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THERMODYNAMICS AND FLUID PROPERTIES

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EXCEPT IN THE MOST established industries, today's chemical engineers will undoubtedly face the problem of designing processes and sizing equipment with little or no reliable thermodynamic or physical property data. This problem will occur more frequently as chemical engineers continue to expand into emerging technologies such as biotechnology, bioprocessing, and electronic materials processing. Even in the traditional industries such as oil and coal, the need for reliable physical property information will increase as these industries strive to meet changing pollution, safety and efficiency standards.

The chemical engineering applied thermodynamics community is quite active in its attempts to "keep pace" with the increased demand for data. While data at the exact conditions of interest are obviously the most desirable, the general trend of thermodynamics research is toward theoretical or semi-theoretical models and property correlations which permit extension of the information to other conditions of temperature, pressure, and composition. A broader trend is toward models which require very limited information. For example, computer simulation and group contribution methods require a knowledge only of the molecular structure to estimate physical properties. However, the basis for reliable correlations remains the accurate measurement of thermophysical properties of interest.

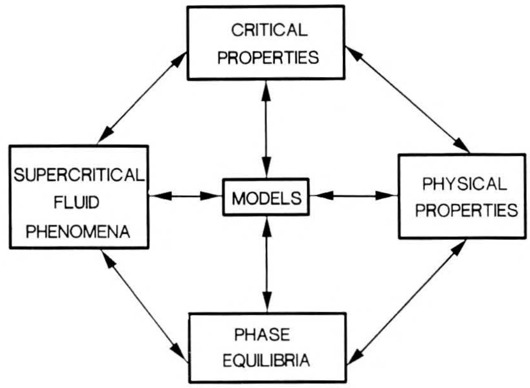

***FIGURE 1.** Interrelationships between thermophysical property research*


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Thermophysical property research at Georgia Tech has a long and distinguished history. Indeed, Professor Waldemar Ziegler was performing solubility studies using supercritical fluids [1] long before this subject became "fashionable." In general terms, our current research is concerned with the measurement, correlation, and prediction of basic properties such as phase equilibria, critical phenomena, enthalpies, specific heats, densities, viscosities, thermal conductivities, diffusion coefficients, and surface tensions. Our ultimate goal is to develop reliable predictive methods for thermophysical properties and phase equilibria and to further the understanding of the underlying molecular phenomena (Figure 1).

The members of our research group consist of the authors, two visiting professors, one post-doctoral fellow, seven graduate students, and two undergraduate students. In addition, we interact closely with research programs in the Schools of Mechanical Engineering, Chemistry, and Applied Biology. In the past four years, six masters degrees and eight PhDs have been awarded for research ranging from experimental studies of hydrocarbon solubilities in supercritical fluids to fundamental equations of state. Our research facilities include equipment for critical point studies, phase equilibrium studies (two at high pressures and one at ambient pressure), several high pressure viscometers, a transient hot-wire thermal conductivity apparatus, a drop calorimeter, two high pressure density apparatuses, and a low pressure densiometer. This equipment is summarized in Table 1. In addition, a wide range of analytical equipment (GC, HPLC, MS, and NMR) is available, as are standards (platinum resistance thermometers, dead weight gauges, *etc.*) for calibration. Our laboratories also have a dedicated microvax II workstation with plotter and laser printer and several PCs for data aquisition, analysis, and report writing. Four current research projects are described in more detail below.

TABLE 1
Experimental Thermophysical Property Capabilities at Georgia Tech

Property	Measurement Technique	Operation Ranges T (°C)	P(bar)
Critical temperature and volume	Rapid heating of a sealed ampoule	25-500	1-100
Critical temperature and pressure	Low residence time flow apparatus	5-400	1-100
Fluid-solid equilibria	Single-pass flow apparatus	-10-90	1-340
Vapor-liquid equilibria	Vapor and liquid recirculation still	25-200	1-340
Vapor-liquid equilibria	Recirculation still	25-200	0.1-2
Thermal conductivity	Transient hot wire method	25-210	1-100
Heat capacity	Adiabatic drop calorimeter	100-500	1-100
Viscosity	Capillary viscometer Rolling ball viscometer Capilary viscometers	25-1100 25-250 -10-250	1-680 1-680 1
Density	High pressure pycnometer Vibrating tube densiometer Vibrating tube densiometer	-10-300 -10-150 -10-50	1-100 1-350 1-10

While critical point measurements have been made for many stable substances, experimental data are almost non-existant for thermally unstable compounds commonly found in heavy oil processing, biochemical separations, and supercritical extraction.

