introduce concepts of thermodynamics of the steady state, dealing with the concept of entropy production and the phenomenological coupling tensor between fluxes and forces. We discuss "Curie's theorem" and its logical basis as a fundamental theorem of tensor calculus,⁶ and the faults of the present state of irreversible thermodynamics (linear "Onsagerist" approach) and its future role in thermodynamics. We conclude by examining real engineering examples of steady-state thermodynamics in coupled systems such as heat-mass transfer, kinetics-fluid flow, and fuel cell technology.

To implement the development of the course, I present, in flow diagram form, apparent interactions in the major areas of thermodynamics. This diagram is shown below. While I do not pretend to imply that this flow diagram is wholly correct or complete, it does serve graphically to illustrate chemical engineering thermodynamics.

T H E R M O D Y N A M I C S



Thermodynamics: Who Cares?

First, it is important that the above program makes no mention of cycles, refrigerators, engines, TS diagrams, Mollier Charts, compressibility curves, etc. This is done deliberately. Emphasis is placed on understanding of underlying mathematical, mechanical, chemical, and physical principles. Interrelationships between thermodynamics, kinetics, and mechanics are continually emphasized and illustrated through engineering examples. Why? It is my belief that rational understanding of the role of thermodynamics in the overall concept of chemical engineering comes, *not* from the ability of the student to calculate coefficients in equations of state—given critical properties, *but* from his ability to understand the usefulness and limitations of the present concepts of thermodynamics. It is his ability to intelligently and rationally question existing practices, *not* blindly calculate and manipulate empirical equations, that will make him a valuable member of the chemical engineering community.

Conclusion

Classical thermodynamicists with their minds intently focussed on new P-V-T correlations or n-th degree refinement in the current Mollier diagram for steam or ammonia, are being by-passed and circumvented by people who *need* to answer thermodynamic questions dealing with biological

metabolism, kidney or fuel cell operation, kinetic-fluid flow interaction, cyclic operation of non-ideal transport systems, thermomechanical foundations of nonlinear viscoelastic media, nonFickian diffusion, sewage disposal and anti-pollution systems. We cannot afford to ignore the challenge of modern chemical engineering by offering material that was designed to support chemical engineering Edisonianism of the 30's.

It is my opinion, then, that Dr. Bates' approach ("First Aid to Ailing Thermodynamics") will eventually lead to the death of thermodynamics as it is traditionally taught. To this, I say, good riddance. For, like the Phoenix of Egyptian mythology, from its ashes shall rise anew a thermodynamics founded on the rational principles of Gibbsian mechanics.

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WHERE ARE THE ENGINEERS?*

T. B. METCALFE

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In spite of our usual confident reliance upon the balance between supply and demand, the relationship between the output of our engineering colleges and the need for practicing engineers does not seem to be following the rule. All of the factors which we would expect to contribute to a great demand for engineers seem to be present. Engineering employment has reached new highs and graduating students of engineering colleges are offered a half dozen or more jobs upon graduation. There are complaints from many potential employers that they are unable to fill their quotas. Indeed, the meteoric rise in the employment of technicians in the engineering field, while largely due to a heretofore unfilled need for this kind of service, is also greatly influenced by the unavailability of young engineers.

Incentives are certainly present in the current situation. The satisfaction to the individual of making a contribution to technical advancement has never been greater and recognition on the part of the general public of the contribution of engineers is well established. Salaries and other remuneration for engineers are at new peaks, higher than those for most other career professionals, at least in the years immediately following graduation. Engineering starting salaries are increasing and at a rate higher than the rate of increase for other professionals.

Thus, the high and unsatisfied demand seems to have created the expected result of increased incentives for the study of engineering. Why then, should there be any shortage of engineers? Many contend that there is no shortage, or rather, they cite statistics to show that there is a consistent increase in the number who choose to study engineering. They conclude that we should not fear a shortage as long as the trends continue.

