ChE laboratory

ON THE APPLICATION OF SIMPLE EXPERIMENTS TO THE TEACHING OF ChE THERMODYNAMICS

KENNETH M. McNEIL
Drexel University
Philadelphia, Pennsylvania 19104

HISTORICALLY, THERMODYNAMICS has been considered one of the most elegant but abstract branches of physico-chemical science. Its fundamental importance in engineering requires that it be taught both at the undergraduate and graduate levels. For that reason, however, it is one of the most difficult subjects to teach effectively. At Drexel University, the undergraduate chemical engineering student is initially exposed to thermodynamics in the common basic thermodynamics course taken by all engineering sophomores, which provides an introduction to the first and second laws, heat engine cycles, and ideal gas relationships. Concurrently, an elementary treatment of thermochemistry, energy balances, and thermodynamic properties is given in the material balances course. Instruction continues in the ChE Thermodynamics course, taken in the second quarter of the sophomore year. Finally, some aspects of statistical thermodynamics are covered in physical chemistry, taken in the second quarter of the pre-junior year. (At Drexel, the B.S. degree requires five years due to the cooperative education program; of the twelve quarters required, three each are attended in the freshman and senior years, two each in the sophomore, pre-junior, and junior years. The student also works in a suitable technical position in industry for six months in each of the three middle years.)

The addition of a series of simple experiments to an established lecture course is a concept novel to ChE curriculum at Drexel University.

Present address: 4000 Gypsy Lane, Philadelphia, Pa 19144

The ChE Thermodynamics course consists of 4 credit hours devoted to such traditional classroom activities as lectures and problem-solving, and a 1-credit hour (2 contact hours) laboratory which was initiated in 1971. The main objective of the overall course is to equip the student with a basic working knowledge of the concepts and practical applications of ChE thermodynamics, thereby also providing an adequate foundation for subsequent undergraduate courses in kinetics and reactor design, transport phenomena, unit operations, and process design, and for graduate courses in thermodynamics and kinetics. The principal purpose of the laboratory is to enhance the students' understanding of an other wise abstract subject; instructional objectives are discussed more fully in the next section.

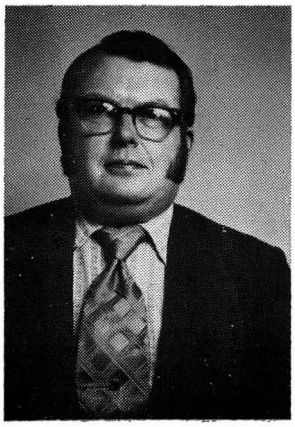
TABLE 1. Lecture Topics

First and Second Laws of Thermodynamics (review)
Thermodynamic analysis of processes
Pressure-volume-temperature relationships for real fluids
Thermodynamic properties of real fluids
Thermodynamics of incompressible and compressible fluid flow
Phase equilibria in pure and multicomponent systems
Chemical-reaction equilibria (homogeneous systems)

The topics covered in the lectures are stated in Table 1. The textbook currently used is by Smith and Van Ness [1].

INSTRUCTIONAL OBJECTIVES OF LABORATORY

THE PRIMARY OBJECTIVE of augmenting the lectures with a series of short laboratory



Kenneth M. McNeil, a consulting chemical engineer, was Assistant Professor of ChE at Drexel University from 1970 to 1976. He is presently Coordinator of the ChE Review course for the P.E. examination. After receiving a B.Sc. from the University of Edinburgh (1962), he studied under Prof. P. V. Danckwerts at the University of Cambridge (Ph.D., 1965). Between 1965 and 1970, he was on the staff of the R. & D. Department of Amoco Chemicals Corp. He is a registered Professional Engineer (Pa.), and is a member of AIChE, ACS, I. Chem. E., and Sigma Xi.

experiments was to improve the pedagogical effectiveness of the course. Thermodynamics is one of the more difficult courses conceptually, but is relatively straightforward (at this level) both mathematically and computationally. Whereas numerous worked examples and homework problems contribute significantly to the learning process, they are of little help in conveying a sense of reality to the student. The experiments fill this void, at the same time exciting curiosity and interest.

The laboratory has several further instructional objectives. It provides an introduction to simple measurements, in particular thermocouple thermometry and differential-pressure flow measurement. This serves as a valuable preparation for subsequent laboratory courses, which include transport phenomena, unit operations, and process control.

