Physical and Chemical Properties Division - Table of Contents

Physical and Chemical Properties Division (838)

W.M. Haynes, Chief

A. Division Overview

Mission

The Physical and Chemical Properties Division serves as the Nation's reference laboratory for measurements, standards, data, and models in the areas of thermophysics, thermochemistry, and chemical kinetics. The Division focuses primarily on:

- thermophysical and thermochemical properties of gases, liquids, and solids, including both pure materials and mixtures;
- rates and mechanisms of chemical reactions in the gas and liquid phases;
- fluid-based physical processes and systems, including separations and low-temperature refrigeration and heat transfer.

The Division outputs include technical reports, Standard Reference Data, internet-based databases, calibrations, and Standard Reference Materials.

In order to carry out this Mission, the Division:

- develops, maintains, and utilizes advanced experimental tools and applies these to problems of scientific and industrial importance;
- compiles, evaluates, correlates, and interprets experimental data;
- develops and evaluates new theories, models, estimation methods, and computational algorithms;
- develops new dissemination mechanisms while maintaining a strong publication record in traditional media;
- carries out research leading to engineering data and models for advanced technologies;
- provides standards and services for fluid flow under cryogenic conditions;
- serves industry by organizing conferences, editing journals, training students, and serving on domestic and international committees.

Programs

The Physical and Chemical Properties Division is organized into six groups: (1) *Experimental Kinetics and Thermodynamics*; (2) *Chemical Reference Data and Modeling;* (3) *Computational Chemistry*; (4) *Experimental Properties of Fluids*; (5) *Theory and Modeling of Fluids*; and (6) *Cryogenic Technologies*. The last three Groups are located in Boulder, CO, as are three Projects, *Properties for Process Separations, Membrane Science and Technology,* and *Thermodynamics Research Center*. The rest of the Division is located in Gaithersburg, MD. These Groups/Projects are engaged in a number of research activities, which arise from several focus areas that cut across

Group/Project boundaries. These focus areas are discussed below, followed by selected Technical Highlights from these activities.

Basic Reference Data

Industry demands reliable and accessible reference data on the physical and chemical properties of a wide variety of compounds. These data are required in the development of models for process design, energy efficiency, and in the evaluation of possible environmental impacts. Basic reference data are also critical to the transportation and storage of fluids, in custody transfer, and for calibration of instruments and processes.

The development of databases for use in industry and academia is a fundamental task of all the focus areas within the Division. Thus, many of the Technical Highlights pertain both to Basic Reference Data and to a specific technical focus area. Several focused data activities of the Division are discussed in Technical Highlights 1-11, but this area permeates the discussion in nearly every report. The strong integration of data activities with the experimental, modeling, and computational programs means that experimental efforts often arise out of needs that these data activities identify. The continuing integration of the Thermodynamic Research Center into NIST activities (Technical Highlight 3) reflects the growing demand for NIST properties data and the Division commitment toward fulfilling this demand. Technical Highlight 9 describes a program in which a means of generating a unique identifier for a chemical compound from a digital representation of its chemical structure is being developed. It is being developed as an IUPAC project with the intention of establishing it as a standard, international means of representing chemical identity. There are also parallel efforts in the Division in the development of XML-based standards for representing physical and chemical property data to promote interoperability in experimental physical and chemical property data collection and management worldwide, as noted in Technical Highlight 2.

- The NIST WebBook - NIST Chemical Reference Data for Industry (Technical Highlight 1)
- Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation (Technical Highlight 2)
- International Standards for Calorimetry and Thermodynamics (Technical Highlight 3)
- Release of Version 7.0 of the NIST REFPROP Database (Technical Highlight 4)
- Properties of Refrigerant Mixtures Near the Critical Point (Technical Highlight 5)
- Viscosity Measurements and Model Comparisons for Second-Generation Alternative Refrigerant Blends (Technical Highlight 6)
- NDRL/NIST Solution Kinetics Database on the Web (Technical Highlight 7)
- Bimolecular Reaction Rates and Mechanisms Relevant to Nano-structure Formation (Technical Highlight 8)
- A Standard Chemical Identifier (Technical Highlight 9)
- Thermal Conductivity of Natural Gas Constituents (Technical Highlight 10)
- Cylinder Filling Ratios for Compressed Liquids (Technical Highlight 11)

Computational Chemistry

The use of modern computational chemistry methodologies in the prediction of molecular properties has become increasingly important mainly due to significant improvements in algorithms and the availability of powerful computer resources. This is particularly true in the area of thermochemistry, where researchers in industry perform *ab initio* quantum chemistry calculations on a routine basis. Progress in this area, however, is hampered by a lack of standards, comparisons, and simplified methodologies. In addition to this external need, the experimental projects within the Division benefit greatly from having a strong computational capability available. These considerations have led us to establish a computational chemistry focus area in the Division. This year, we have continued to make significant progress in the compilation, evaluation, and dissemination of information about computational techniques. The results of this project have led to the continued development of a computational chemistry comparison and benchmark database. In addition, improved methodologies for calculating thermodynamic and kinetic parameters and predicting chemical reactions have been developed and applied to a variety of problems of interest in industry and in our own Division. Technical Highlight 12 describes exploratory work on the pyrophoric combustion of silane. In the semiconductor industry, combustion of pyrophoric gases such as silane (SiH_4) and phosphine (PH_3) is an important safety hazard. Although the combustion can have explosive force, it is initiated by relatively slow reactions. Similar chemistry may be responsible for initiating the autoxidation of organic compounds, including plastics, elastomers, lubricants, and edible fats and oils. An understanding of how these reactions occur may lead to new ways of suppressing undesirable oxidative reactions. Both processes involve oxidation by atmospheric oxygen and chain reactions that follow a much slower, unknown initiation step.

More recently, increasing interest in the semiconductor industry in rational design of materials leading to the manufacture of novel electronic components at the nanometer scale has prompted us to initiate a program studying the validation of state-of-the-art *ab initio* quantum chemical methodologies in the area of molecular electronics (Technical Highlight 14). Given that the nanofabrication of these materials will likely entail the use of self-assembly monolayers containing molecules interacting via long-range forces, it is important to have a fundamental understanding of the nature of these forces. Although quantum chemistry could offer the appropriate tools to achieve this goal, there is a significant lack of validation of these methodologies.

A new, robust and computationally efficient exchange functional for density functional theory has been developed and implemented (Technical Highlight 15). It eliminates serious problems encountered in most of the exchange functionals used currently by the scientific community. The use of the new methodology will allow scientists to compute physical and chemical properties of complicated chemical systems in a reliable and cost-effective manner. The development of this methodology constitutes a major advancement in the area of density functional theory, a computational chemistry technique widely used by scientists in industry. The surface structure and properties of chromium oxide are keys to its performance in a wide variety of technological applications, ranging from passivation of stainless steel to catalytic reduction of pollutants. Despite its importance, the surface structure and stoichiometry of chromium oxide is not well understood because its insulating character renders analytical techniques based on electron spectroscopy problematic. The phase diagram of the α-Cr_2O_3 surface in equilibrium with O_2, H_2O, and O_2 has been calculated from first principles, and is consistent with experimental observations (Technical Highlight 16). Formation of a strong Cr=O bond upon exposure to oxygen can account for the passivation of stainless steel and oxygen poisoning of catalysts.

- The Initiation Step in Pyrophoric Combustion of Silane (Technical Highlight 12)
- Conference on Biophysics from First Principles: From the Electronic to the Mesoscale, September 7-12, 2002, San Feliu, Spain (Technical Highlight 13)
- Molecular Electronics. Negative Differential Resistance Explained: Guidelines and a Model to Design New Molecules (Technical Highlight 14)
- An Efficient Model to Compute the Exact Exchange Potential in Density Functional Theory (Technical Highlight 15)
- Environmental Control of α-Cr_2O_3 (0001) Surface Chemistry (Technical Highlight 16)

NIST played a key role in the organization of the Conference on Biophysics from First Principles: From the Electronic to the Mesoscale described in Technical Highlight 13. The purpose of this conference was to bring together theoretical and experimental researchers from physics, chemistry, biological sciences, and industry to foster interdisciplinary approaches to the study of living systems. The principal focus was on the application of theoretical physics – from first principles to classical simulations, as well as statistical approaches – to understanding biological processes. The major challenge identified was the integration of time and length scales, particularly to treat complex problems such as protein folding, biochemical pathways, toxicology, and ion transport through membranes.

Fundamental Studies of Fluids

In support of the Division mission to provide U.S. industry with thermophysical properties of gases, liquids, and solids, the Division maintains a focus area on the fundamental studies of fluids, with strong theoretical (Technical Highlights 17 and 18) and experimental (Technical Highlight 19) components. The goals are to develop and utilize unique experimental, theoretical, and simulation capabilities to study fluid systems under equilibrium and nonequilibrium conditions. Much of the work relates to phase boundaries, vapor-liquid and solid-fluid equilibria, simulation of real and model systems (Technical Highlights 17 and 18), virial coefficients for mixtures, etc., including complex interactions associated with nanocomposites. In this area, we both respond to current industrial needs and develop capabilities that anticipate future needs. It is anticipated that the theoretical work, such as that related to solid-fluid equilibria, mixture virial coefficients, molecular simulation, etc., can lead to models upon which future data evaluation, prediction, and database efforts will be based. Some of our work on processes and structures at the micrometer and nanometer length scales may lead to broader programs in these areas to support industrial requirements as they are identified. Some of the areas of focus are:

- **Industrial Fluid Properties Simulation Challenge: Benchmark Standards (Technical Highlight 17)**

- **Molecular Simulation of Solute Diffusion (Sodium Chloride) in Supercritical Steam (Technical Highlight 18)**
- **Double-Sinker Densimeter for High-Accuracy Fluid Density Measurements (Technical Highlight 19)**
- **Conference on Biophysics from First Principles: From the Electronic to the Mesoscale, September 7-12, 2002, San Feliu, Spain (Technical Highlight 13)**

Technical Highlight 17 describes the outgrowth of a workshop that was organized by our division to identify industrial fluid property needs that could be addressed using molecular simulation methods and to ensure that industry has the tools necessary to employ molecular simulation methods as reliable options for the longer term. The First Industrial Fluid Properties Challenge has been organized to promote and to advance the status of molecular simulation for the calculation of properties of interest to industry. In particular, NIST has coordinated activities related to establishing benchmark standards against which competition entries will be compared. The simulation contest will serve to assist in the transfer of the technology to prospective industrial users, to identify strengths and weaknesses of the various techniques, to begin the process for systematic development of force fields, and to initiate general protocols for the assessment of property prediction techniques.

Technical Highlight 19 describes an apparatus that defines the new best-in-the-world instrument for wide-ranging, high-accuracy P-ρ-T measurements. Density as a function of temperature and pressure is one of the most important properties for the determination of a thermodynamic equation of state of a fluid. Density is also vital in fluid metering applications in research and industry. This new apparatus extends our capabilities to higher temperatures and lower densities and reduces the uncertainties by an order of magnitude. We will use these capabilities to provide data on key industrial fluids and mixtures and develop standard reference materials (SRMs) for fluid density. The SRM work will include extensive tests to investigate possible systematic errors and establish strict traceability of fluid P-ρ-T properties to fundamental standards. This is important since the new densimeter surpasses the capabilities of all existing instruments, rendering moot any comparison with published data.

Tools for Chemical Analysis

Central to all of chemistry is the analysis of complex mixtures and the identification of the individual chemical constituents. These analyses are usually derived from basic physical/chemical properties of the species, and knowledge of these properties is thus critical to the reliability of the information. The Division strives to produce evaluated data, predictive algorithms, and analysis software to assist in the identification and quantitation of a range of species under diverse conditions. The NIST WebBook plays a central role in this, but current Division activities also include measurements and data acquisition designed to expand the gas chromatographic and mass spectrometric databases (Technical Highlight 20). A major update of this database was released during the past year. Spectra for over 54,000 compounds were added to the new version, for a total of 174,948 spectra of 147,198 compounds. Another important activity in the Division is the development of complex algorithms for the rapid and automatic analysis and deconvolution of GC/MS data for the identification of chemical-weapon agents.

A program has been initiated to extend the coverage of the widely-used NIST Mass Spectral Library to MS/MS and ion trap mass spectra (Technical Highlight 21). The existing NIST mass spectral library is composed entirely of 'classical' electron ionization mass spectra. Spectra generated by ion trap and MS/MS instruments, which are becoming widely used for chemical identification, may not match these classical spectra. The work has also led to improvements in the automated extraction of mass spectra by the NIST AMDIS program. One particular application area, pesticide analysis, has been targeted for initial development. A comprehensive gas phase retention index library for capillary columns is nearing completion (Technical Highlight 22). It contains approximately 70,000 data points for 12,000 compounds on widely used nonpolar capillary columns. The evaluated data collection will be provided along with the NIST Mass Spectral Library to confirm the identity of compounds in chemical analyses.

- The NIST Mass Spectral Library: A Major Update (Technical Highlight 20)
- Laying the Foundation of MS/MS and Ion Trap Libraries (Technical Highlight 21)
- Gas Chromatograhy Retention Index Library: A Major New Resource Nears Completion (Technical Highlight 22)

Cryogenic Technologies

Cryogenic technologies are critical to a wide variety of technically and industrially important areas. These include the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics, magnets, and power systems, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas, and many other existing and potential applications. The research of the Division in this area involves the application of thermophysical concepts and measurements for temperatures below 120 K. Research in this area has focused primarily on improved measurement and modeling techniques involved in the development and characterization of novel and improved cryocoolers (Technical Report 23), studies of microscale heat transfer, development of a cryogenic materials database, and the maintenance and improvement of the national standard for cryogenic flow measurements. As part of an upgrade, the cryogenic flow loop has been brought into compliance with ISO Guide 25 requirements.

