General Comments:

As this was the final year of the research contract, most of the activities centered on completing some of the research in progress, and an orderly transition to other activities. Overall, the recent years of the project have been successful as evidenced by the accomplishments listed below and the papers published between 2005 and the present, as well as their impact and the cooperation they have encouraged with people at other universities and industry.

Research Findings

There have been two major research activities during the recent years of this contract period. One centered on adsorption and transport of gases through nanoporous materials related to gas separations, such as the energy-intensive oxygen-nitrogen separation and also carbon dioxide-nitrogen separations for greenhouse gas sequestration. The second area of continuing work has been on the COSMO-SAC method of using computational quantum mechanics to make a priori predictions of mixture and pure component phase behavior.

Our research has contributed to the fields of chemical engineering/physical chemistry/simulation in two important ways. First, our COSMO-SAC model and the associated data base have allowed chemical engineers to now routinely make quantum-based predictions of the properties of pure fluids, vapor-liquid and liquid-liquid equilibrium in mixtures, and the partitioning of chemicals between phases without knowing much about quantum mechanics. Also, we have developed an easy-to-use Windows-based interface so users need only point-and-click to make predictions. Consequently, engineers now have a completely new theoretically-based tool that is not a simple extension of group contribution models, and indeed is very different from such models. Further, the method is applicable to a more compounds and classes of compounds than the pre-existing group contribution methods, and allows properties predictions for classes of compounds not usually considered by such methods, such as pharmaceuticals and environmental pollutants.

The quantum mechanics-based method we have developed is now being used to predict octanol-water partition coefficients (Kow) of various chemicals and pharmaceuticals. This parameter is part of the rule of five (i.e., Log Kow<5) for a drug candidate molecule acceptable. Also, our work has shown, based on quantum mechanics, how to make changes to drug molecules to make them more hydrophobic or hydrophilic for improving drug delivery. One of our studies dealt specifically with corticosteroids. An application of our results has been with civil/environmental engineers in predicting the properties of environmental pollutants, especially polychlorinated biphenyls (PCBs), relevant to determining their fate in the environment. Experimental data for the PCBs, because of the number of congeners and the extreme values of their octanol-water
partition coefficients and Henry’s law constants, are quite inaccurate, sometimes spanning one or two orders of magnitude for the same property and the same temperature from different investigators. Our predictions, having been shown to be in agreement with accurate experimental data, and are now being used to make better environmental fate predictions.

To make this work publically available, we have collaborated with Professor B. Y. Liu and his students at the Virginia Polytechnic Institute and State University to establish a database of the results of quantum mechanics calculations needed to use the COSMO-SAC method we have developed. Professor Liu has developed a Web site and has posted the results of our joint calculations for others to use. This data base has been made available to the world for free. Also, the window-based programs we have developed are available on request.

Our second area of research, on adsorption and transport through nanoporous carbon-based materials has helped explain previously inexplicable experimental observations, and have led to collaborative experimental work and membrane design specifically for gas separations at the National University of Singapore and the University of Melbourne (Australia). The experimental results we have been able to explain are the high gas separation factors found with nanoporous carbon membranes. We have shown that this occurs because of irregularities in the pore structure of these materials. This has led to suggestions for designing carbon nanotubes and other materials with specific constrictions (defects) to produce separations of, for example carbon dioxide from nitrogen in flue gas (for carbon dioxide sequestration) and oxygen from nitrogen for a variety of applications including breathing-assist apparatuses and commercial applications. More recently, we have become part of a major experimental and modeling effort on gas separations at the National University of Singapore.

Participants and Collaborators

At various times over the duration of the project, four graduate students were involved. Jianwen Jiang is now on the faculty of the Department of Chemical and Biomolecular Engineering at the National University of Singapore and is our collaborator there on gas separations. Jeffrey Klauda is now a faculty member in chemical engineering at the University of Maryland. Gaurav Arora is employed as a chemical engineering at Air Products and Chemicals, Allentown PA, and Shu Wang is employed by Aspen Technology, Cambridge MA.

We have also worked closely with Chau-Chyun Chen at Aspen Technology (Cambridge, MA) and Professor B. Y. Liu and his research group at Virginia Polytechnic Institute and State University. Aspen Tech has provided support in kind in terms of making available software and physical properties data bases, and the VPI group has provided the manpower needed to improve and complete the quantum mechanics data base. In addition, we are now working closely (and co-supervising a graduate student) with Professors Geoffrey Stevens and Sandra Kentish of the Department of Chemical and Biomolecular Engineering of the University of Melbourne. This latter group is doing experimental work in support of our theoretical and simulation studies. The first of our publications with this group will appear shortly. Our most recent collaboration in this area is with Neal Chung at the National University of Singapore.

To a lesser extent we have also collaborated with Professor Berend Smit at the University of Amsterdam (Holland and now at the University of California, Berkeley) and Professor Ilja Siepmann of the University of Minnesota. More recently, we have entered into a collaborative arrangement with the SCM (Scientific Computing and Modeling) Group in Amsterdam helping
them use our published results and models. Finally, we are beginning a collaboration with
Steven Lustig of the DuPont Company to couple our COSMO-SAC method with his intelligent
molecular design methods to develop a tool that would allow an chemist or engineer to specify
desired properties of a chemical or chemical mixture, and the program would then provide a list
of candidate chemical and/or mixtures with the desired properties. Using this method, it will be
possible to identify chemicals for which no data exists, such as chemicals that have not yet been
synthesized. Of special interest are single chemicals or mixtures that could be replacements for
less environmentally industrial chemicals. Related to this, we had started a research activity on
the prediction of properties ionic liquids. However, as a result of loss of funding, this project has
been terminated.

**Publications (2005 to the present)**

In addition to the data base now publically available on the Web that we developed with the VPI
group develop, we have published numerous papers supported by this contract on both the
quantum mechanics-based research as well as the adsorption/transport in nanoporous materials
research. A list appears below.

"Hierarchial Modelling of N\textsubscript{2} Adsorption on the Surface of and Within a C\textsubscript{60} Crystal: From
Quantum Mechanics to Molecular Simulation" by J. W. Jiang, J. B. Klauda and S. I. Sandler, J.

"Adsorption and Phase Transitions on Nanoporous Carboneaous Materials: Insights from
Molecular Simulations" by J. W. Jiang and S. I. Sandler, Fluid Phase Equilibria **228**, 189-195
(2005).

"Air Separation by Single Wall Carbon Nanotubes: Thermodynamics and Adsorptive

"Adsorption and Separation of Linear and Branched Alkanes in Carbon Nanotube Bundles from
Configurational-bias Monte Carlo Simulation" by J. W. Jiang, S. I. Sandler M. Schenk and B.

"Separation of CO\textsubscript{2} and N\textsubscript{2} by Adsorption in C\textsubscript{168} Schwarzite: A Combination of Quantum

"A Comparative Study of Nitrogen Physisorption on Different C\textsubscript{70} Crystal Structures Using an

"Effects of Conformational Distributions on Sigma Profiles in COSMO Theories” by S. Wang, J.

"Shape Versus Inverse-shape Selective Adsorption of Alkane Isomers in Carbon Nanotubes" by

"Air Separation by Single Wall Carbon Nanotubes: Mass Transport and Kinetic Selectivity" by
Virtual Journal of Nanoscale Science and Technology **13**(9), March 6 2006.