In this course, the students receive their first experience in the planning of experiments, the analysis of data, and report writing, albeit at an elementary level. This, too, is helpful preparation for subsequent laboratory courses, in which considerably more detail is required.

The class is divided into several groups which retain their identity throughout the course. Each group consists preferably of three students, one of whom is appointed group leader for a particular experiment; each student acts as group leader for at least two experiments. The course thus exposes the students to the interpersonal relationships involved in group work, from the viewpoint of both the group leader and the team member.

EXPERIMENT DESCRIPTIONS

THERE IS ONE experiment corresponding to each major lecture topic, as listed in Table 2. There follow brief descriptions of the experiments, with comments on typical results that have been obtained.

TABLE 2. List of Experiments (with Corresponding Lecture Topics)

EXPERIMENT	LECTURE TOPIC
Flow Calorimeter	First Law
Hilsch Vortex Tube	First and Second Laws
Refrigeration Cycle*	Thermodynamic analysis
P-V-T Behavior of CO_2	P-V-T relationships
Throttling Calorimeter	Thermodynamic properties
Maximum Flow in Nozzle	Thermodynamics of fluid flow
Triple Point of Nitrogen	Phase equilibria
Ethanol-Acetic Acid-Ethyl Equilibrium	Chemical equilibria

*Planned

Flow Calorimeter. The equipment consists of a simple calorimeter incorporating an electrical resistance which enables electrical energy to be converted to heat and dissipated in the liquid stream. The liquid (water) is fed to the calorimeter at a constant rate from a header tank, in which the level is maintained manually. The flowrate is determined by measuring the volume of effluent in a given time interval, and the inlet and outlet temperatures are measured with mercury-in-glass thermometers (Fig. 1). By comparing the input

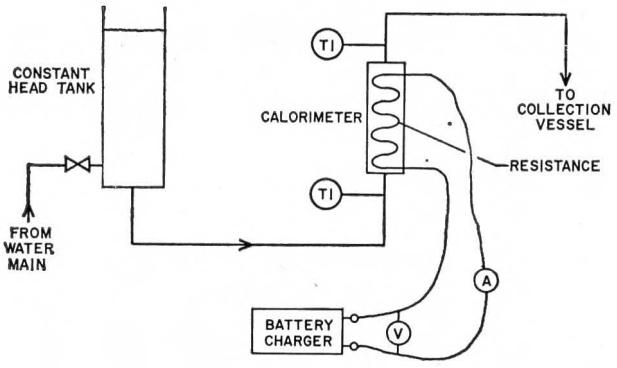


FIGURE 1
FLOW CALORIMETER

of electrical energy to the increase in enthalpy of the water, the electrical equivalent of heat can be calculated. Reasonably accurate results for this relatively crude device have been obtained by the more careful students (within 10% of the correct value).

Hilsch Vortex Tube. In this apparatus, high-pressure air is led tangentially into a tube (constructed of Plexiglas) where it expands, giving rise to a high-speed circumferential motion. As a result of this expansion, the air as a whole gains kinetic energy at the expense of its internal energy, and the temperature therefore falls. The air near the axis is withdrawn in an axial direction. It has relatively low kinetic energy (the angular velocity does not vary greatly with radial position, and the tangential velocity near the axis is therefore low), and thus remains cooler than the inlet air. The air near to the tube wall, on the other hand, has a high tangential velocity and hence kinetic energy. This air is withdrawn in the opposite axial direction. As it passes down the tube, most of the kinetic energy is dissipated by turbulent mixing and the internal energy consequently increases. The temperature of this stream becomes higher than the inlet air, as nearly all the internal energy initially converted to kinetic energy reappears as internal energy in only this part of the original stream.

The apparatus, which is illustrated in Fig. 2, is provided with means of measuring the temperatures and pressures of all three air streams, and the flow-rates of the hot and cold effluent streams. From these data, entropy and enthalpy balances

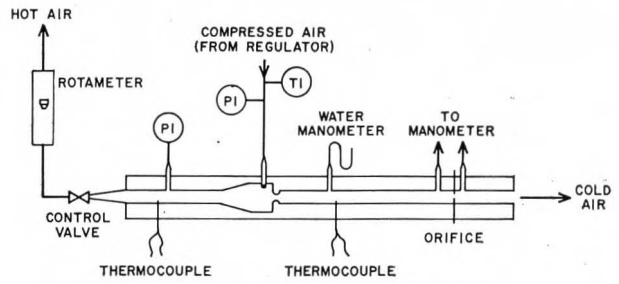


FIGURE 2
HILSCH VORTEX TUBE

can be carried out over the vortex tube. The experiment has been successful in demonstrating the applicability of the entropy function to considerations of irreversibility, as well as giving practical experience in the construction of entropy and enthalpy balances. Furthermore, it provides an introduction to important measuring techniques: thermocouple thermometry, pressure measurement by bourdon gauge and manometer, and flow measurement by orifice meter and rotameter. Typical experimental results are presented in Table 3.