- **Properties and Processes for Cryogenic Refrigeration (Technical Highlight 23)**

Measurements for the Environment

The use of chemicals in American industry is ubiquitous and, thus, the fate and disposal of these industrial chemicals and their byproducts are of great concern. A wide variety of physical and chemical data are essential to understand the fate and impact of chemicals in the environment, to develop strategies for the removal or destruction of harmful byproducts, and to *design processes and products that minimize environmental impact. A major consideration in the choice of chlorination chemistry as the first of our targeted evaluation projects was the concern over the unintentional formation and release of chlorinated species in industrial processes. Our kinetics and thermodynamics databases have always been of particular importance in the development of environmental models and the needs of this community was a consideration in the web-based kinetics database. The mass spectral database is a key tool in environmental analysis (Technical Highlight 20), and the tools we are developing for use in the decomposition and analysis of GC/MS data files will provide powerful new methods in that area. During the past year our program on the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions (Technical Highlight 23) has expanded. These Green 'designer solvents' that can serve as both catalyst and solvent are attracting increasing attention from industry since they promise significant environmental benefits.*

In conjunction with our data activities, we have ongoing programs to generate key physical and chemical data for the environment. Our long-term program on the atmospheric degradation of industrial compounds has, in recent years, focused on halon replacements. This experimental activity has been closely tied to a computational effort, which has allowed us considerable leverage in providing needed information to industry and other agencies. Our experimental studies have involved the reactions of the hydroxyl radical with industrial gases in order to assess their potential environmental impact. Reactions of the hydroxyl radical in the gas phase are central to atmospheric chemistry and combustion processes.

The accumulation of CO_2 in the atmosphere from fossil fuel burning leads to global warming. Various strategies are being considered to mitigate this problem. One of the more promising is to mimic nature and carry out the photochemical conversion of CO_2 into useful products, a strategy of photochemical reduction. In order to successfully design production systems based on these catalysts, detailed fundamental information is needed on their photochemical and chemical properties, including their stability under operating conditions. Although studies (Technical Highlight 25) on iron and cobalt porphyrins have shown that they can serve as efficient homogeneous catalysts for the photochemical reduction of CO_2, the decomposition of these substances has proven to be an intractable problem. A more promising route is to investigate heterogeneous systems using semiconductor nanoparticles as light absorbers and catalysts.

Another means to reduce the amount of CO_2 in the atmosphere is, of course, to develop more energy-efficient industrial processes. Much of the data provided by the Division, especially that described in the Focus Area on Properties of Energy-Related Fluids can have huge impact on the energy efficiency of industrial processes. Increasing the energy efficiency of an industrial process, for example, not only translates to less CO_2 emitted into the environment, but also represents a fuel cost savings and makes the process more economically viable. This goes hand in hand with maintaining our economic vitality and high standard of living. It is certain that in the coming decades the most successful economies will be those that develop innovative, sustainable solutions to technological problems.

Our long-term effort to provide thermodynamic information necessary for prediction of movement of heavy metals through ground waters (aquifers) and surface waters, and for prediction of remediation yields in treatment methodologies continues. During this past year work has continued on arsenic and chromium properties; both of these substances fall high on the 1999 CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) List of Priority Hazardous Substances. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a critical issue in a broad array of applications including pollution prevention and remediation (Technical Highlight 26). Our measurements on liquid systems will allow prediction of pollutant entry into ground waters. Studies also continue on the properties of electrolytes in aqueous and mixed solvents (important for waste-water and other environmental applications).

The potential impact of the release of chlorofluorocarbons in the upper atmosphere on ozone depletion, and the concomitant effects on human health and the environment, is well documented. Our Division has conducted a program on the properties of alternative refrigerants since the mid-1980s to provide highly reliable date for selection of new alternatives and for optimization of the efficiency and capacity of refrigeration and air-conditioning systems. Recent work in this area is described in Technical Highlights 4, 5, and 6.

- Kinetics and Thermophysical Properties of Ionic Liquid Systems (Technical Highlight 24)
- **Photochemical Reduction of CO_2 Catalyzed by Metalloporphyrins (Technical Highlight 25)**
- **Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes (Technical Highlight 26)**

Data for Process and Product Design

At some point in the manufacture of almost all the products that we use, there is a physical or chemical separation process involved. In modern industry, the products and processes are designed or optimized by process simulators. These rely on fundamental physical and chemical property data. The Division's goal is to provide the data that industry needs to effectively apply process modeling and simulation at all appropriate points in the manufacturing cycle, from the separation and treatment of raw feedstock, through the manufacturing process, to the ultimate treatment and disposal of waste streams. This has led to a wide variety of projects in the Division, some of which are strongly focused on a specific problem. Areas of current interest include:

- High-Throughput Liquid Transport Properties Measurements in Membranes and Films (Technical Highlight 27)
- Measurements, Modeling and Data for Pressure-Driven Membrane Separations (Technical Highlight 28)
- Stability of Potential High-Temperature Heat Transfer Fluids (Technical Highlight 29)
- Far-Ultraviolet Spectra of Compounds Important in Next-Generation Lithography (Technical Highlight 30)
- Bimolecular Reaction Rates and Mechanisms Relevant to Nano-structure Formation (Technical Highlight 8)
- The Initiation Step in Pyrophoric Combustion of Silane (Technical Highlight 12)
- Environmental Control of α-Cr_2O_3 (0001) Surface Chemistry (Technical Highlight 16)
- Properties and Processes for Cryogenic Refrigeration (Technical Highlight 23)

Properties of Energy-Related Fluids

Energy-related fluids include both those which are primary sources of energy – the fuels; and those which inter-convert heat and useful work – the working fluids. In several key areas, industry requires accurate and comprehensive equilibrium and transport property data and models for these fluids. These areas include the design and optimization of working cycles in refrigeration or power production systems; the design and control of gas processes; custody transfer; and development of new, cleaner energy systems. Efforts in the Division to meet these needs include the development of experimental apparatus for thermophysical property measurements; the acquisition of data; and the development and dissemination of accurate correlations. Recent work has focused on the thermodynamic and transport properties of refrigerant mixtures near the critical point (Technical Highlight 5), viscosity measurements and models for refrigerant blends (Technical Highlight 6), the thermal conductivity of natural gas components (Technical Highlight 10), and the stability of high-temperature heat transfer fluids for solar energy applications (Technical Highlight 29). An important facet of this focus area has been participation in the development of internationally accepted standards for the properties of water and steam, natural gas, and alternative refrigerants. Examples of activities under study in this focus area include:

- Chemistry and Properties of Trace Components in Fuel Gas (Technical Highlight 31)
- Release of Version 7.0 of the NIST REFPROP Database (Technical Highlight 4)
- Properties of Refrigerant Mixtures Near the Critical Point (Technical Highlight 5)
- Viscosity Measurements and Model Comparisons for Second-Generation Alternative Refrigerant Blends (Technical Highlight 6)
- Thermal Conductivity of Natural Gas Constituents (Technical Highlight 10)
- Molecular Simulation of Solute Diffusion (Sodium Chloride) in Supercritical Steam (Technical Highlight 18)
- Stability of Potential High-Temperature Heat Transfer Fluids (Technical Highlight 29)

Organizational Structure

Division-Office Projects (Gaithersburg and Boulder)

- Studies the behavior of fluid systems under both equilibrium and nonequilibrium conditions using unique experimental, theoretical, and simulation capabilities.

Properties for Process Separations Project (Boulder)

- Performs research and provides critically evaluated data and models on a variety of fluid-based separation processes, including distillation, adsorption, and supercritical fluid extraction.

Membrane Science and Technology Project (Boulder)

- Performs research on characterization techniques and provides fundamental data and models needed to design and/or select more efficient and robust materials for membrane-based separations.

Thermodynamics Research Center Project (Boulder)

- Collects, evaluates, and disseminates thermophysical property data for a very large number of fluid systems of interest to the chemical industry and related customers.

Experimental Kinetics and Thermodynamics Group (Gaithersburg)

- Develops and uses state-of-the-art measurement techniques to determine the rates and mechanisms of chemical reactions in the gas and liquid phases and the thermodynamic properties of industrially and environmentally important chemical species and materials.
- Develops new measurement methods for detecting and characterizing reactive intermediates.
- Certifies Standard Reference Materials for thermodynamic properties important to industry and science.

Chemical Reference Data and Modeling Group (Gaithersburg)

- Develops and evaluates new theories, models, and estimation methods for thermodynamic properties, rate constants, and molecular spectra.
- Compiles, evaluates, correlates, and disseminates Standard Reference Data.
- Develops and disseminates electronic databases and software on thermodynamics, chemical kinetics, and analytical mass and infrared spectra.

Computational Chemistry Group (Gaithersburg)

- Develops and applies computational methods for calculating the chemical and physical properties of selected species and systems.
- Critically compares computational predictions with the best available experimental data to establish the accuracy and reliability of computational methods.
- Develops resources to provide guidance to non-experts on methods, reliability, and resource requirements.

Experimental Properties of Fluids Group (Boulder)

- Performs experimental research and develops and maintains high-accuracy apparatus for measuring the full complement of thermodynamic and transport properties of fluids and fluids mixtures over wide ranges of temperature, pressure, and composition.
- Provides comprehensive thermophysical property measurements for technically important pure fluids and mixtures, including common organics and inorganics, hydrocarbons, refrigerants, and aqueous systems.

Theory and Modeling of Fluids Group (Boulder)

- Performs theoretical and simulation research on the thermophysical properties of fluids and fluid mixtures, including regions of fluid-fluid and fluid-solid phase separation.
- Develops models and correlations of high accuracy to describe and predict the thermophysical properties of fluids and fluid mixtures.

- Provides comprehensive and evaluated Standard Reference Data and electronic databases for the properties of technically important fluids and fluid mixtures.

Cryogenic Technologies Group (Boulder)

- Develops improved measurement and modeling techniques for characterizing basic cryocooler components and processes.
- Develops prototype state-of-the-art cryocoolers for specific applications.
- Provides measurement standards and services for flow under cryogenic conditions.

Staff Recognition for Fiscal Year 2002

- Laurell Phillips **received the CSTL Secretarial Achievement Award for exceptional administrative support of NIST and the Physical and Chemical Properties Division**
- Jennifer Scott and Mike Lewis **received Certificates of Appreciation for affirmative employment and diversity activities in recognition of their nominations for the Building Tomorrow's Workplace Award.**
- Anneke Sengers **was elected a Fellow of the American Association for the Advancement of Science for meritorious efforts to advance science.**
- Michael Frenkel, Dan Friend, and Arno Laesecke **were selected as Fellows of the International Union of Pure and Applied Chemistry for their service to the Union.**
- W. M. Haynes **received the U.S. Department of Commerce Silver Medal for leadership and management of the Physical and Chemical Properties Division.**
- Jan Sengers **was elected Academician Emeritus of the International Academy of Refrigeration.**
- Ray Radebaugh **received the Federal Laboratory Consortium Technology Transfer Award for the transfer of cryocooler technology to private industry and, in particular, for collaborations with a small medical company to develop a cryogenic catheter to treat heart arrhythmias.**
- Jeff Manion **was the Division 838 nominee for the CSTL Technical Achievement Award for his paper entitled "Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons,"** ***J. Phys. Chem. Ref. Data*** 31, **123-172 (2002).**
- **The** NIST Chemistry WebBook **was voted as the winner in the "Portals and Information Hubs" category of the Best Chemical Sites in a Web contest sponsored by ChemIndustry.com Inc., John Wiley & Sons, Inc., and the Royal Society of Chemistry, UK.**

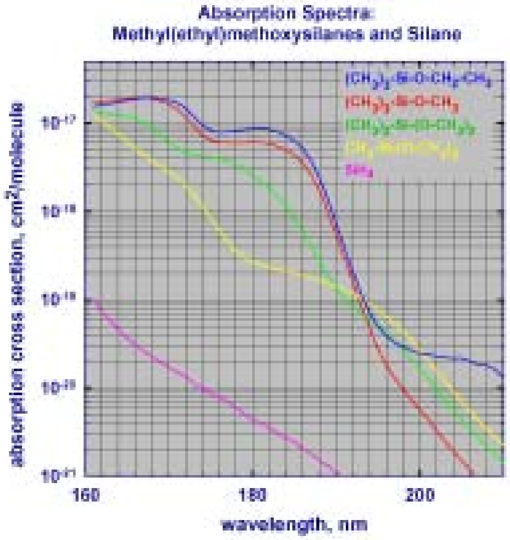
Far-Ultraviolet Spectra of Compounds Important in Next-Generation Lithography

CSTL Program: Microelectronics
Author: *V.L. Orkin*

Abstract: Atmospheric pressure deep UV lithography using fast chemically amplified photoresists will be the mainstay of semiconductor production into the foreseeable future. The development of materials and techniques for both 193 nm (based on ArF excimer lasers) and 157 nm (based on F_2 excimer lasers) exposure tools for UV lithography should soon become available. A challenge for the utilization of these shorter wavelengths is photodeposition on the surfaces of the many lenses required to focus and direct the light. These deposits cause light scattering and poorer imaging. Although the problem has been observed to some extent at longer wavelengths, it becomes very serious for the deep UV radiation. The control of this problem requires a quantitative understanding of the photochemical properties of the gases that are likely to be present in the lithography apparatus. To help address these problems, we have measured the deep UV spectra of a set of silicone-containing compounds likely to be used in next-generation lithography.

Purpose: The objective of this project is to provide far-UV spectra of species identified as important contamination sources in lithography. These compounds were selected based on input from the first Lithography Contamination Control and Monitoring Roadmap Workshop, held in 2001

Major Accomplishments: The absorption spectra of nine different silicone-containing compounds were measured down to 160 nm (the limit of our apparatus). With the exception of silane, all the Si-containing gases studied exhibit very strong absorption at shorter wavelengths. At 193 nm, the absorption cross sections are relatively small, except for hexamethyldisilazane. For hexamethyldisiolxane and the alkyl-methoxysilanes, the absorption cross section increases by more than two orders of magnitude between 193 nm and 160 nm.



All of the spectra can be found at http://www.nist.gov/kinetics/spectra

Impact: The substances whose far-UV spectra were measured represent the most important likely contaminants as chosen by the Lithography Workshop. This information will now allow plans for the design of next-generation lithography equipment to proceed with quantitative information on the photochemical behavior of this compound set.

Future Plans: If funding can be obtained, we intend to extend the range of the vacuum UV monochromator down below 157 nm, since this is the wavelength of the fluorine laser. This will be particularly important for substances with absorption features that are increasing rapidly in the region above 160 nm, our present measurement limit.