A comprehensive study published in the January, 1966 *Journal of the American Society for Engineering Education*, by the ECAC (committee for analysis of engineering enrollment) presented data in total engineering enrollments between 1949 and 1962. They note the large contribution of veterans under the government educational

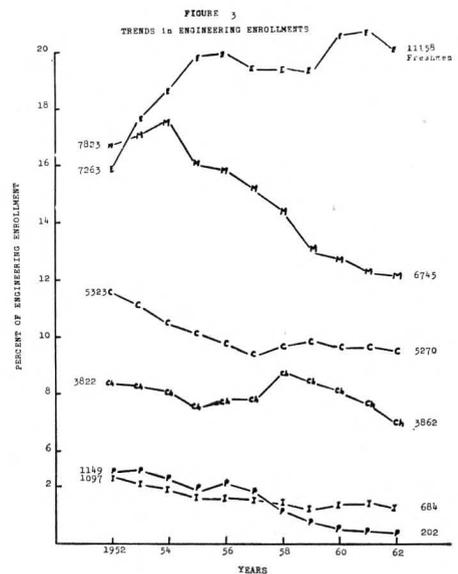
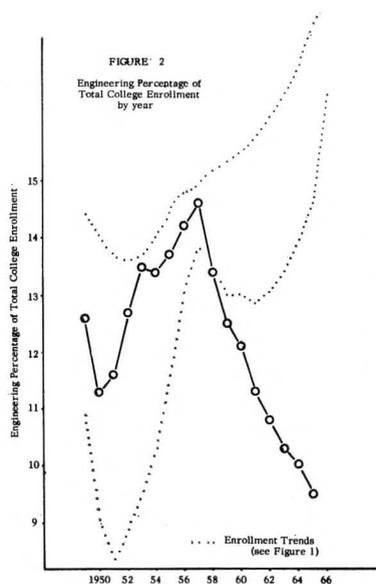
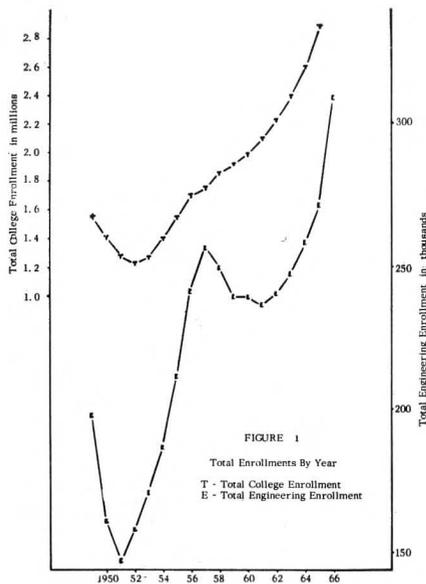
*Presented to the Spring Meeting of the Gulf-Southwest Section ASEE, College Station, Texas, 21 March 1968.



Dr. T. B. Metcalfe is Head of the Department of Chemical Engineering at the University of Southwestern Louisiana. His background and experience includes degrees from Georgia Institute of Technology and the University of Texas; faculty positions at West Virginia Institute of Technology and the University of Houston; and professional experience with Shell Oil Company, U. S. Naval Reserve (WW II) and Dow Chemical Company.

programs who swelled the enrollment in the years immediately following World War II and also during 1954-56 subsequent to the Korean military involvement. This analysis illustrated that if the enrollment of veterans was not included in the totals, the fluctuations in enrollment of engineering students are much reduced and a definite and consistent trend was evident. It was concluded that the apparent appreciation in engineering enrollments of about 13,500 each year (during the entire thirteen-year period covered) might be confidently extrapolated for another few years.

It becomes the responsibility of engineering educators to perceive the changes in trends, and to exert the necessary influence to reverse undesirable ones. Two conditions which contribute markedly to the rate of output of engineers are (1) the number of entering college students choosing engineering as a career and (2) the retention of those students through graduation from engineering college. The desirability of, and the incentive to, study engineering must be communicated to the high school and junior high school public (student, parent, and counselor). Depending upon the success of this contact, more (or fewer) students may choose the profession of engineering. The statistics upon which Figure 1 is based illustrate that in the years 1949 to 1952 there was indeed a marked decrease in the total enrollment in universities in our country. This was undoubtedly due both to the then declining number of World War II veterans enrolling and the decrease in the enrollment of younger men



students due to the Korean involvement. Subsequent to that period, however, from 1952 to the present no disregard of veterans or any other group is necessary to allow the recognition of a consistent, rapidly upward trend in the total enrollment of college men students in our colleges and universities. Comparison of trends in the total college enrollment and in engineering enrollments show the same fluctuations, with variations in the trend for the most part occurring at the same times. However, the variations are greater in the case of the engineering enrollment and the ECAC prediction of an appreciation of 13,500 each year has been exceeded considerably each of the last 4 years, with an ever increasing rate. A significant difference in total enrollment and engineering enrollment is the occurrence of a peak in engineering enrollment in 1957 and a subsequent four-year decline in that enrollment, during which four years, the rise in total college enrollment slowed only slightly.