TABLE 3. Hilsch Vortex Tube: Typical Operating Conditions and Results

Inlet air, temperature	82°F
pressure	45-90 psia
Hot stream, temperature	90-97°F
pressure	20-30 psia
Cold stream, temperature	76-71°F
pressure	~ 0.5 psig
Flow ratio, hot stream: cold stream	~ 1:2
Entropy generated	2.0-3.0 Btu lb mole^{-1}°R^{-1}
Error in enthalpy balance (adiabatic conditions assumed)	-1.5 to 4.0 Btu lb mole^{-1}

Refrigeration Cycle (Planned). A standard vapor-compression refrigeration cycle, with temperature and pressure sensors before and after each major component (compressor, condenser, throttling valve, evaporator), will be used to illustrate the thermodynamic analysis of a cycle using a pressure-enthalpy diagram. A secondary objective is to determine the overall and volumetric efficiencies of the compressor.

P-V-T Behavior of Carbon Dioxide. The objectives of this experiment are to measure the P-V-T behavior of CO_2 over a wide range of pressure (50-900 psia) at room temperature, to determine how accurately the data can be fitted by a simple equation of state such as the van der Waals, and to compare the results with values predicted from a generalized compressibility-factor chart and also with published data. A lecture bottle of known volume is evacuated and weighed, and then charged with CO_2 at various pressures; the corresponding masses of CO_2 are measured by difference.

The results that have been obtained by the more meticulous experimenters agree well with published data, and also serve to exemplify the validity of the predictive methods under the range of conditions investigated. The non-ideal behavior of a real gas at elevated pressures is convincingly demonstrated.

Throttling Calorimeter. This simple device causes wet, high-pressure steam to be throttled

isenthalpically to atmospheric pressure. Provided that the high-pressure steam is not too wet, the expanded steam will be superheated. The quality of the high-pressure steam can then be determined from a Mollier diagram (or steam tables) if the line pressure and expanded steam temperature are known.

The experiment has proved valuable in illustrating the use of thermodynamic diagrams for a pure substance, and in clarifying the nature of the isenthalpic flow process.

Maximum Flow in Nozzle. In this experiment, the occurrence of a maximum mass flowrate of a gas through a converging-diverging nozzle is verified. In addition, the observed flowrate and critical throat pressure are compared with values predicted from theoretical isentropic flow equations. The equipment used is a Scott-Armfield Compressible Flow Bench, Model A.E.C.1. The pressure upstream of the nozzle is atmospheric, and a variable subatmospheric pressure on the downstream side is generated by a compressor controlled by a throttle on its discharge.

The concept of a maximum flowrate, which remains constant as the downstream pressure continues to be reduced below a certain value, is very difficult to present convincingly in a lecture. After having performed this experiment, students can hardly deny the evidence, even if they remain skeptical.

Triple Point of Nitrogen. The apparatus, illustrated in Fig. 3, consists of an unsilvered Dewar flask, which permits observation of the contents connected to a mercury manometer and vacuum pump. Temperature inside the flask is measured by a copper-constantan thermocouple, the reference junction being liquid nitrogen boiling at atmospheric pressure in a second, silvered Dewar flask.

Vapor is withdrawn continuously by the vacuum pump from the unsilvered Dewar flask, which contains boiling nitrogen. As the nitrogen is thermally insulated, vaporization causes its temperature to fall. Provided that the rate of vaporization is not too high, the vapor and liquid are approximately in equilibrium. Thus, simultaneous readings of pressure and temperature can be plotted to yield a saturated vapor pressure curve. When the pressure and temperature have been lowered sufficiently, the triple point is attained, as signified by the sudden appearance of a solid phase.