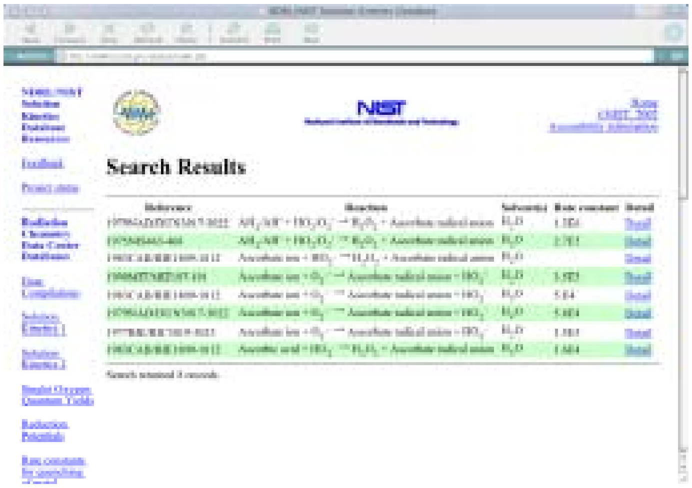
NDRL/NIST Solution Kinetics Database on the Web

CSTL Program: Chemical and Allied Products
Authors: *T.C. Allison, R.E. Huie, and P. Neta*

Abstract: As part of an effort to make NIST data products as widely available as possible, the NDRL/NIST Solution Kinetics Database has been made accessible on the Internet at http://kinetics.nist.gov/solution. The database contains over 23,000 rate constants, primarily for free radical reactions. More than 11,000 unique species in more than 150 solvents or mixtures of solvents are included. The data have been abstracted from nearly 4,000 literature sources. A powerful search engine is part of the web site allowing rapid searching of the database, and subsequent links to additional NIST databases will make this a particularly important source of information on free radical chemistry in solution to such areas as physiological and radiation chemistry.

Purpose: To provide data on the kinetics of reactions taking place in solution to a wide audience via the Internet; to make these data readily searchable; and to deliver the data to the user in a useful and clear form.

Major Accomplishments: The database was converted from an older format to one more appropriate for use in conjunction with a web environment, and a web site was established. The web site incorporates useful information and links in addition to the implementation of the database. A search engine was integrated into the web site allowing for fast and accurate searching of the database. Results of queries are returned in a useful summary form with access to full details available with a single click. All records are indexed such that data are intuitively linked (e.g., one can go directly from a single reaction record to all records reported within a journal article).

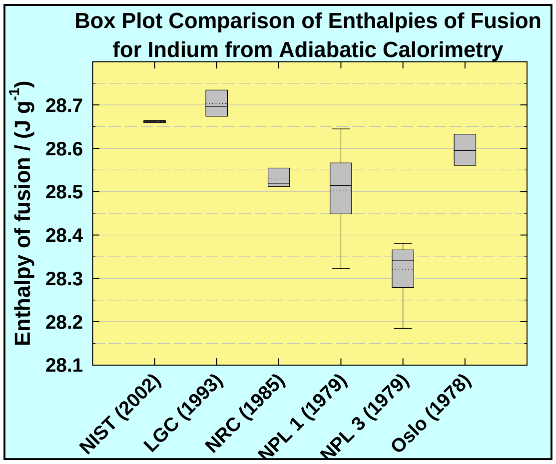


Impact: The rates of free radical reactions in solution are important in many parts of chemistry and biology, particularly with the increased understanding of their role in the causes and cures of disease and in aging. The NDRL/NIST Solution Kinetics Database is one of the few databases with this type of information available.

Future Plans: Over the next fiscal year, the database will be linked to the NIST Chemical Kinetics Database (gas phase) and the NIST Chemistry WebBook and *vice versa*. This will be done to provide maximum linking of similar data, which will lead to a more user-friendly experience for those using the database. A new tool for data entry will be developed this year to enable distributed data entry to facilitate new data projects. The first of these will be to add reactions of phenoxyl radicals to the database; alkoxyl radicals will follow these. In developing a new data entry tool and gathering new data, the types of information contained in the database will increase. This expanded definition of database fields will be used as the basis for an XML schema for solution kinetics data. The web site will have the ability to return data in the XML format for further processing by the database users. This functionality will ultimately be implemented as a web service allowing automated queries of the database.

International Standards for Calorimetry and Thermodynamics

CSTL Program: Industrial and Analytical Instruments and Services
Authors: *D.R. Kirklin, and D.G. Archer*



Abstract: Thermodynamic and calorimetric measurements have wide usage, ranging from product specification and quality control to research. Many calorimetric or thermodynamic instruments must be calibrated and methods validated for proper operation. We develop Standard Reference Materials and other highly accurate property data for calibration and/or validation of calorimetry and other thermodynamic measurements. A high-temperature adiabatic calorimeter has been made operational this year. This new instrument was used to measure enthalpies and temperatures of fusion of two certified reference materials (indium and tin) from the Physikalisch-Technische Bundesanstalt (PTB) for differential scanning calorimetry. The collaborative project with PTB was conducted under the Memorandum of Understanding signed between NIST, PTB, and BAM. The newly determined enthalpy of fusion value for indium has an uncertainty that is about an order of magnitude better than that for the best previous measurements (see box plot). This new calorimeter will be used for certification of the temperatures and enthalpies of fusion of two more SRMs for calibration and validation of DSC.

New and better measurements for the enthalpy of combustion of SRM 217 were undertaken this year so as to provide reference data for precision and bias statements required by some organizations such as ASTM. Certifications of SRM 2233, cyclopentane for calibration of DSC, and SRM 2234, gallium for calibration of DSC, were completed this year.

Purpose: To provide reference materials and reference data of the highest accuracy for calibration and/or validation of calorimetric and thermodynamic instruments, procedures, and measurements. To provide assistance in the development of consensus standards, the development of international standards, and the removal of standards-related barriers to trade.

Use of calorimetric and thermodynamic measurements ranges from product specification and quality control of manufacturing to state-of-the-art research. In response to these needs, we are responsible for at least 14 current Standard Reference Materials (SRMs) for calorimetry. We have also developed several non-SRM standards used for calorimetry, densimetry, and isopiestic determination of vapor pressure. The Group continues to develop new standards and participates with voluntary standards organizations.

Differential scanning calorimetry (DSC) is perhaps the most widely used of the calorimetric methods. DSC requires calibration of both the enthalpy-flux and temperature scales of the instrument. Currently, the limitations of the accuracy of DSC are uncertainties in the reference materials used to calibrate the instruments. We are currently working to improve the accuracy of established properties for the reference materials for DSC.

Major Accomplishments: 1) A high-temperature adiabatic calorimeter was put into service. This calorimeter was used to determine the enthalpies and temperatures of transition of two of PTB's certified calorimetric reference materials, indium and tin. The measurements for indium are about an order of magnitude less uncertain than previous certified reference material determinations and other reference values. These measurements were conducted with a staff member from the PTB of Germany whose four-month visit was made under the terms of the Memorandum of Understanding that was signed between NIST, BAM, and PTB. His visit was for observation of our state-of-the-art calorimetric methods and for an assessment of their certified values for their certified calorimetric reference materials for DSC. 2) This fiscal year, the certification process for two new SRMs was completed. The two new SRMs are the first of four new SRMs that will serve as a calibration basis for DSC and other thermal analysis methods for temperatures from 100 K to 700 K. The two new SRMs, cyclopentane and gallium, can be used to calibrate DSC over the temperature range of 100 K to 300 K. These two SRMs are particularly important because low-temperature calibration of DSC must be accomplished with organic materials, which are not generally available in sufficient purity to be used in concert with literature values of temperatures and enthalpies of phase changes. 3) New measurements for the enthalpy of combustion of SRM 217 have been started. These new measurements are being made with a more accurate method than that used previously, so as to provide information for an ASTM International Precision and Bias Statement. 4) Articles were published on the enthalpy of fusion of gallium and on the two new SRMs developed for DSC.

Impact: These accomplishments will allow NIST customers to perform more accurate calibrations of instrumentation and perform validation determinations of measurement methods.

Future Plans: In FY2002, we expect to complete certification of SRMs 2235 and 2236. These two SRMs are for calibration of differential scanning calorimeters for temperatures up to 700 K. We also expect to conduct an interlaboratory study of a standard method for determination of the heat of reaction of thermally reactive materials.

Photochemical Reduction of CO_2 Catalyzed by Metalloporphyrins

CSTL Program: Chemical and Allied Products

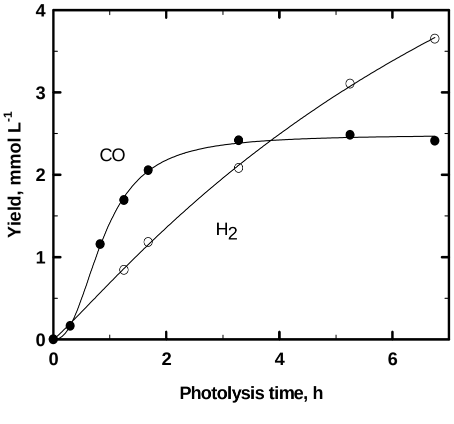
Authors: *P. Neta (838)*; *and J. Grodkowski (Institute of Nuclear Chemistry and Technology, Warsaw)*

Abstract: The accumulation of CO_2 in the atmosphere from fossil fuel burning leads to global warming. Various strategies are being considered to mitigate this problem. One of the more promising is to mimic nature and carry out the photochemical conversion of CO_2 into useful products, a strategy of photochemical reduction. Reduction of CO_2 can lead to the formation of various useful chemical compounds, such as CO, HCOOH, CH_2O, CH_3OH, and CH_4, which can either be used as fuels or as chemical feedstocks. Iron and cobalt porphyrins and related metal complexes have been proposed as catalysts for the photochemical reduction of CO_2. In order to successfully design production systems based on these catalysts, detailed fundamental information is needed on their photochemical and chemical properties, including their stability under operating conditions. Our approach has been to utilize them in model photochemical systems, to demonstrate formation of CO and/or HCOOH from CO_2, and then to examine the mechanism of catalysis and to determine the relevant rate constants by pulse radiolysis.

Purpose: To obtain kinetic and mechanistic information on the elementary reactions involved in the photochemical reduction of CO_2 and to develop strategies for the reduction of CO_2 into fuel or feedstock materials. This fundamental investigation into the photochemical reduction of CO_2 in the presence of metal porphyrins provides the Department of Energy with the information required for them to decide how and if process design based on homogeneous photocatalysis should go forward.

Major Accomplishments: We have found that iron and cobalt porphyrins (MP) catalyze the photochemical reduction of CO_2 to CO in dimethylformamide or acetonitrile solutions containing triethylamine (TEA) as a reductive quencher. In these solutions, $M^{III}P$ is reduced ultimately to M^0P, which reacts with CO_2, to form CO. In these photochemical studies, the quantum yields were low. We have found that the yield can be dramatically increased by the use of *p*-terphenyl (TP) as a photosensitizer. TP is very effectively photoreduced by TEA to form the radical anion, $TP^{\bullet -}$, which can reduce Co and Fe porphyrins very rapidly to their M^0P state. While this highly reduced state reacts with CO_2 to form CO, it also reacts with protons (formed in the photolysis) leading to production of H_2 and also to hydrogenation of the porphyrin. After the metalloporphyrin is hydrogenated in

Photolysis of iron porphyrin in acetonitrile solution containing triethylamine and p-terphenyl and saturated with CO_2



several successive steps, it decomposes and the catalytic reaction stops. Metal complexes of similar structures exhibit similar behavior; phthalocyanines and corroles have similar catalytic efficiencies whereas corrins are more efficient than porphyrins. In all cases, however, after the metal complex participates in many cycles of CO_2 reduction, it decomposes and the reaction stops. Attempts to protect the metal complexes against decomposition by embedding them in zeolytic materials did not succeed; CO_2 reduction was accompanied by the same side reaction and the hydrogenated complex within the zeolyte could not be reactivated. It appears that photochemical reduction of CO_2 with metal complexes as homogeneous catalysts suffers from the side reaction due to photochemically produced protons, and it may be that the only way to achieve more long lasting photochemical catalysis of CO_2 reduction is by using heterogeneous catalysis, for example, with semiconductor nanoparticles.

Impact: Although iron and cobalt porphyrins are capable to serve as efficient homogeneous catalysts for the photochemical reduction of CO_2, the decomposition of these substances has proven to be an intractable problem. Thus, we have recommended that there be no attempt to use this approach in subsequent process design.

Future Plans: Transition metal ions complexed to macrocyclic ligands are clearly efficient at gathering light energy and as electron transfer agents to catalyze the reduction of CO_2. Nature has done this for millennia. The present work has shown that a simple homogeneous approach is not likely to succeed. A more promising route is to investigate heterogeneous systems using semiconductor nanoparticles as light absorbers and catalysts. Besides being more stable, such systems could lead to better charge separation, possibly leading to the simultaneous reduction of CO_2 and the oxidation of water.

Bimolecular Reaction Rates and Mechanisms Relevant to Nano-structure Formation

CSTL Program: Exploratory Research Project
Author: *J.W. Hudgens*

Abstract: Gaseous organometallic compounds are used during manufacturing processes to deposit metals in semiconductor, optical, fuel cell, MEMS, and NEMS devices. The metal deposition rates and film quality are governed by the chemical environment above substrate surfaces formed by precursor compounds, by their decomposition products, and by the secondary products formed through bimolecular reactions with free radicals. Chemical modeling of any MOCVD process is difficult due to the absence of reliable kinetic rate equations for organometallic species. Moreover, useful reference mass spectra are unavailable. This project comprises two laboratory activities. The first uses a novel "beam-swallowing" mass spectrometer to measure the first reference mass spectra of organometallic compounds. These data will become available through the NIST Mass Spectral Database web site. The second uses mass spectrometry to measure bimolecular reactions between organometallic precursors and free radicals. The fundamental rate data will become available through the NIST Chemical Kinetics Database web site.

Purpose: Through a program of advanced measurements, this project measures and disseminates reference mass spectra and fundamental chemical kinetic properties of organometallic compounds. These data will facilitate reactor design, improve process monitoring accuracy, and enhance the safety of processes used to fabricate semiconductor, optical, fuel cell, MEMS, and NEMS devices.

Major Accomplishments: During FY2002 the novel laboratory apparatus was designed and its components were procured. The apparatus uses a pulsed molecular beam valve to introduce organometallic molecules for analysis. The design uses a series of apertures to shape the molecular beam so that thermally labile species never contact a hot ionizer surface. Because this "beam-swallowing" geometry inhibits the formation of pyrolysis products, the apparatus can measure high-quality reference mass spectra of radicals and unstable chemical species. By mounting a small pulse-heated, high-pressure flow reactor to the molecular beam valve, fundamental bimolecular mechanisms and reaction rates will also be measured.