CRITICAL PROPERTIES OF THERMALLY UNSTABLE AND STABLE FLUIDS

In addition to its fundamental importance in molecular theory, the critical point of a substance forms the basis for the corresponding states and equation of state calculations of thermodynamic properties and phase equilibria. A knowledge of the critical point is also required in supercritical fluid extraction, retrograde condensation, and supercritical fluid power cycles.

While critical point measurements have been made for many stable substances, experimental data are almost non-existent for thermally unstable compounds commonly found in heavy oil processing, biochemical separations, and supercritical extraction. At Georgia Tech, we have developed two methods for determining the critical properties of thermally unstable fluids. The first method involves the rapid heating in a platinum furnace of a sealed glass ampoule containing the substance. By observing the changing meniscus disappearance-reappearance phenomena characteristic of the critical point with time, and by extrapolation to a thermally stable state, the critical temperature and critical volume can be obtained (Figure 2). The

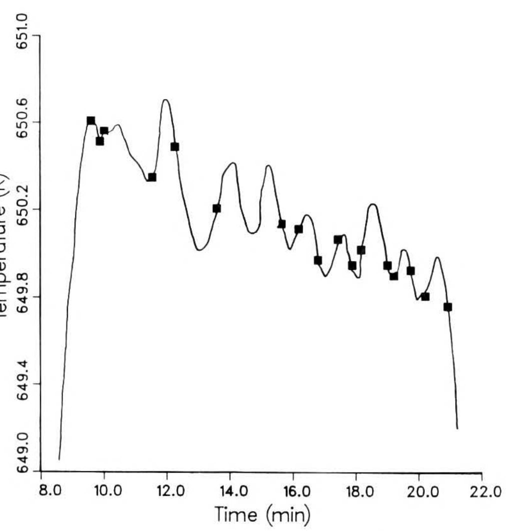

***FIGURE 2.** Temperature-time history of a thermally unstable substance (octan-1-ol) showing points of meniscus disappearance and reappearance*

second method is a low-residence time technique in which the fluid is pumped rapidly through a view cell in a heated oven. In this apparatus, critical opalescence is observed by manipulating the pressure, temperature, heating rate, and flow rate of the fluid. The combination of these two methods provides all three critical properties (P_c, V_c, and T_c) of pure fluids and fluid mixtures. New methods, including one involving rapid heating with a CO_2 laser, are being developed to extend the range of fluids which can be studied.

The critical properties of several homologous series of compounds have been measured in our laboratories including the alkanes, 1, 2, 3, 4, and 5-alkanols, aldehydes, carboxylic acids, perfloroalkanes, and mercaptans. We estimate that some 8% of all experimental critical properties have been measured in our laboratories. Part of this research is funded by the AIChE through DIPPR (Design Institute for Physical Property Research) and part by the National Science Foundation. Several correlations for critical properties have also been developed, as well as a method for estimating the effect of impurities using continuous thermodynamics [2].

BIOSEPARATIONS INVOLVING SUPERCRITICAL FLUIDS

The advantages of supercritical fluids for bioseparations have been noted by many researchers [3]. In particular, physiologically inert solvents with moderate critical temperatures (such as CO_2) are well-suited to the separation and isolation of biochemicals. Our interest in supercritical fluid extraction is multifaceted. We are interested in the phenomenological aspects of phase equilibria at high pressure as well as in the modelling and prediction of these phenomena. For example, a recent PhD thesis [4] successfully demonstrated that multicomponent high pressure phase equilibria could be predicted using generalized equations of state with only a knowledge of the chemical structures of the components (Figure 3). We are also very interested in separations with potential applications in biotechnology. Towards this end, we are carrying out joint research with the natural products group of Dr. Leon H. Zalkow in the School of Chemistry and Dr. Leslie T. Gelbaum of the School of Applied Biology at Georgia Tech. This joint work has included the separation and isolation of several chemotherapeutic compounds of interest to the National Cancer Institute.