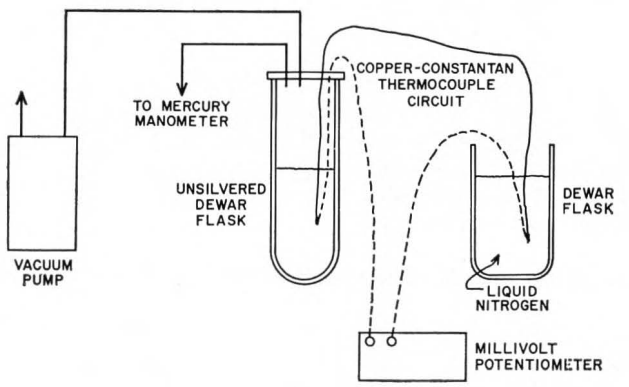


FIGURE 3
APPARATUS FOR TRIPLE POINT DETERMINATION

Results have been surprisingly good in view of the lack of experimental sophistication; values of temperature within 10%, and of pressure within 15% of their accepted values (63.2°K, 0.124 atm [2]) having been obtained by most students. Careful experimentation by the author yielded a temperature within 2% of the accepted value, and a pressure within 3%. The experiment serves both to demonstrate phase behavior of a pure substance and to provide practice in thermocouple thermometry.

Ethanol-Acetic Acid-Ethyl Acetate Equilibrium. The equilibrium

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is approached very slowly at room temperature, but can be achieved in a reasonable time in the presence of a strong acid catalyst such as hydrochloric acid. The equilibrium constant (defined in terms of mole fractions) can then be calculated from the weights of the reactants, and the total acid in the equilibrium mixture as determined by acid-base titration. The mixtures, which are stored at room temperature in small stoppered weighing

The main objective of the overall course is to equip the student with a basic working knowledge of the concepts and practical applications of ChE thermodynamics, thereby also providing an adequate foundation for subsequent undergraduate courses in kinetics and reactor design, transport phenomena, unit operations process design, and for graduate courses in thermodynamics and kinetics.

Despite these shortcomings, however, the concept of reinforcing the classroom experiences with short experiments has proved successful, and should be extended to other suitable courses in the curriculum such as transport phenomena, and chemical kinetics and reactor design.

bottles, are assumed to be equilibrated after one week.

The principal point that this experiment is intended to demonstrate is that the value of the equilibrium constant is independent of the initial and final compositions. Three different initial compositions are employed, two being ethanol and acetic acid in different proportions, the third being ester and water.

As the apparent value of the equilibrium constant is very sensitive to analytical inaccuracies [3], results of the less meticulous students have been considerably scattered. More careful experimenters have achieved remarkably consistent results. However; in the best set of results, the values ranged from 3.7 to 4.1. These results are in accord with published data, which themselves exhibit substantial scatter [3]. Disadvantages of the experiment are its relatively tedious nature (two class periods are required, cf. one period for the other experiments), and the necessity for a relatively skillful experimental technique if consistent results are to be obtained.

INSTRUCTIONAL PROCEDURES

THE LABORATORY PART of the course is introduced by means of several lectures. The first lecture consists of a general orientation, in which the course objectives, physical facilities, safety procedures, and required reports are described. This information is also supplied in a course manual, which includes general information and instructions, experimental instructions including basic references, and a detailed list of lecture topics to which the experiments correspond. In three subsequent lectures, techniques of temperature, pressure, and flow measurement are described. The students are required to augment this information with assigned readings from a reference [4].

As indicated previously, the students work in groups of three, one student being appointed group leader for the duration of the experiment, which is one class period in most cases. Assignment of group leaders is on a rotating basis within the group. Several days before the experiment is to be performed, all members of the group attend a preliminary conference with the instructor, at which the group leader presents the experimental plans, which he is responsible for developing. The preliminary conference fulfills several functions: it motivates the group leader to prepare adequately, it serves as a forum to clarify misconceptions (which are not infrequent at this early stage in the curriculum), and it enlightens the other group members. Due to the inexperience of the students, fairly close supervision is given during the actual laboratory period.

All students are required to submit a short written report of each experiment. The required format is described by the following excerpt from the instructions.