Impact: These activities will enable CSTL to provide reliable fundamental reference data of organometallic compounds, fulfilling data needs of the chemical vapor deposition (CVD) equipment manufacturers and device production facilities. Since CVD precursor usage continues to grow rapidly within several industries, we expect that the demand for these data will increase proportionately.

Future Plans: Future plans include measurements of reference mass spectra and bimolecular reaction rates. Reference mass spectra of organometallic compounds will become available through the NIST Mass Spectral Database web site. Bimolecular reaction rate coefficients, initially for $M(CH_3)_n$ (M= Sn, Cu, Ga, Zn) species, will become available through the NIST Chemical Kinetics Database web site.

Kinetics and Thermophysical Properties of Ionic Liquid Systems

CSTL Program: Environmental Technologies and Services
Authors: *P. Neta, J.W. Magee, M. Frenkel, A. Laesecke, M.O. McLinden, and R.A. Perkins (838); J. Grodkowski (Institute of Nuclear Chemistry and Technology, Warsaw); and G. Kabo (Belarusian State U., Belarus)*

Abstract: Ionic liquids, a class of organic salts that are liquid at room temperature, have been proposed as solvents for "Green Processing." To provide U.S. industry with the knowledge base to exploit these solvents, we have begun to study the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions. Published and unpublished physical properties measurements are being compiled and evaluated, and experimental measurements have been initiated on ionic liquids representing broad classes of compounds. Rate constants for several oxidation and reduction reactions as well as for addition and hydrogen abstraction reactions in ionic liquids have been measured by pulse radiolysis and compared with rate constants for the same reactions in classical solvents. The rate constants often are lower in ionic liquids due to the high viscosity of these solvents limiting the diffusion rate. From additional effects on the rate constants, conclusions are drawn on the polarity and specific solvation effects of several ionic liquids.

Purpose: Ionic liquids are a class of organic salts that are liquid at or near room temperature. They are generally composed of a large asymmetric organic cation and either an organic or inorganic anion. As such, they are nonvolatile and nonflammable. Therefore, they have been proposed as solvents for "Green Processing." The physical properties of ionic liquids may be tuned, for example, by altering the hydrophobicity, and this affects the solubility, reaction rate, and selectivity. However, in spite of the many advantages that these fluids are predicted to offer, fundamental data on their physical and chemical properties are scarce. To provide U.S. industry with the knowledge base to exploit these solvents, we have begun to study the physical properties of ionic liquids and their effects on rate constants of fundamental chemical reactions.

Major Accomplishments: A physical properties database is being developed that will provide industry with access to evaluated physical property data, validated models to interpolate the available measurements, and structure-property tools to predict physical properties not yet measured. Measurements of physical property data are being collected for properties including melting point, density, electrical conductivity, refractive index, viscosity, heat capacity and surface tension. The focus of this data collection is on ionic liquid compounds that are liquid-phase at room temperature and are air and moisture stable, since they will have many practical applications. Though all possible sources are under consideration to uncover both published and unpublished measurements, it is becoming clear that measurements are scarce for most physical properties and are nearly nonexistent for vapor pressure or thermal conductivity. A single compound, 1-butyl-3-methylimidazolium hexafluorophosphate, has been systematically studied, but not its vapor pressure or thermal conductivity. We have initiated experimental measurements with a focus on five physical properties – density, heat capacity, vapor pressure, viscosity, and thermal conductivity. A preliminary study has shown that the choice of either the cation or the anion strongly influences the physical properties of the ionic liquid. For our experiments, we have acquired 100 mL pure samples of six compounds. We will explore the effects of length of the alkane side-chain attached to the cation, which has a rather bulky, asymmetric alkane-based structure that accounts for the low-temperature freezing points. Measurements have shown, for example, that doubling the chain length from butyl to octyl in 1-R-3-methylimidazolium hexafluorophosphate reduces the salt's freezing point by 84 ˚C. The influence of the anion on physical properties is also very strong and will be explored by selecting three anions $[PF_6]^-$, $[BF_4]^-$, and $[(CF_3SO_2)_2N]^-$ for experimental studies. We have begun a long-range collaboration with investigators in Belarus who are measuring heat capacities with a triple heat bridge calorimeter and vapor pressures with a Knudsen effusion apparatus. In our labs, we are measuring densities with a pycnometer, viscosities with Ubbelohde-type capillary viscometers and thermal conductivities with a transient hot-wire apparatus for the six compounds.

The pulse radiolysis technique was utilized to measure rate constants for several oxidation, reduction, addition, and hydrogen abstraction reactions in ionic liquids. In most cases the rate constants in ionic liquids are lower than those in classical solvents, in part because of the higher viscosities of ionic liquids, which limits the diffusion rate. In addition to this effect, significantly lower rate constants for redox reactions indicate that the ionic liquids behave as solvents of low polarity, suggesting a high degree of ion-association. Certain reduction and oxidation reactions are found to behave very differently in ionic liquids as compared with other solvents, both in the rate of the reaction and sometimes even in the direction in which the electron is transferred. These strong effects were found to be due to differences in the energy of solvation of the reactants and products in the various solvents, which affect the driving force of the reaction and thus its rate constant. Hydrogen abstraction and addition reactions, in general, are only slightly slower in ionic liquids compared with water and organic solvents.

Impact: This project will provide industry with essential data on physical properties and reaction kinetics to help accelerate the development of industrial processes that exploit the unique properties of ionic liquids.

Future Plans: Structure-property relationships for physical properties will be explored by analyzing evaluated data in our database. Based on the measurement trends that are found in the data, a group-contribution correlation will be developed for each key physical property to serve as a guide for future work in this area. Rate constants will be determined for reactions that are expected to be diffusion-controlled, and the viscosities of the ionic liquids will be measured, in order to establish the relationship between the viscosity and the diffusion-limited rate. The use of ionic liquids for the preparation and stabilization of colloidal metal nanoparticles will be explored.

Publications:

Behar, D., Neta, P., and Schultheisz, C., ***"Reaction Kinetics in Ionic Liquids as Studied by Pulse Radiolysis: Redox Reactions in the Solvents Methyltributylammonium***

Bis(trifluoromethylsulfonyl)imide and N-Butylpyridinium Tetrafluoroborate," J. Phys. Chem. A 106, 3139 (2002).

Grodkowski, J. and Neta, P., ***"Reaction Kinetics in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide. Pulse Radiolysis Study of*** $^{\bullet}CF_3$ ***Radical Reactions,"*** J. Phys. Chem. A 106, 5468 (2002).

Grodkowski, J. and Neta, P., ***"Reaction Kinetics in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide. Pulse Radiolysis Study of 4-Mercaptobenzoic Acid,"*** J. Phys. Chem. A 106, 9030 (2002).

Grodkowski, J. and Neta, P., ***"Formation and Reaction of*** $Br_2^{\bullet-}$ ***Radicals in the Ionic Liquid Methyltributylammonium Bis(tri-fluoromethylsulfonyl)imide and in Other Solvents,"*** J. Phys. Chem. A 106, in press (2002).

Paulechka, Y.U., Kabo, G.J., Blokhin, A.V., Vydrov, O.A., Magee, J.W., and Frenkel, M., ***"Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Ideal Gas State,"*** J. Chem. Eng. Data (in press).

Release of Version 7.0 of the NIST REFPROP Database

CSTL Program: Energy Systems
Authors: *E.W. Lemmon, M.O. McLinden, and M.L. Huber*

Abstract: A major revision of the NIST REFPROP database has been completed and is now being distributed by the NIST Standard Reference Data Program. Previous versions of this database have become the *de facto* standard for refrigerant properties worldwide. The new version includes additional fluids and mixtures, improved property models, increased calculational speed, and an enhanced user interface with additional properties and calculation and plotting options. Support is provided for using the property routines with other applications, including Excel spreadsheets and Visual Basic programs.

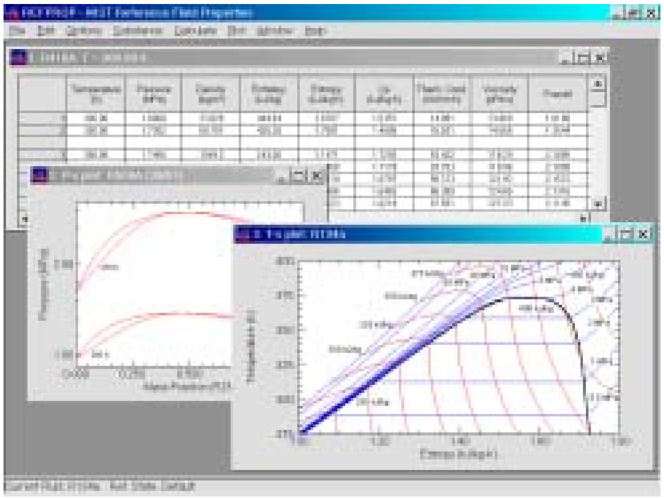
Purpose: Industry requires high accuracy thermophysical properties for the pure fluids and fluid mixtures used as working fluids in refrigeration and air conditioning systems. Property databases are widely needed for the design and analysis of refrigeration systems and are also used for other applications such as flow metering, calibrations, and the design, optimization, and innovation of chemical processes. High accuracy equations of state for pure fluids and their mixtures have been implemented along with models for the transport properties into a database entitled Reference Fluid Thermodynamic and Transport Properties (REFPROP, Version 7.0). This database incorporates the recent experimental and modeling results of the Division as well as the work of other laboratories published in the literature. By combining these sources into one package, industrial users have at their fingertips the most accurate properties available.

Major Accomplishments: Version 7.0 represents a major revision and upgrade of this database. New features include additional fluids and mixtures. The revision adds the main air constituents nitrogen, oxygen, and argon, and, thus, REFPROP 7.0 supplants the NIST 72 database on the properties of air. Ammonia/water mixtures are also included, incorporating a model which had been previously planned as a separate database. Arbitrary mixtures of up to 20 components may be specified, up from the five-component maximum in previous versions. Properties of HFC mixtures are calculated with a new Helmholtz energy model, and experimentally based values of the mixture parameters in this model are now available for 145 binary pairs. The viscosity and thermal conductivity models for 19 fluids have been updated based on recently published data.

The new graphical user interface (GUI) retains the overall look and feel of the Version 6 GUI, but incorporates enhanced usability and many new features and options, greatly improved speed of calculation, and many more options to prepare plots of thermodynamic surfaces. Support for Excel spreadsheets, Visual Basic programs, and other applications is also provided. Additional properties, including dielectric constant, freezing lines, and sublimation lines have been added where data are available. A wide variety of property diagrams may be automatically generated, including pressure-enthalpy and temperature-entropy diagrams and (for binary mixtures) temperature-composition and pressure-composition plots.

Impact: Previous versions of REFPROP have become the *de facto* standard for refrigerant properties. The REFPROP subroutines have been embedded in many industrial and commercial applications and provide consistent property values. Version 7.0 provides additional capabilities, increased accuracies, and additional pure fluids and mixtures.

Future Plans: The new title for REFPROP (Reference Fluid Thermodynamic and Transport Properties) with "Reference Fluid" replacing the "Refrigerant" of earlier versions indicates our direction: we will merge the NIST12 and NIST14 databases into REFPROP. Thus, a single database would encompass refrigerants, cryogenic fluids, hydrocarbons, and simple inorganics.



Properties of Refrigerant Mixtures Near the Critical Point

CSTL Program: Energy Systems
Authors: *M.O. McLinden, R.A. Perkins, E.W. Lemmon, A. Laesecke, and J.W. Magee*

Abstract: The refrigerant blends now seeing commercial application as replacements for HCFC-22 in air-conditioning equipment can operate near the refrigerant critical point. This exacts a performance penalty, and this project is supplying improved property data and models in support of the equipment testing and simulation work being carried out in BFRL to elucidate the causes of the performance penalty. Measurements of heat capacity, density, viscosity, and thermal conductivity have been completed. It has also resulted in significant advances in our equation-of-state models and fitting procedures. These results have improved the accuracy of our refrigerant mixture models, which are transferred to industry primarily through the NIST REFPROP database.

Purpose: HCFC-22 is the refrigerant presently used in most residential and small commercial air-conditioners and heat pumps, but it must be phased out under international treaty. Refrigerant mixtures are the likely replacement, and systems using mixtures are now on the market. These blends, typically composed of HFCs 32, 125, 134a, and/or 143a, have much lower critical temperatures than HCFC-22 and normally operate at considerably higher pressures. Under extreme conditions, the blends can operate near or above the refrigerant critical temperature and pressure, with major losses in capacity and efficiency. An understanding of the causes of such losses is a high priority of the Air-Conditioning and Refrigeration Technology Institute's industry-sponsored 21-CR research program. There are very few property data for the blends near their critical points. This work has focused on the measurement of new data for R-410A (a blend of HFC-32 and HFC-125) near its critical temperature. The new data, together with other available measurements for HFC mixtures, have been used to develop improved models for the entire class of HFC blends over wide ranges of conditions.

Major Accomplishments: We have completed P-ρ-T and heat capacity measurements for pure HFC-125 and a gravimetrically prepared mixture of R-410A at temperatures up to 400 K. The measurements on pure HFC-125 in the critical region have enabled the development of an improved equation of state. The new mixture measurements have been used along with other available experimental data for mixtures of HFCs-32, 125, 134a, and 143a to develop an improved, wide-ranging mixture model. The new model, explicit in the excess Helmholtz energy of the mixture, calculates all thermodynamic properties in the liquid, vapor, and supercritical regions with typical uncertainties of 0.1% in density and 0.5% in heat capacities and the speed of sound. Calculations of the bubble or dew point pressure along the vapor-liquid equilibrium boundary have uncertainties of 0.5%. Calculations in the critical region of the R-410A mixture have been greatly enhanced. In the course of this effort, significant advances in our modeling and fitting procedures have been made. These include nonlinear fitting techniques and theoretical constraints, resulting in models with fewer parameters that are yet more accurate with improved extrapolation behavior.

Viscosity and thermal conductivity measurements on R-410A and a blend of HFCs 125 and 143a, have been completed over the temperature range 300 to 420 K. Significant enhancement of the measured thermal conductivity is observed in the vicinity of the critical point. These new data will enable the development of improved models for the transport properties of these refrigerant mixtures.

Impact: Increasingly, refrigeration systems are using refrigerant blends, and the new models developed here have improved the accuracy of HFC mixture properties. The models are applicable to ternary and higher-order mixtures, without the need to fit additional parameters, and allow a complete description of all refrigerant mixtures. The advances in equation-of-state modeling have enabled us to provide better property models for a wide range of fluids. These improved models have been incorporated into the recently released Version 7.0 of the NIST REFPROP database.