In 1961, while total college enrollments continued to climb (due, no doubt, to the coming of college age of the unusually large number of post-war babies), engineering enrollments began again to rise. Each year since, the rise has been at a larger rate.

Since our analysis of incentives has been discussed earlier in terms of comparison to other professions and careers, it is logical to evaluate the trends in engineering enrollments in terms of comparison to the overall enrollment. The significance of the 1957 reversal in the upward trend of engineering enrollments is clarified by the curve of Figure 2 which represents the fraction

of total enrollment represented by engineers. The percentage of engineers in the total college population reached a peak in 1957 after having risen consistently during the post-Korean period. Subsequent to 1957, this percentage has persistently dropped, until at the present time, it is little more than half of the 1957 value of nearly 15 per cent.

This is taken to be a clear indication of a serious and dangerous lack of rapport with the potential college student on the part of engineering educators. There is small comfort in the existence of an upward trend in engineering enrollments in view of the fact that the shortage of engineers is not being relieved and the increase in engineering enrollments falls so far short of the increase in total college enrollment.

To be most meaningful the statistics must be expressed in terms of the various disciplines. The classical disciplines of Chemical, Civil, Electrical, and Mechanical Engineering account for about half of all engineering students. Industrial and Petroleum Engineering are the only other disciplines with appreciable fractions of total engineering enrollments. In 1952, there were in ECPD accredited departments 3,822 entering freshmen students who wished to study Chemical Engineering, and in 1962, at the end of the reporting by ASEE, there were 3,862, an only slightly larger number (see Figure 3). Reflecting the difference in total engineering enrollments at the start and at the end of this period, the nearly equal numbers of students in Chemical Engineering represented 8 per cent (of total engineering enrollment) in 1952 and hardly more than 7 per cent in 1962. Thus, while maintaining the num-

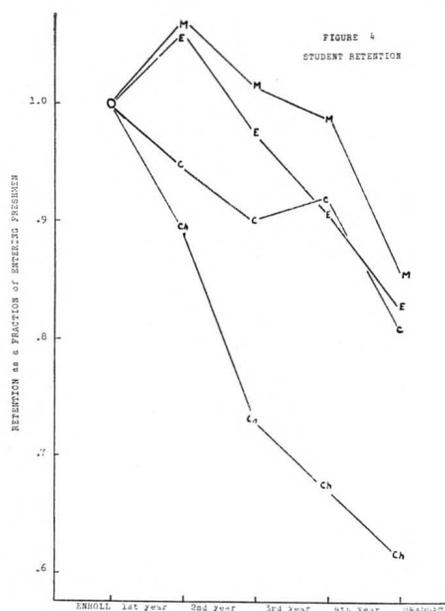
ber of its students, Chemical Engineering has declined slightly in public acceptance as an engineering discipline.

By comparison, and considering the absolute numbers for the beginning and end of the ten-year span as well as the trends, it is evident from the curves (Figure 3) that enrollments in Civil Engineering have dropped slightly, while their percentage has dropped from $11\frac{1}{2}$ to $9\frac{1}{2}$ per cent. There has been a more marked drop in the number of Mechanical Engineers and their percentage is down from 17 to 12 per cent of the total. Both Industrial and Petroleum Engineering disciplines have shown large decreases in the number of students and in their fraction of the total engineering enrollment during this period. Only Electrical Engineering has shown a marked increase in number of students. This has resulted in an increase in its fraction of the total from 16 to 20 per cent.

It becomes evident that the classical disciplines are not generally increasing in spite of the marked increase in total engineering enrollments. The increase is distributed among the newer disciplines, each representing smaller numbers of engineering students. These newer disciplines, while offshoots of the classical disciplines, have completely divorced themselves from the parent departments except in the case of Electrical Engineering. The growth of the Electrical Engineering discipline can be attributed to their absorption of a number of new interests such as Electronics and Communications.

This action on the part of Electrical Engineers to retain within a single discipline the widely varied interests which represent different applications of the same engineering principles is considered a wise one and one which should be emulated by other disciplines. New branches of engineering often are created because of the recognition on the part of their practitioners that their interests stem from more than one of the classical disciplines, and therefore, they consider themselves separate from both. Preferable to this proliferation of engineering disciplines would be an interdisciplinary interest on the part of the parent disciplines. This would tend to unify and strengthen engineering instead of weakening it as does the current practice of splintering.