> **Introduction—State purpose of investigation, and briefly describe the appropriate theory including the principal equations and the procedure for calculating the final results from the experimentally-measured quantities.**
>
> **Experimental—Describe the equipment verbally, and by means of a sketch (which should be on a separate sheet of paper). State the variables that were measured, and the instruments used. Indicate what ranges of independent variables were studied, and the basis whereby these ranges were chosen.**
>
> **Results and Discussion—Present all final results (not raw data) in tables, graphs, or verbally depending on which method affords the greatest clarity. Include a sample calculation. All tables and figures should have a number and title. Discuss the meaning, significance and validity of the results. State possible sources of error.**
>
> **Conclusions—State concisely all significant information obtained from the experiment. Present each conclusion in a separate, numbered paragraph.**

The reports are graded; the cumulative marks count *pro rata* to the overall course grade.

CONCLUSIONS

THE ADDITION OF A series of simple experiments to an established lecture course is a concept novel to the ChE curriculum at Drexel University. In quantitative terms, there has been a

From a quantitative standpoint, there has been a most definite improvement in the students' motivation and interest.

significant upward trend in grade point average, which has recently been in the region of 2.8/4.0 compared with about 2.0/4.0 before the inception of the laboratory. This is not of course a true A-B comparison, but it is generally felt that the average ability of our students has not changed noticeably in recent years. Moreover, ten out of fourteen classes were taught by the author over a period of seven years, which included the transition from a lecture course to the combined lecture-laboratory course. Consistency in standards and grading were thus maintained.

From a qualitative standpoint, there has been a most definite improvement in the students' motivation and interest. The only complaint of substance concerns the lack of multiple set-ups, which results in students performing some of the experiments before the corresponding topics have been covered in the lectures. This situation is dictated by lack of facilities rather than pedagogical philosophy. Whereas students are obliged to study unfamiliar material by themselves, which is salutary to some extent, it would be more effective from the point of view of reinforcement, if multiple set-ups were available to permit parallel operation of the lectures and experiments.

Despite these shortcomings, however, the concept of reinforcing the classroom experience with short experiments has proved successful, and should be extended to other suitable courses in the curriculum, such as transport phenomena, and chemical kinetics and reactor design. □

ACKNOWLEDGMENTS

The author is grateful to many of his colleagues for helpful discussions and suggestions, and in particular to Professor Bernard D. Wood of Syracuse University, who designed the Vortex Tube and Triple Point experiments, and Professor C. William Savery of Drexel University, who designed the P-V-T experiment.

REFERENCES

1. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3rd edition (McGraw-Hill, New York, 1975).
2. B. R. Brown in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VIII, Supplement I, p. 37 (Wiley, New York, 1964).
3. S. Glasstone, *Textbook of Physical Chemistry*, 2nd edition, pp. 842-3 (Macmillan, London, 1956).
4. R. P. Benedict, *Fundamentals of Temperature, Pressure and Flow Measurements* (Wiley, New York, 1969).

CARNEGIE-MELLON

Continued from page 106.

well as with people in computer science, applied mathematics and operations research. Art is the Director of the DRC which currently has 17 members. As one cooperative project, they are developing the nonnumeric processing capability of computers to do design.

Prof. Powers is actively studying the use of fault trees, a technology growing out of the aerospace industry, to evaluate process safety and reliability. He is developing methods to synthesize and then analyze fault trees, given the process components and their interconnection. He and Prof. Westerberg are also developing process synthesis techniques. They work on such problems as total process flowsheet synthesis, reaction path synthesis (getting the computer to do chemistry), separation system synthesis, energy recovery network synthesis, and control system synthesis—in each case the idea is to get the computer into the act of suggesting alternative flowsheets. Prof. Westerberg is also working on advanced approaches for performing computer-aided process analysis coupled with optimization.

OVERALL IMPRESSIONS

WHILE CARNEGIE-MELLON University may not be all things to all people, the programs in the areas of Industrial Administration, Drama, Computer Science and Engineering are strong with an unusual emphasis on professionalism. The urban surroundings of Oakland—an area filled with parks, a wide selection of ethnic restaurants, the Carnegie Library and Museum, and Scaife Art Gallery—provide a pleasant setting in which to live and work. Within the Department of Chemical Engineering, the research interests of faculty are diverse, from the abstract to the practical. Although our size is expanding, personal contacts among faculty members, and between the faculty and students, are frequent and continuous. From those first impressions of 1974, as well as from my experience of living here for three years, I conclude that Carnegie-Mellon University, as well as Pittsburgh, is "someplace special." □

ChE news

Dr. Billy L. Crynes, professor of ChE at Oklahoma State University, has been approved to head OSU's School of Chemical Engineering. Crynes received his B.S. from Rose-Hulman Institute. His M.S. and his Ph.D. are from Purdue University.