Future Plans: Although this contract (jointly funded by ARTI and DoE) has been completed, improved models for the transport properties of these refrigerant mixtures will be developed using the present data as part of a renewal contract with DoE.

Viscosity Measurements and Model Comparisons for Second-Generation Alternative Refrigerant Blends

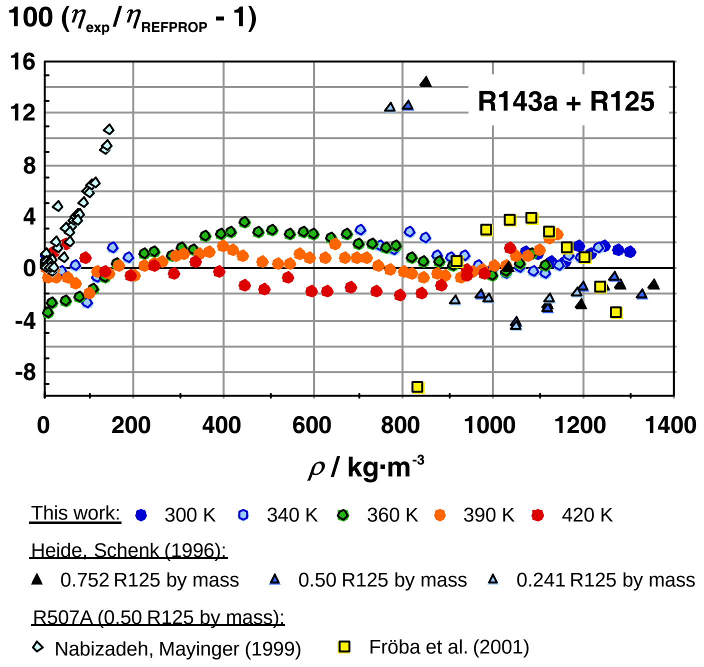
CSTL Program: Energy Systems
Author: *A. Laesecke*

Abstract: Wide-ranging viscosity measurements of the blends R507A (0.5 R143a + 0.5 R125 by mass) and R410A (0.5 R32 + 0.5 R125 by mass) were carried out in the torsional crystal viscometer at two subcritical and three supercritical isotherms with pressures up to 68 MPa. The subcritical measurements were conducted at the nominal temperatures 300 K (liquid only) and 340 K (liquid and vapor). Supercritical measurements included the nominal temperatures 360 K, 390 K, and 420 K. For reference, the viscosity of the blend R410A was measured at saturated liquid conditions between 240 K and 350 K with a sealed gravitational capillary viscometer because in that instrument the sample is not exposed to an electric field. The measurement results were compared with literature data and with values estimated *via* the extended corresponding states model in NIST Standard Reference Database 23 (REFPROP, Version 7).

Purpose: Significant energy penalties have been measured in HVAC systems with next-generation alternative refrigerant blends operating at condenser temperatures that are closer to their critical temperatures. To understand the causes of these energy penalties, working fluids have to be characterized not only at subcritical saturated vapor and liquid states but also at supercritical conditions. Literature viscosity data for such blends and working conditions are very sparse. Accordingly narrow is the basis on which predictive viscosity models for such mixtures have been developed. Also, substantial errors have been identified frequently in literature viscosity data for hydrofluorocarbon systems. Therefore, additional viscosity measurements are needed to built a broader base of validated and reliable data for these important fluids. Measurements on the blend R410A in two different viscometers presented an opportunity to discern the susceptibility of this fluid to an applied electric field and to quantify its effect on the results of the torsional crystal viscometer in an effort to extend the application range of this instrument.

Major Accomplishments: The measured viscosity data fill large gaps for both alternative refrigerant blends. They serve as a reference to examine literature data for measurement errors, and they give indications where the predictive model may be improved. As an example, the deviation plot compares the range and deviation of the experimental results and literature data for mixtures of R143a + R125. The blend R507A exhibited very low electrical conductance (< 0.62 μS) and the measured viscosities agree with predicted viscosities over the entire density range within the mutual uncertainties of measurement and model. The three available literature data sets deviate from the model systematically and in opposite directions. While the saturated liquid data of Heide and Schenk (1996) are up to 14 % higher, those by Fröba et al. (2001) tend to be up to 9 % lower. Good agreement between predicted and experimental data exists in the limit of zero density. However, with increasing density, the data of Nabizadeh and Mayinger (1999) are systematically up to 11 % higher than the present results and the predicted values.

The blend R410A exhibited substantially higher electrical conductances (< 5.7 μS) as were observed consistently with R32 (difluoromethane) and its mixtures. While the data obtained with the torsional crystal viscometer are systematically higher than predicted viscosities, the results from the sealed capillary viscometer agree with them very well. This suggests an additional flow impedance besides Newtonian shear at the crystal surface when the torsional crystal viscometer is employed with polar fluids where charge carriers may be present. An explanation takes into account an electrokinetic secondary flow perpendicular to the crystal surface whose intensity depends on the electrical conductance of the sample.



Impact: The results of this intramural round robin reduce uncertainties in several areas and improve the thermophysical property basis for the design of advanced HVAC systems. The measured viscosities cover considerably wider ranges than the previously available literature data. They corroborate the extended corresponding states model as a predictive tool and indicate possible refinements. They eliminate bias of the predictive model due to literature data, some of which are shown to be burdened with systematic errors. Besides their industrial relevance, the results of this study lay the foundation for the development of the torsional crystal viscometer to probe flows under combined molecular and electroviscous friction as occur frequently in microfluidic systems.

Publication:

Laesecke, A., ***"Sub- and Supercritical Viscosity Measurements of Binary and Ternary Hydrofluorocarbon Mixtures with a Torsional Crystal Viscometer,"*** presented at the Third Halocarbon Workshop during the 17th IUPAC Conference on Chemical Thermodynamics, July 28 – August 3, 2002, Rostock, Germany, Proceedings of the Workshop will be published in a Special Issue of *Fluid Phase Equilibria* in 2003, Guest editors: U. K. Deiters (Cologne, Germany) and A. Laesecke (NIST).

Thermal Conductivity of Natural Gas Constituents

CSTL Program: Energy Systems
Author: *R.A. Perkins*

Abstract: Knowledge of the thermal conductivity of natural-gas mixtures is required to optimize heat exchange surfaces in processes for power conversion, liquefaction, separation, and purification. This work focuses on the thermal conductivity of pure propane, butane, and isobutane at temperatures from their triple points to 600 K at pressures up to 70 MPa. New transient hot-wire measurements of thermal conductivity cover the vapor, liquid, and supercritical gas phases with reduced uncertainty and fill regions where data were not available. The thermal conductivity data are used to develop accurate correlation surfaces for these three pure fluids that form the basis of improved models and standards for natural-gas mixtures.

Purpose: Natural gas and liquefied petroleum gas are abundant and clean burning fuels that typically consist of mixtures of light hydrocarbons with nitrogen and carbon dioxide. Examination of these light-hydrocarbon constituents reveals the need for improved knowledge of the thermal conductivity of propane, butane, and isobutane over a wide range of conditions. This improved knowledge of the thermal conductivity of the pure constituents will form the basis for improved mixture models. In particular, propane is an ideal reference fluid for extended corresponding states models of the transport properties of natural gas mixtures since its liquid state exists over an exceptionally wide range of reduced temperature.

Major Accomplishments: We have measured the thermal conductivity of pure propane, butane, and isobutane at temperatures from their triple points (86 K for propane) to 600 K with pressures up to 70 MPa with the transient hot-wire technique. The measurements were made with extremely small tungsten wires of 4 μm diameter to reduce uncertainty due to corrections. For the dilute vapor, the transient measurements were supplemented with steady-state measurements with the same hot wires. Significant enhancement of the measured thermal conductivity was observed in the vicinity of the critical point for each gas. These data revealed errors in the best available correlations for thermal conductivity that were greater that 10 % near the critical density of each fluid and again approaching the triple point of butane and isobutane. These new data were used to develop reliable models for the thermal conductivity of these important constituents of natural-gas mixtures. These improved models were developed in collaboration with the International Association for Transport Properties and are recommended as interim standards.

Impact: Natural gas and liquefied petroleum gas are multicomponent blends with a wide variation in composition. Corresponding states models are applicable to ternary and higher-order mixtures and allow a complete description of the thermal conductivity of natural gas and liquefied petroleum gas mixtures. The improved knowledge of the thermal conductivity of propane, butane, and isobutane enables the development of better thermal conductivity models for these fuel mixtures. In addition, these three gases are considered to be “natural refrigerants” and their use has been proposed in alternative refrigerant blends. These improved models for thermal conductivity have been incorporated into the recently released Version 7.0 of the NIST REFPROP database.

Future Plans: The present correlations for the thermal conductivity of propane, butane, and isobutane are considered to be interim recommendations since the analysis was based on calculations from equations of state with known limitations in the critical region. These interim recommendations will be replaced with reference quality correlations when improved equations of state are developed and accepted as consensus standards for each gas.

Industrial Fluid Properties Simulation Challenge: Benchmark Standards

CSTL Program: Chemical and Allied Products

Authors: *D.G. Friend, J.W. Magee, A.M. Chaka, R. Mountain, R.D. Johnson III, L.A. Watts, E.W. Lemmon, R.D. Chirico, M.O. McLinden, A. Laesecke, and T. Bruno*

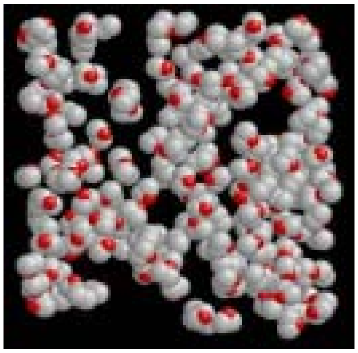
Abstract: The First Industrial Fluid Properties Challenge was sponsored by the Computational Molecular Science and Engineering Forum Group (CoMSEF Group) of the American Institute of Chemical Engineers (AIChE) in order to promote and to advance the status of molecular simulation for the calculation of properties of interest to industry. NIST has had a key role in organizing this contest, together with industrial participants from such companies as Dow Chemical, BP, DuPont, etc. In particular, NIST has coordinated activities related to establishing benchmark standards against which competition entries will be compared. Questions posed by the competition were prioritized by the industrial participants and included the calculation of certain vapor-liquid equilibrium properties, densities, and viscosities. Evaluations and measurements have been completed in the last year. A total of twelve supporting documents were created, involving about 35 benchmark points with uncertainties. Contest entries are now being evaluated in a double-blind protocol, with the announcement of results and discussion scheduled for a special symposium at the National AIChE Meeting in November 2002.

Purpose: Molecular simulation is widely perceived to be a tool of the future in the determination of thermophysical properties of interest to industry. In some contexts, it is currently considered as an alternative to measurements or conventional theoretical approaches. However, this tool has limited value because of the absence of a critical evaluation of its capabilities: no one knows how good the results are. More general applicability awaits the development of standardized validated force fields and careful objective evaluation of simulation algorithms. A workshop on this subject was held at NIST in 2001, and the framework for the simulation challenge was established. The simulation contest will serve to assist in the transfer of the technology to prospective industrial users, to identify strengths and weaknesses of the various techniques, to begin the process for systematic development of force fields, and to initiate general protocols for the assessment of property prediction techniques.

Major Accomplishments: With partners on the benchmarking committee from the Dow Chemical Company, twelve benchmark documents were created for the challenge problems involving vapor-liquid equilibrium, density, and viscosity. In some cases, the benchmarks were based on a careful evaluation of published or unpublished experimental results. For other challenge questions, experimental measurements were conducted for the density and viscosity of specified pure fluids and mixtures conducted at Dow Chemical and at NIST. The NIST measurements, in particular, required analysis and purification of available specimens, extension of the temperature/density range of a vibrating tube densimeter apparatus, and establishment of calibration points at high densities using a new double-sinker densimeter.

Impact: Entries to the First Industrial Fluid Properties Challenge are currently being evaluated against the benchmark standards discussed above; the evaluation protocol ensures that the contestants had no access to the benchmark standards and the judges are not made aware of the identities of the authors of each entry. The most successful entries will be presented an award, including a monetary prize provided by industry, at the Fall AIChE Meeting. A transfer of the most appropriate and successful tools to industrial users is anticipated through site visits and publications. The successes and challenges for the various techniques will be discussed at the meeting, and common paths towards future positive developments in the techniques are envisioned.

Future Plans: Plans are being considered for a second challenge to be completed in 2004; the results from the first competition and input from industry and practitioners will serve as input. The paths toward systematization of force field development and evaluation of algorithms will be identified as this project progresses.



Double-Sinker Densimeter for High-Accuracy Fluid Density Measurements

CSTL Program: Chemical and Allied Products

Authors: *M.O. McLinden (838); and C. Lösch (Rubotherm Präzisionsmesstechnik, Bochum, Germany)*

Abstract: A new apparatus for high-accuracy fluid density measurements over wide ranges of temperature, pressure, and density (–180 to +250 ˚C; 0 to 40 MPa; 5 to 1700 kg/m^3) has been completed and put into operation. This new apparatus extends our capabilities to higher temperatures and lower densities and reduces the uncertainties by an order of magnitude. We will use these capabilities to provide data on key industrial fluids and mixtures and develop standard reference materials (SRMs) for fluid density.

Purpose: Density as a function of temperature and pressure is one of the most important properties for the determination of a thermodynamic equation of state of a fluid. Density is also vital in fluid metering applications in research and industry. The objective of this work is to improve our density capabilities to best-in-the-world class.

Major Accomplishments: This new instrument employs an Archimedes (buoyancy) technique using two sinkers immersed in the fluid of interest. The use of two sinkers leads to a cancellation of effects, such as surface adsorption, which can affect the accuracy of single-sinker techniques, making this instrument especially useful for the measurement of complex mixtures and vapors near saturation.

The compact double-sinker densimeter is complete and operational. The apparatus consists of six key subsystems: (1) the two sinkers which together with a balance, a magnetic suspension coupling, and a mechanism to pick up each sinker constitute the density measuring system; (2) a measuring cell (pressure vessel) which contains the fluid of interest; (3) pressure and temperature measuring instruments; (4) a thermostat incorporating liquid nitrogen or fluid cooling and electrical heating; (5) a computer which controls the entire system and records the experimental data; and (6) auxiliary systems such as a sample charging manifold and a vacuum system.