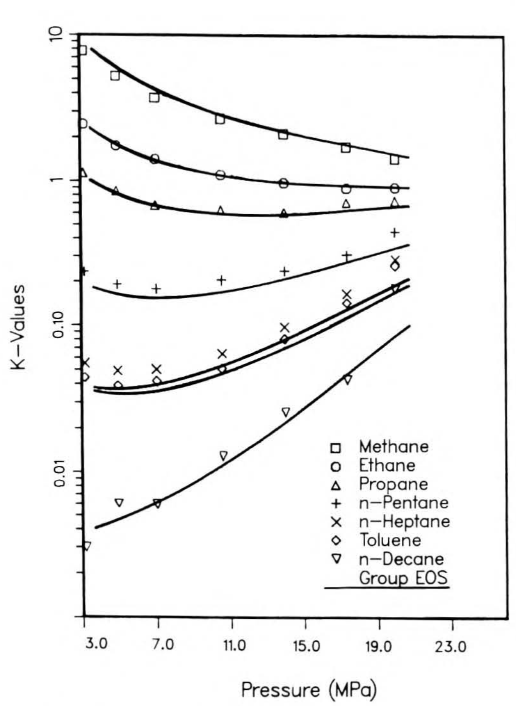

***FIGURE 3.** Predicted phase equilibria using a group contribution equation of state [4] at 360K*

We have recently completed a study of the extraction of the anti-cancer alkaloid monocrotaline (Figure 4) from the seeds of *Crotalaria spectabilis* using supercritical carbon dioxide and ethanol mixtures [5]. It was found that pure carbon dioxide extracted only the non-polar lipid materials from the seeds, which is to be expected in view of the chemical nature of carbon dioxide. By adding ethanol, the alkaloid of interest could be removed, although the lipids were still present in the extracts. In order to reduce the downstream separation requirements of a potential commercial process, a second stage separation employing a novel adsorbent was used to separate the components in the supercritical fluid phase. Using this technique, alkaloid purities of almost 100% were obtained. This process offers significant economic as well as regulatory (FDA) advantages over conventional separation processes and is being patented.

A study has also been recently completed involving the separation of fructose from glucose in aqueous solutions, again using carbon dioxide–ethanol mixtures [6]. Fructose has nutritional advantages for normal, controlled diabetic and reactive hypoglycemic persons. In this study, it was found that high fructose purities could be obtained in the vapor phase. Currently, using this same apparatus, an investigation is under way to separate taxol from Indian Yew tree bark. Taxol is a very effective anticancer drug which is difficult to separate from its natural source. Indeed, the conventional separation technique is so elaborate and has such low yields that effective clinical testing of the drug is difficult. It is our hope that an alternative carbon dioxide based separation process will result from our study.

THERMOPHYSICAL PROPERTIES OF CONCENTRATED ELECTROLYTE SOLUTIONS

Two pairs of working fluids are in common use in commercial absorption chillers and heat pumps: ammonia-water and lithium bromide-water. The thermodynamic properties and phase equilibria of these binary working pairs determine the energy flows

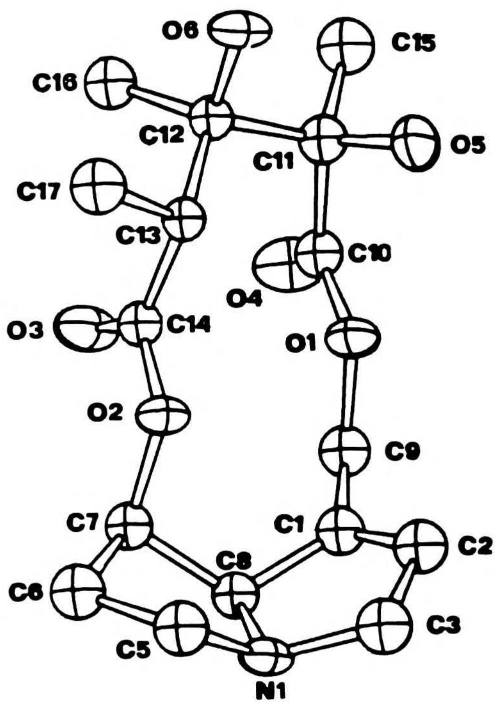

FIGURE 4. ORTEP drawing of monocrotaline from a single crystal X-ray diffraction

necessary to drive the dissolution and separation steps in the absorption cycle. Efforts to quantify the performance of absorption cycles have, however, been hindered by a lack of consistent thermophysical property data for lithium bromide-water systems, particularly at high temperatures and high concentrations.

The American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) is supporting an extensive investigation of the properties of these concentrated electrolyte solutions (concentrations approaching 65 wt %) at temperatures up to 473K. We are measuring heat capacities, densities, viscosities, thermal conductivities, and vapor pressures of these solutions. The system also serves as a model for the development of correlations for concentrated electrolyte solutions and is part of a collaborative effort with Dr. Sheldon Jeter of the School of Mechanical Engineering at Georgia Tech.