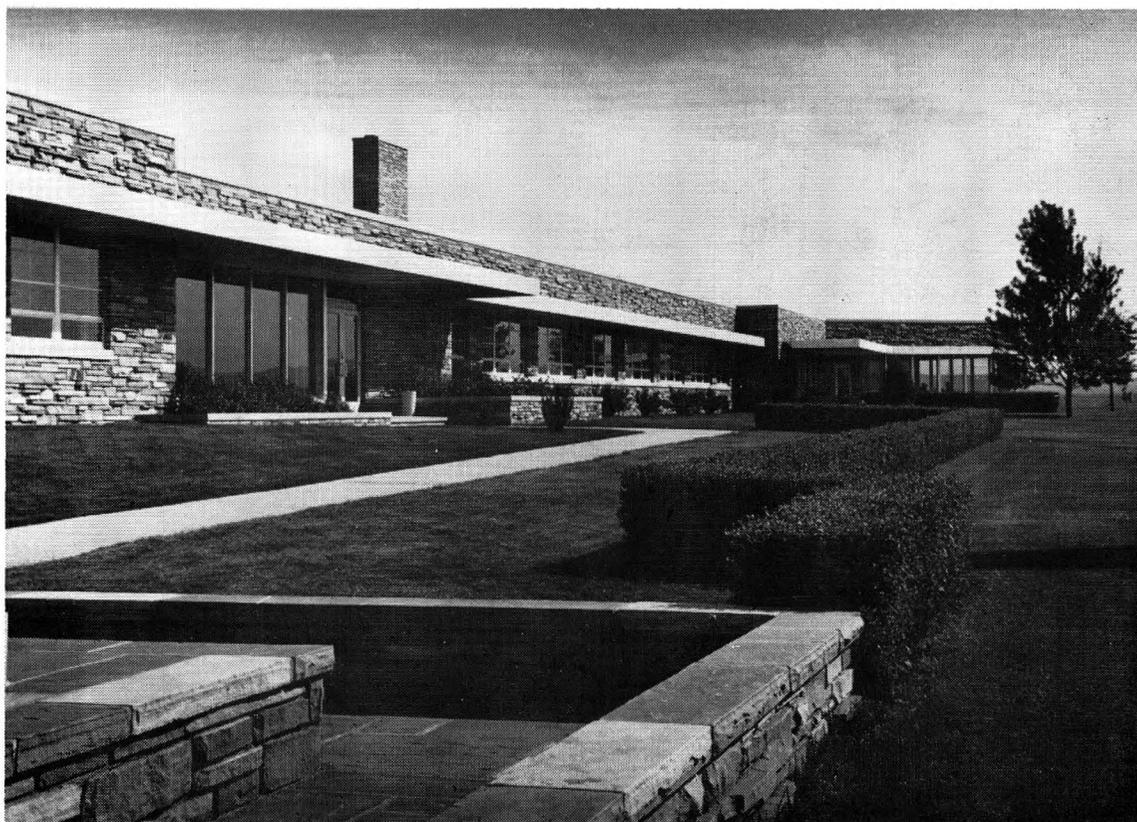
Having determined the total enrollments as the potential with which we have to work, it is now interesting to observe the retention of this group of students. Over a ten-year period, the average retention for Chemical Engineering



(Figure 4) shows that after the first year the number of students enrolled for their second year is only 90 per cent, and those persisting to the third year only 73 per cent of the entering freshmen. Sixty-seven per cent persisted to their fourth year, and finally 61 per cent were graduated with the B.S. degree after four years. In Civil Engineering, 5 per cent were lost in the first year, with 95 per cent remaining; 90 per cent remained for their third year and a slight appreciation then resulted in the fourth year class of 92 per cent of their entering freshmen. At the end of four years, 80 per cent of the entering Civil Engineering classes were graduated. Mechanical and Electrical Engineering appreciated 6 and 7 per cent, respectively, in the second year after which their number declined so that Mechanical Engineering Departments graduated 85 per cent of their entering freshmen and Electrical Engineering, 83 per cent. Thus, among these disciplines only Chemical Engineering shows no increase at any level during the college career. Rather, the number dropping out of Chemical Engineering during each year is significant.

We can conclude that engineering educators must face up to the fact of a declining acceptance of engineering as a course of study by college students. Instead of fatalistic acceptance, we must strive to reverse this trend and provide greater numbers of graduated professionals by stronger recruitment of high school and junior college graduates and by greater retention of entering students who choose an engineering course of study.

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