The density measuring system was developed in collaboration with Rubotherm, Inc. of Bochum, Germany. Their components were integrated with the bulk of the system, which was fabricated in the NIST Instrument Shops. The magnetic suspension coupling has proven stable and reproducible to better than 5 μg; this yields a reproducibility in density of 0.0005 kg/m^3 (*i.e.*, 5 ppm or less for gases of moderate density as well as liquids). The volumes of the sinkers have been determined to an uncertainty of 20 ppm by comparison to silicon density standards. The final uncertainty in the density depends on both the weighings and the sinker volumes, and we are confident that we will achieve our goal of 0.01 % (100 ppm) uncertainty in density. Although originally designed for measurements on low-density gases, the apparatus has proven capable on liquids with densities as high as 1700 kg/m^3.

Impact: This apparatus defines the new best-in-the-world instrument for wide-ranging, high-accuracy P-ρ-T measurements. Furthermore, it provides an absolute measure of density, *i.e.*, no calibration fluids are needed.

Future Plans: This new instrument will be used to develop toluene as a density SRM over the temperature range –50 ˚C to +150 ˚C and the pressure range 0.1 MPa to 30 MPa. The SRM work will include extensive tests to investigate possible systematic errors and establish strict traceability of fluid P-ρ-T properties to fundamental standards. This is important since the new densimeter surpasses the capabilities of all existing instruments, rendering moot any comparison with published data. The properties of propane will be measured as part of a project to develop an improved equation of state. Measurements on numerous other fluids and mixtures of industrial importance are planned for FY'04 and beyond.

Sinkers and magnetic suspension coupling comprising the heart of the densimeter. The electromagnet at the top hangs from the balance and levitates the permanent magnet below it. In this photo, the bottom sinker is being weighed, while the top sinker sits on its rest. This assembly is normally contained within a pressure vessel.

The Initiation Step in Pyrophoric Combustion of Silane

CSTL Program: Exploratory Research Project

Authors: *K.K. Irikura (838); and M.S. Gordon, I. Adamovic, and H.M. Netzloff (Iowa State Univ.)*

Abstract: In the semiconductor industry, combustion of pyrophoric gases such as silane (SiH_4) and phosphine (PH_3) is an important safety hazard. Although the combustion can have explosive force, it is initiated by relatively slow reactions. After an induction period, the primary products react rapidly to produce the characteristic flame or explosion. Silane combustion has been the subject of significant kinetics modeling efforts at NIST and elsewhere, but the initial step remains conjectural. We have suggested some new mechanisms for this reaction and are evaluating them using advanced methods of quantum chemistry. In addition to its importance for pyrophoric combustion, similar chemistry may be responsible for initiating the autoxidation of organic compounds, including plastics, elastomers, lubricants, and edible fats and oils. An understanding of how these reactions occur may lead to new ways of suppressing undesirable oxidative reactions.

Purpose: Oxidative degradation of hydrocarbon derivatives is the organic equivalent of rusting. Unwanted oxidation of plastics, of which the USA produces 100 billions pounds annually, presents an important economic burden. Likewise, lubricating fluids no longer function properly if oxidized. Edible fats and oils become rancid and unfit for consumption. These chemical processes are all characterized by slow initiation followed by a faster chain reaction. Despite the practical interest, most purported progress has been merely speculative.

Superficially, the pyrophoric combustion of semiconductor-processing gases might not appear to be related to autoxidation. Both processes, however, involve oxidation by atmospheric oxygen and chain reactions that follow a much slower, unknown initiation step. In this project, we chose silane combustion as a model system for autoxidation due to the following advantages: (1) silane is a well-defined compound, (2) experimental data on ignition delays are available for comparison with models, (3) kinetic models have already been developed, (4) it is a small molecule amenable to high-level theory, and (5) it is of practical interest in its own right. We consider initiation reactions involving singlet and triplet oxygen, and also the "two-state" mechanism discovered recently in the gas-phase oxidation of saturated hydrocarbons by FeO^+.

Major Accomplishments: A contract to Iowa State University (ISU) was awarded in August. Nonetheless, we have already obtained a preliminary transition structure for the singlet reaction. The preferred theoretical method has also been identified. Although this capability is unavailable in standard software packages, it has been programmed into the developmental version of the ISU software.

Impact: An understanding of the initiation step in silane pyrophoricity may lead to procedures for retarding this unwanted reaction.

Future Plans: This project is in its early stages. We intend to evaluate the alternative mechanisms over the coming year, which will include kinetics modeling elsewhere in CSTL. If this project is successful, future work will address the major, long-standing problem of hydrocarbon autoxidation.

Conference on Biophysics from First Principles: From the Electronic to the Mesoscale, September 7-12, 2002, San Feliu, Spain

CSTL Programs: Biomaterials, and Pharmaceuticals and Biomanufacturing
Authors: *A.M. Chaka (838); and F. Seno (Department of Physics, University of Padova, Italy)*

Abstract: The purpose of this conference was to bring together theoretical and experimental researchers from physics, chemistry, biological sciences and industry to foster interdisciplinary approaches to the study of living systems. The principal focus was on the application of theoretical physics – from first principles to classical simulations, as well as statistical approaches – to understanding biological processes. Session topics included: Understanding Biological Mechanisms; Transition Metal Chemistry; Predicting the Biological Activity of Chemicals; Structure and Function of Biological Macromolecules; and Molecular Interactions and Solvation: Short- and Long-range Forces. Challenges facing industry and the environment were presented by invited plenary speakers from Dupont (Daniel Kleier, pesticide invention), BASF (Hugo Kubinyi, drug design and virtual screening), and the U.S. Environmental Protection Agency (EPA) (James Rabinowitz, understanding health effects of environmental chemicals). The maximum capacity of 135 researchers from academic and government institutions around the world attended, as well as industrial participants from companies such as Dupont, BASF, Unilever, Toshiba, and IBM. There was a waiting list of over 150 people hoping to attend. The conference was deemed so successful and the interdisciplinary need so timely that the European Science Foundation has decided to initiate a new conference series entitled "Computational Biophysics: Integrating Theoretical Physics and Biology" to be held every two years.

Purpose: Physicists and biologists have few opportunities to interact, yet such interaction has the potential to contribute greatly to progress in both fields. No single simulation or experimental approach will provide all the answers, and solving life science problems requires the skills and knowledge from across traditional disciplines. Advances in physics, such as electronic structure and *ab initio* dynamics, have the potential to play a vital central role in the study of biological systems. The size and complexity of biological problems have driven development of classical approaches such as molecular mechanics and force field methods, and the calculation of free energy of solvation. Theoretical models and numerical simulations from both disciplines need to be integrated to achieve the synergy that is necessary to make real predictions.

Major Accomplishments: This conference represents the first time leading researchers in the field of biological simulations (M. Karplus, K. Schulten, M. Klein), experimental biology (C. Dobson, H. Schrempf), theoretical physics (M. Parrinello, R. Car, B. Lundqvist), and experimental physics (B. Kasemo W. Zinth) have been brought together for a week-long, intensive conference and discussions. Several challenges were identified, such as a continuing mechanism to foster interdisciplinary research between biologists and physicists. The importance of chemistry as a key link between biology and physics was also stressed. The major challenge identified is the integration of time and length scales, particularly to treat complex problems such as protein folding, biochemical pathways, toxicology, and ion transport through membranes.

Impact: A new international conference series has been initiated to address needs identified by this meeting. A general consensus was that those attending knew less than 10% of the other participants, thus learning a great deal regarding problems and methods in other areas. Many new collaborations were initiated.

Future Plans: A.M. Chaka will continue to serve on the steering committee for the new EURESCO Computational Biophysics: Integrating Theoretical Physics and Biology Conference series. The Computational Chemistry Group will develop plans to address key modeling challenges identified such as integrating time and length scales, validating current simulation methods, mesoscale phenomena, and improving robustness of biological simulations through increased use of first principles techniques.

Molecular Electronics. Negative Differential Resistance Explained: Guidelines and a Model to Design New Molecules

CSTL Program: Chemical and Allied Products

Authors: *C.A. Gonzalez (838); Y. Simón-Manso (Universidad de Chile); and Y. Aray (Instituto Venezolano de Investigaciones Científicas)*

Abstract: The observation of abrupt changes in the slope in the current-voltage (I-V) characteristics of molecular devices formed by molecule-metal interfaces is one of the most promising phenomena in the field of molecular electronics that could potentially lead to the manufacture of molecular electronic devices at the nanoscale such as diodes, gates, etc. In this work a simple quantum-chemical model that provides insight into the understanding of the observed negative differential resistance (NDR) in current-voltage characteristics of molecule-metal tunneling junctions has been developed and validated. The model is based in quantum chemical calculations of the electronic structure of bridge molecules in a capacitor-like electric field that mimics the potential spatial profile of the junction. The results show that a plausible mechanism for NDR behavior in planar molecular bridges, like the prototype molecule π-conjugated phenyl-ethylene oligomer 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate (PEO) involves a substantial rearrangement of the charge density of the neutral bridge at a threshold voltage. The model developed in this work provides a simple and powerful tool for the rational design of other molecular systems that could exhibit similar NDR behavior.

Purpose: This work focuses on the study of molecular systems that exhibit NDR behavior, a property necessary for the fabrication of molecular diodes and electronic circuits. Given the prospects of manufacturing more powerful and versatile electronics components based on molecules, the microelectronics industry has expended significant interest in novel technologies that can lead to the design and fabrication of such devices. Although there has been significant progress in the synthesis of such systems, the mechanisms leading to this behavior are not well understood. In order to understand the fundamental mechanisms leading to NDR in molecules and to develop theoretical tools that can complement the experimental efforts leading to the rational design of such systems, a reliable and simple theoretical model based on density functional theory calculations of the isolated molecule in the presence of an external electric field has been developed. The model has been compared to predictions based on more rigorous and computationally expensive calculations that take the metallic electrodes into consideration. The results indicate excellent agreement between the model and the rigorous calculations.

Major Accomplishments: The theoretical model was able to explain the dominant mechanisms for NDR behavior in the π-conjugated PEO molecule, the first molecule known to exhibit NDR. According to our results, NDR in this molecule is due to substantial charge density rearrangements caused by external voltage increases. These changes are highly affected by the presence of the nitro group, which acts as an electron basin of attraction that forces the system to behave as a quantum well trapped between two barriers. Predictions based on the model indicate that substituting the nitro group for electron withdrawing groups such as fluorine atoms will also lead to NDR behavior. Currently, these predictions are being validated by measurements performed on the recently synthesized π-conjugated phenyl-ethylene oligomer 2’-amino-4,4’-di(ethynylphenyl)-5’-fluoro-1-benzenethiolate.

Impact: It is expected that the researchers will start using the theoretical tools developed in this work in order to guide their designs of new NDR systems. Scientists from different microelectronics companies have indicated their interest in simple models like the one presented in this work, since it would help them “screen” a potentially large number of candidate molecules.

Future Plans: The model will be tested on other molecular systems as soon as new measurements are available. To this end, this phase of the project will be conducted in close collaboration with experimental groups at CSTL.

An Efficient Model to Compute the Exact Exchange Potential in Density Functional Theory

CSTL Programs: Microelectronics, and Energy Systems
Authors: *C.A. Gonzalez, and T.C. Allison (838); E. Ludena, V. Karasiev, and I. Gonzalez (Instituto Venezolano de Investigaciones Científicas); and Y. Simón-Manso (Universidad de Chile)*

Abstract: A robust and computationally efficient exchange functional for density functional theory has been developed and implemented. This functional is computed variationally through the standard Kohn-Sham procedure and does not require parameters. It is shown that this functional (and its potential) reproduces the "exact exchange" behavior and that it eliminates serious problems such as lack of self-interaction correction, non-variational character, and existence of spurious electron correlation, encountered in most of the exchange functionals used currently by the scientific community. Methods such as the one described in this work will allow scientists to compute physical and chemical properties of a large variety of chemical systems, complementing the metrology of these properties based on expensive and complicated experimental setups.

Purpose: The use of state-of-the-art electronic structure calculations based on *ab initio* quantum chemical methodologies has become widely popular. Today, scientists in industry and academia make use of this technology to guide complicated experimental work in a large variety of areas including chemical reactivity, catalysis, chemical kinetics, combustion chemistry, environmental chemistry and organic synthesis. Density functional theory (DFT) has become one of the most widely used methods mainly due to its relatively low computational expense. The electronic energy within the DFT formalism is a functional of the electron density that consists of an "exchange" energy term and a "correlation" energy term. Although, in principle, there exists a universal DFT functional that can describe the electronic problem exactly, the discovery of such functional has eluded scientists around the world for years. In practice, arbitrary forms for the DFT functionals are parameterized in order to reproduce the experimental energetics of a relatively small set of molecular systems. Systematic validation conducted by the Computational Chemistry Group of CSTL indicates that most of these functionals are not transferable to the computation of different chemical properties, where they show a marked erratic behavior. The results of the work presented here indicate that the major source of error can be traced back to the "exchange" functional. It has been found that these functionals are non-variational and do not eliminate serious self-interactions of the electrons. In addition, the parameterization used to generate these functionals includes spurious electron "correlation." In this work, we have developed a method called "Self-Consistent Alpha" (SC-α) that eliminates all these problems and does not introduce further parameterization. The SC-α method involves the correction of the DFT exchange energy and its corresponding potential at each Kohm-Sham cycle by a factor computed as the ratio between the Hartree-Fock exchange and the DFT exchange.

Major Accomplishments: The SC-α method has been successfully implemented and tested on a series of atoms and diatomic molecules for which values for the "exact exchange" energies are available. The results show excellent agreement between the SC-α values and the “exact exchange” results.

Impact: The use of the SC-α methodology will allow scientists to compute physical and chemical properties of complicated chemical systems in a reliable and cost-effective manner. The development of this methodology constitutes a major advancement in the area of DFT, a computational chemistry technique widely used by scientists in industry.

Future Plans: Further work leading to validation of the SC-α method in the calculation of different physical and chemical properties of polyatomic systems is under way. In particular, properties such as potential energy barriers critical for kinetic studies of chemical reactions will be studied. A similar study in order to improve the current correlation functionals will also be conducted.