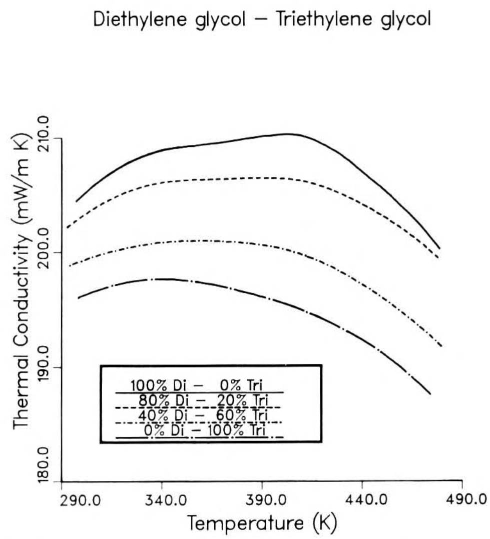

FIGURE 5. Thermal conductivity of diethylene and triethylene glycol mixtures

FLUID PROPERTIES RESEARCH INSTITUTE

Much has been written about industrial support of thermophysical property research [7]. One cost-effective way in which industry supports such research is by participation in consortia such as the Fluid Properties Research Institute. FPRI is an industrially sponsored co-operative research organization which was founded in 1973 for the purpose of acquiring sound thermophysical property data. It was originally based at Oklahoma State University but was relocated to Georgia Tech at the end of 1985. The industrial members of FPRI include petroleum companies (Amoco), specialty chemical (Hoechst-Celanese) and chemical companies (Dow), as well as contracting companies (UOP, Stearns-Catalytic, JGC, Sasakura Engineering). Basic data on heat capacities, densities, thermal conductivities (Figure 5) and viscosities of classes of compounds (*e.g.*, glycols, crude oils, aqueous solutions) are being measured and computer data banks are being developed. Graduate students and postdoctoral fellows participate in the FPRI research effort. Thus program funding produces two outputs: technical information and talented chemical engineering graduates. The program sponsors benefit by "leveraging" their research funds for basic studies, gaining access to experimental data and correlations, and by

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in the United States, a fundamental strength, should not be compromised, and perhaps could even be encouraged. For example, a student might be asked to submit a short proposal on extensions of his research to another field, which would be appended to his thesis with appropriate keywords for location by researchers who might otherwise never examine his or her work. For the MS degree, on the other hand, coursework is overemphasized, and a greater emphasis on research contributions would be desirable.

Both Japan and the United States have serious issues of access to higher education in technical fields for women and minorities. While the situation for women in the U.S. has improved significantly in recent years, in Japan the attitude toward women in technical and supervisory positions remains highly prejudicial. As the percentage of women in these positions in the U.S. continues to grow, discomfort will be experienced in cross-national dealings, *e.g.*, joint ventures. While change will be slow, it is to be hoped that Japan will eventually take its place among the leading societies in this regard. In the U.S., continuing efforts must be made not only to attract minorities and women into the scientific and engineering professions, but to deal with the fundamental causes underlying reduced participation by these groups.

In summary, although some would argue that each system serves the unique needs of its country adequately, comparing the systems of engineering education in Japan and the United States offers food for thought on possible improvements to each. While a significant number of Japanese students and faculty spend some time within the U.S. educational system, it is unfortunate that a much smaller number of Americans participate in the Japanese experience. It is to be hoped that in the future, more American students and faculty will view first-hand the workings of Japanese education. To stimulate this, it would be desirable for engineering departments of major universities to develop student and faculty exchange programs and to incorporate courses in Japanese language and technical Japanese into their curricula. In Japan, the focus for the future must be on stimulating creativity, while in the United States the educational system does not appear to wholly meet needs for research management capability and solution of pressing social concerns, including industrial competitiveness. In particular, concrete measures directed at increasing the prestige of manufacturing among engineering graduates may be warranted. While the job market for scientists and engineers frequently appears to be supersaturated, *stable* growth in scientific and engineering enrollments with production of good-quality graduates can be expected to benefit the nation in the long term. Both countries still face some very real issues of access and fairness. In the U.S., there is a clear need for professional societies to assist in monitoring statistics relating to women and minority enrollments. Finally, the nation's corporations can do their part by taking an active interest in education, promoting stable hiring policies, and maintaining affirmative action goals.

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interacting with high-quality students prior to graduation. The students benefit by interactions with industrial sponsors and by working on industrially-relevant research.

CONCLUSIONS

Thermodynamics and fluid properties research is a thriving activity at Georgia Tech. Although based mainly in the School of Chemical Engineering, there are joint projects with the Schools of Chemistry, Mechanical Engineering, and Applied Biology. There is also significant industrial participation via the Fluid Properties Research Institute. It is obvious from some of the work described that the need for thermophysical properties and for fundamental understanding of molecular behavior which determines these properties, will continue to grow as new technologies emerge and established technologies change.

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