Environmental Control of α-Cr_2O_3 (0001) Surface Chemistry

CSTL Programs: Chemical and Allied Products, and Technologies for Future Measurements and Standards
Authors: *A.M. Chaka (838); N. Harrison (Imperial College and Daresbury Laboratory); A. Wander (Daresbury Laboratory); and X.-G. Wang (Delphi)*

Abstract: Surface structure and properties are key to the performance of chromium oxide in a wide variety of technological applications, ranging from passivation of stainless steel to catalytic reduction of pollutants. Yet, despite considerable experimental and theoretical efforts, the surface structure and even the surface stoichiometry are matters of strong controversy. We have developed a method of *ab initio* thermodynamics that enables us to link 0 K density functional theory electronic structure and vibrational calculations to finite temperatures and pressures to calculate the free energy of a surface in equilibrium with multiple species in the environment. The resultant phase diagram of the α-Cr_2O_3 (0001) surface in the presence of O_2, H_2O, and O_2 indicates a complex surface chemistry with an extreme sensitivity to environmental conditions, which can account for much of the variability and controversy in previous studies. Upon exposure to sufficient oxygen pressure, exposed Cr atoms on the surface react to form strong chromyl Cr=O bonds. This chromyl group is extremely stable and can explain how oxygen poisons the surface of chromia catalysts and passivates the surface of stainless steel, which is primarily chromium that has segregated to the surface. The calculated phase diagram also indicates that this chromyl group can be removed by low oxygen pressure and high temperature, which is consistent with experimental observations of catalyst regeneration and susceptibility to corrosion in stainless steel after exposure to heat and vacuum.

Purpose: Chromium oxide is very important for a wide variety of technological applications such as catalysis and surface passivation of metal alloys like stainless steel. Chromium is also added to aluminum alloys because it will segregate to the surface, oxidize, and provide an almost universal foundation for primer and coatings for subsequent surface engineering. Despite its importance, the surface structure and stoichiometry of chromium oxide is not well understood because its insulating character renders analytical techniques based on electron spectroscopy problematic. It is also difficult to obtain clean, well-ordered surfaces for investigation under ultra-high vacuum, let alone interpret experimental observations of systems under industrial conditions. Hence, there is a need for theoretical models that can identify the most likely surface structures, and predict how they will react under realistic conditions in a complex environment. These models can then be used to guide experiment and interpret complex results.

Major Accomplishments: The phase diagram of the α-Cr_2O_3 (0001) surface in equilibrium with O_2, H_2O, and O_2 has been calculated from first principles, and is consistent with experimental observations. Formation of a strong Cr=O bond upon exposure to oxygen can account for the passivation of stainless steel and oxygen poisoning of catalysts.

Impact: Understanding and controlling surface chemistry of chromium oxide has a broad impact on the catalyst, automotive, steel, and aluminum manufacturing industries.

Future Plans: Alcoa is very interested in using this technique to engineer surfaces of chromium-aluminum alloys. Hence, we will be extending this technique to calculate the phase diagrams for mixed-metal oxide surfaces and to identify processing conditions that favor formation of desirable surfaces. In addition, due to the great sensitivity of the chromium oxide surface structure and bonding to the environment, we plan to explore the potential of this oxide as a chemical sensor.

Stability of Potential High-Temperature Heat Transfer Fluids

CSTL Program: Energy Systems
Authors: *D.G. Friend, T.J. Bruno, and W.C. Anderson*

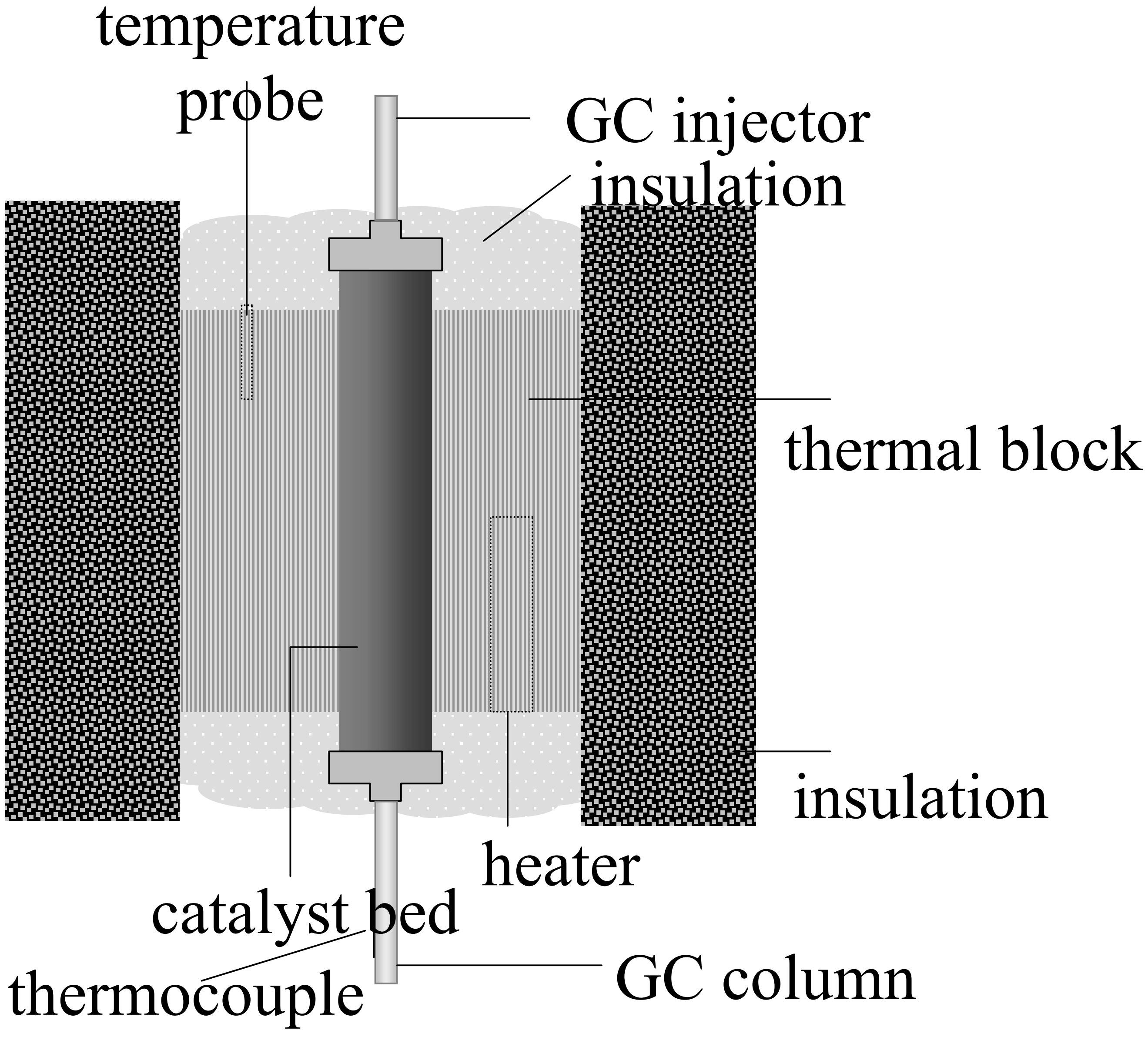
Abstract: The thermophysical properties of light hydrocarbons of between 5 and 8 carbons make this family of compounds attractive as heat transfer fluids for solar panels used in electric power generation. In this solar energy application, heat transfer fluids are subjected to high temperatures and pressures on the order of 315 °C and 4.1 MPa (600 °F and 600 psia). At these temperatures and pressures, the stability of many such fluids is uncertain, especially long term, and in contact with potentially catalytic surfaces. We are working with the National Renewable Energy Laboratory (NREL) to establish the best values for key thermophysical properties of the pentanes, and, especially, to determine the stability of pentanes and light aromatics. We are also measuring the kinetics of decomposition at 315 °C and 4.1 MPa in the presence and absence of catalytic materials. The experimental results, based on reaction chromatography and ampoule decomposition kinetics measurements, indicate that these fluids may not be sufficiently stable for the intended application.

Purpose: There has been growing interest in integrating parabolic trough solar systems with organic Rankine power cycles (ORC); this integration of technologies would open a new market niche where solar technologies have been too expensive. Although ORC technology is very mature, the existing plants operate at temperatures below about 200 °C. Preliminary analysis at NREL showed that pentanes (and fluids with similar thermophysical properties) as working fluids could provide high cycle efficiencies. Unfortunately, these fluids had not been tested at high temperatures, and there were concerns about decomposition of the working fluids. NIST was asked to respond to concerns raised by the solar and ORC industry to assist in determining the suitability of pentane isomers in parabolic trough solar systems by study of the stability of the fluids at high temperatures with and without catalytic materials.

Major Accomplishments: We have completed our initial efforts to establish key properties for the pentane isomers to be used in cycle design calculations. The stability measurements are based on two techniques: (1) reaction chromatography, a method developed at NIST (see illustration), and (2) ampoule decomposition kinetics measurements. These methods allow the reaction to be measured as a function of temperature in the presence and absence of catalytic surface materials. Results for n-pentane, for example (with residence reaction times up to about 10 days), indicate a rate constant for decomposition of about 8.4×10^{-5} min^{-1}. Isopentane, neopentane, and toluene have also been shown to decompose at the conditions of interest.

Impact: The results to date indicate that most of the common fluids examined are not suitable as heat transfer fluids in solar trough applications. Thus, these fluids will not be studied further in laboratory scale or pilot demonstration facilities. However, the integrated technology is still of interest, and alternative heat transfer fluids are being considered.

Future Plans: In conjunction with researchers at NREL, several additional heat transfer fluids and mixtures have been identified. Uncatalyzed reaction screening measurements will be performed on two candidates, and continued study depends, in part, on results from these experiments.


temperature
probe
GC injector
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thermal block
insulation
heater
catalyst bed
thermocouple
GC column

Cylinder Filling Ratios for Compressed Liquids

CSTL Program: Chemical and Allied Products
Authors: *M.L. Huber, and D.G. Friend*

Abstract: The filling ratio is the ratio of the mass of a fluid to the mass of water at 15 ˚C that would completely fill a pressure receptacle. Depending on the fluid involved, there are different restrictions placed on the filling ratio to ensure safety. For example, it is important that cylinders exposed to high temperatures that may be encountered during storage or transportation, do not develop high pressures that could exceed safety limits. Therefore, it is important to be able to determine the filling ratio accurately for a wide variety of fluids. For this project, models were developed to compute the filling ratio using several different methods. When available, high-accuracy equations of state, such as those in NIST Standard Reference Databases were used. For fluids where dedicated, high-accuracy equations of state were not available, a predictive model based on the theory of extended corresponding states was used. This method has been used successfully in the past for modeling hydrocarbons, cryogens, and refrigerants. The results were verified by comparison with experimental data where available and existing or proposed international or domestic guidelines. The information was then provided to the U.S. Department of Transportation (DOT) as input into proposed United Nations (UN) recommendations and domestic DOT guidelines.

Purpose: As the UN Committee of Experts on the Transport of Dangerous Goods performs its mandated study on safety issues related to international commerce, DOT provides input related to domestic industrial requirements and the domestic regulatory environment. NIST has been asked to assist in the development of cylinder filling ratio guidelines to be used in domestic and international commerce of certain fluids. Specifically, the purpose of this project was to provide reliable values of the filling ratio for a wide variety of industrially important fluids including fluids such as refrigerants, hydrocarbon gases, welding gases, semiconductor processing fluids, odorants, and other commercially available fluids.

Major Accomplishments: Filling ratio calculations for a wide variety of fluids were made and the results presented in the form of a spreadsheet. The best models available were used for the calculation of the fluid density required in the computation of the filling ratio. Results were compared with the existing DOT 49 CFR, § 173.304 and the proposed UN Model regulation, Twelfth Edition.

Impact: This project provides a reliable model for the calculation of the filling ratio for liquefied gases required for the safe handling of gas cylinders. The results are expected to be incorporated into a UN Model Regulation and to be used in international and domestic commerce of certain hazardous materials. In the U.S., these calculations are part of the process to develop consensus standards and will be considered by interested industrial participants in the process.

Future Plans: Depending upon the needs of the Department of Transportation and industrial parties (especially through the Compressed Gas Association), this project may be expanded to provide customized information to the industry through a computer program tailored to cylinder specifications, filling conditions, and regulatory guidelines.

Molecular Simulation of Solute Diffusion (Sodium Chloride) in Supercritical Steam

CSTL Program: Environmental Technologies and Services

Authors: *A.H. Harvey, and R.D. Mountain (838); and J.C. Bellows (Siemens Westinghouse)*

Abstract: Essentially no experimental measurements exist for the diffusivity of solutes in supercritical steam, despite the importance of these data for understanding deposition in steam turbines and for design of supercritical water oxidation processes. In this work, molecular dynamics simulation was used to calculate the diffusion coefficient of the sodium chloride ion pair at infinite dilution in supercritical steam. Potentials from the literature were used; a polarizable model for the water molecule was chosen to accurately represent water in the vapor phase. The results of the simulations are estimated to be accurate to within 20%, which is a great improvement over current semiempirical estimation methods. The results can be fitted satisfactorily to the form of a simple kinetic-theory expression, allowing extrapolation to conditions other than those simulated. The results from this work now provide the best values available for the diffusivity of sodium chloride in steam.

Purpose: A large fraction of electric power is generated in facilities that employ steam turbines, either in the primary power cycle or as a secondary heat-recovery cycle following a combustion turbine. A major problem in these systems is the deposition of impurities from the steam. The deposition process is believed to be governed by mass transfer, but further understanding of the process requires diffusivities of the solutes and these data do not exist. The most important solutes in this context are NaCl, NaOH, and silica. In addition, the diffusivities of solutes in supercritical water is of interest for the environmental technology of supercritical water oxidation (SCWO). Experimental measurement of these data is difficult if not impossible. Previous work has attempted to estimate these diffusivities with hard-sphere kinetic theory, which is likely to be inaccurate for strongly interacting systems such as water with salts.

Our approach is to calculate the diffusivity directly from molecular dynamics simulation, which provides rigorous results if the intermolecular potentials are sufficiently accurate. Good potentials (incorporating polarizability, which is needed for accurate description of water in the vapor phase) are available for water with sodium chloride. Advances in computing power have brought this calculation into the range of feasibility.

Major Accomplishments: The method was tested by successfully reproducing data for the diffusivities of pure water and of sodium nitrate in water at higher densities than those of interest here. The diffusivity of sodium chloride in steam was then simulated at seven state points representing typical steam turbine conditions. The results are estimated to be accurate within 20%. The simulation results show that the simple hard-sphere expressions others have used to estimate diffusivities in these systems overpredict the diffusion coefficient by approximately a factor of three. Our results were fitted to a simple kinetic-theory expression that allows calculation of the diffusivity of NaCl in steam at conditions other than those simulated.

Impact: This work provides the first reliable data for the diffusion coefficient of a solute in steam at turbine conditions. These data will support industrial and academic researchers who are seeking to better understand and control problems associated with impurities in steam turbines; industrial water treatment experts have estimated that costs to the electric power generation industry of efforts to prevent and repair damage due to these impurities amount to hundreds of millions of dollars per year.

Future Plans: The other solutes of most interest are NaOH and silica, so in coming years we intend to simulate their diffusivities in steam. NaOH should not pose too many difficulties, but for silica the identity of the diffusing species is not known because of uncertainties in the thermochemistry of the steam/silica system. Collaborations with the Computational Chemistry Group are planned to calculate reliable thermochemical data for hydrated silica species and to determine which species will need to be incorporated in our simulations. This project is one of a series aimed at evaluating the utility of computer simulation methods for problems for which experimental data are not available.

Properties and Processes for Cryogenic Refrigeration

CSTL Programs: Chemical and Allied Products, and Energy Systems
Authors: *R. Radebaugh, P. Bradley, and M. Lewis (838); R. Gates, and L. Reynolds (Univ. of Colorado); J. Gary, and A. O'Gallagher (891); and J. Pfotenhauer (Univ. of Wisconsin)*

Abstract: The objectives of this research are (1) to use measurement and modeling techniques for evaluating and improving performance of cryocoolers and their components, such as heat exchangers and pulse tubes, (2) to develop new and improved refrigeration and heat transfer processes for the temperature range below about 230 K, and (3) to provide a database on material properties at cryogenic temperatures. A book chapter on the thermodynamics of regenerative refrigerators was completed and reviewed this year. Development of our regenerator test apparatus has begun with components designed and fabricated. A prototype pulse tube neon liquefier to provide 500 W at 30 K was developed and tests performed on several geometry options. A low temperature of 30 K has been obtained, but for liquefaction of neon a no-load temperature of about 20 K is required. Further tests and data analysis are underway under a CRADA with an industrial sponsor. Under another CRADA a 15 K two-stage pulse tube refrigerator was designed for use with a thermoacoustic driver. We have assisted the sponsor in the fabrication and testing of the system. Under a third CRADA we have designed and have partially fabricated a test two-stage pulse tube refrigerator for cooling superconducting motors and for comparisons with our models. A microscale heat exchanger of parallel plate geometry was optimized, developed, and tested for use in a Joule-Thomson cryocooler for the Air Force. We have added Young’s modulus of materials at cryogenic temperatures to our web site as well as a complete set of properties data for many new materials.

Purpose: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics, magnets, and power systems, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas, and many other existing and potential applications. The use of these technologies has been hampered because of problems with existing cryocoolers. These problems include short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas. Proper measurements need to be identified that will characterize losses within these cryocoolers, and models need to be developed to optimize the design of such systems. Material properties at cryogenic temperatures are needed by industry for the design of cryogenic equipment, but the data are difficult to find and often in out-of-print reports.

Major Accomplishments: A book chapter on the thermodynamics of regenerative refrigerators was written and underwent review. The chapter is to be the first chapter in a book on low temperatures and refrigeration to be published in Japan. The chapter lays the foundation of thermodynamics for oscillating fluid systems such as Stirling, Gifford-McMahon, and pulse tube refrigerators. A large (500 W at 30 K) prototype pulse tube neon liquefier was developed under a CRADA with an industrial sponsor. Extensive instrumentation has been added to understand the physics and the source of losses in the scale-up of pulse tube refrigerators. Tests with several geometries of pulse tubes and regenerators have been conducted with a low temperature of 30 K being achieved. A low temperature of about 20 K is required to match the design conditions and to provide 500 W at 30 K. A small two-stage pulse tube refrigerator was designed and the technology for its development was turned over to the sponsor who plans to use it as the first step in the development of a system for subcooling liquid hydrogen to 15 K for use in the next-generation space vehicle. Another two-stage pulse tube refrigerator was designed for a superconducting company for use in cooling large superconducting motors. Part of the prototype system has been developed. We expect the results of the tests with this system to be compared with our modeling of two-stage pulse tube refrigerators. A microscale heat exchanger of parallel plate geometry was designed, developed, and tested between temperatures of 40 K to 300 K. An effectiveness value of 97.5% was obtained compared with the calculated value of 99.5%. We expect the difference is due to flow maldistribution. A method for reducing the flow maldistribution has been devised but not tested yet. Over 15 new materials have been added to our cryogenic materials database as well as the addition of Young's modulus to the set of properties. These material properties have been added to our web site.

Impact: Our accomplishments during the past year have provided industry with new tools to improve the performance of cryocoolers, particularly those operating at temperatures below about 20 K. The chapter on thermodynamics will aid the entire cryocooler industry to improve the performance of their cryocoolers. Our work on two-stage pulse tubes at 30 K will aid the superconductor industry in the development of superconducting systems that can be marketed to a larger customer base. Our materials properties database is now getting more attention and is useful to all industries dealing with cryogenic temperatures.

Future Plans: Activity in this area is continually expanding as more industrial customers are requiring our models, data, and technical expertise in the development of cryocoolers for an ever-increasing range of applications. To improve efficiency of these coolers, we are continuing the development of a test apparatus to measure nearly all types of losses in cryocoolers and to measure how they are influenced be various parameters. We are seeking further funding for these tests. The results will be used in the development of improved models.

The NIST WebBook* - NIST Chemical Reference Data for Industry

CSTL Program: Chemical and Allied Products, and Microelectronics
Authors: *P.J. Linstrom, and W.G. Mallard*

Abstract: The NIST Chemistry WebBook remains one of the most used resources for chemical and physical property data. Usage has continued to grow at about 20% per year with over 500,000 distinct IP addresses accessing the WebBook in the last year. The high rate of return users indicates a high level of satisfaction. For the first time a predictive tool has been added to the WebBook. The well established group additivity method for enthalpies of formation as well as heat capacity and entropy has been added as a tool for users who need data for which there are no experimental data. The group additivity tool has been developed using the most recent analysis of the data on the WebBook. .

Purpose: There is an enormous amount of thermochemical data (heats of formation, entropies, heat capacities, heats of reaction) as well as thermophysical property data (vapor pressure, viscosity, boiling points, melting points, etc) that are unavailable to the technical community. One part of this project is to find and evaluate those data. The second part is to make this and other data such as infrared (IR), ultraviolet (UV) and mass spectra available and easy to access. The WebBook is being used by a very wide variety of users in industry, government and academia.

Major Accomplishments: During 2002 the eighth edition of the NIST Chemistry WebBook* was released. The major changes were in the addition of the predictive tools rather than a major increase in the data. Additional new fluids were added for the high precision fluid properties section.

Impact: The WebBook continues to be widely used – during FY02, the total number of distinct Internet addresses that accessed the WebBook was in excess of 500,000. Growth in usage has been fairly steady from year to year – with same period usage increasing by about 20% in each of the last four years. The numbers of users, between 10000 and 20000 per week, and the variety of users, in industry, government and academia is a clear indication of the success of the WebBook. The fraction of returning users, typically between 45 to 55%, is a good indication that the user community feels that the resource is valuable. The WebBook is also a tool to aid future evaluation projects both at NIST and in collaboration with outside organizations. Ongoing work on developing standard protocols for transmission of chemical data has included work with IUPAC and ASTM groups associated with developing standards for data transmission.

Future Plans: The goal of the WebBook is to have a single point of entry for access to all chemical data at NIST and to make that data available in formats needed by both individual scientists and engineers as well as by computer tools serving these users. It is anticipated that during FY2003, there will be one or two releases of the NIST WebBook. In addition, ongoing work on making the WebBook an entry point for other kinds of chemical data is continuing.

***http://webbook.nist.gov/chemistry**

Laying the Foundation of MS/MS and Ion Trap Libraries

CSTL Program: Industrial and Analytical Instruments and Services
Authors: *J. Klassen, Q.-L. Pu, and S.E. Stein*

Abstract: A program has been initiated to extend the coverage of the widely-used NIST Mass Spectral Library to MS/MS and ion trap mass spectra. This has involved the creation and evaluation of an MS/MS library as well as the first NIST measurements of these spectra for inclusion in the library. Measurement conditions have been established and variations of spectra depending on instrument type and operating conditions have been studied. This guides the way for developing a searchable MS/MS library that can provide useful results over a range of instruments. Also, a collection of ion trap spectra has been developed that includes specific varieties of compounds whose spectra are known to be different in ion traps than in conventional mass spectrometers. This will enable users of ion traps to be able to employ the NIST Library with fewer 'corrections' for ion trap behavior.

Purpose: The existing NIST mass spectral library is composed entirely of 'classical' electron ionization mass spectra. Spectra generated by ion trap and MS/MS instruments, which are becoming widely used for chemical identification, may not match these classical spectra. Additions to the NIST library are being made to enable its use with these two varieties of instruments.

Major Accomplishments: Many of the varieties of compounds that produce electron ionization mass spectra in ion traps that differ significantly from those in traditional instrument types (e.g., quadrupole and magnetic sector instruments) have been identified. Approximately 200 such spectra have been measured in two ion trap instruments. This work has been done in close cooperation with the two instrument manufacturers. These substances are primarily relatively small organic molecules with low ionization energies and/or high proton affinities. The work has also led to improvements in the automated extraction of mass spectra by the NIST AMDIS program.

A significant start has been made in the creation of an MS-MS library. A diverse MS-MS collection of 1,000 has been donated for use in our program by a major instrument vendor. One particular application area, pesticide analysis, has been targeted for initial development, and 600 spectra of 75 compounds have been examined on ion-trap instruments over a range of collision energies. We are now actively engaged in a round-robin exercise involving these pesticides with a number of environmental laboratories. A variety of measurements on a newly acquired triple quadrupole instrument have been made for both common calibration and internal standards and simple peptides. An important finding is that while the ion collision energy needs to be considered and controlled, variations in spectra between instruments are not too great to prohibit effective library searching.

Impact: While ion trap and MS-MS spectra are routinely generated in laboratories in a wide range of application areas, reliable reference libraries are unavailable. With the addition of a limited number of carefully selected spectra to the current library, a major increase in the reliability of library searching is expected to result, especially for laboratories that are involved in the identification of small compounds. MS-MS spectra often involve different starting species than present in the current NIST library, so library searching requires new spectra. With the initial focus on the most significant compounds and the inclusion of a broad base library, we hope to provide the first evaluated, comprehensive library for this critical measurement device.

Future Plans: The ion-trap library will be tested with blind or unknown GC/MS data to ensure that the database is large enough to improve identification of ion trap spectra. An MS-MS round-robin study with selected pesticides and conditions will be undertaken to further establish limits of variability in these spectra. Available ion trap and MS-MS spectra will be made available to current NIST library users.

The NIST Mass Spectral Library: A Major Update

CSTL Program: Chemical and Allied Products
Authors: *A. Mikaya, S.E. Stein, D. Tchekhovskoi, C.L. Clifton, and Q.-L. Pu*

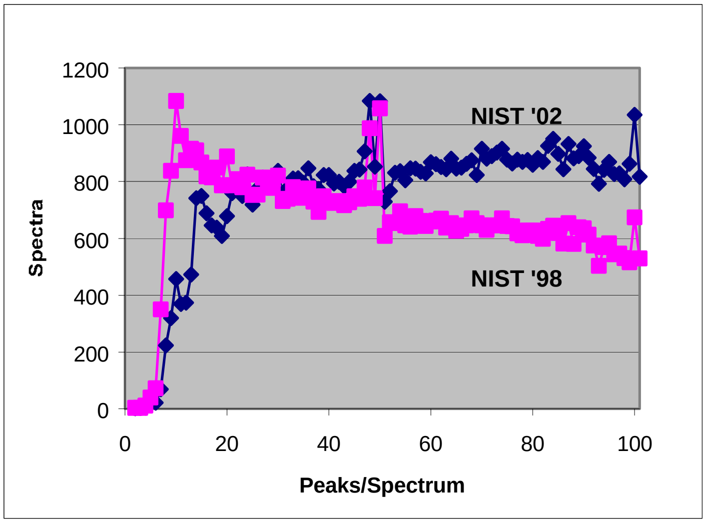
Abstract: After four years of intensive evaluation and measurement, a new version of the NIST Mass Spectral Library has been completed and delivered to distributors. The number of spectra has increased by over one-third, with each spectrum subjected to a published evaluation method. A variety of quality improvements have been made throughout the Library in which names were re-checked, edited and added. Also, 40,000 new CAS registry numbers were added to assist linkage with other chemical databases. A re-ranking of replicate spectra and replacement of lower quality with higher quality spectra has led the replacement of thousands of spectra in the main library with higher quality spectra. These enhancements in coverage and quality will improve the reliability of this library for identifying unknown, volatile chemical compounds using the technique of gas chromatography/mass spectrometry (GC/MS).

Purpose: To provide mass spectrometrists with a comprehensive, reliable library of mass spectral 'fingerprints' to assist the task of compound identification using the method of gas chromatography/mass spectrometry (GC/MS).

Major Accomplishments: The new release features major improvements in both coverage and quality.

Coverage: Spectra for over 54,000 compounds were added to the new version, for a total of 174,948 spectra of 147,198 compounds. This includes large numbers of spectra specifically measured for the library, including derivatives (compounds 'volatilized' through chemical reaction), chemical weapons related compounds, and pesticides as well as replicate measurements for selected compounds. Spectra for 1,735 commercially available compounds of special interest were measured by GC/MS at NIST.

Quality: All new spectra were subjected to published quality control procedures. Moreover, a variety of quality improvements were made throughout the library. All chemical names were re-examined to discover errors and to select the best name. IUPAC names were generated by software from structures for approximately 100,000 compounds. Over 16,000 spectra formerly in



the main library were replaced by either higher quality replicates or newly acquired spectra. This led to a significant change in the distribution of peaks per spectra in the Library, as illustrated in the accompanying figure.

Names for hundreds of salts were converted to a more correct ‘free base’ form, and hundreds of ambiguous structures were corrected or improved. All CAS registry numbers were verified with the assistance of Chemical Abstracts Services and over 40,000 new Registry numbers were added. Finally, a number of structure-spectral consistency checks were made leading to the discovery and resolution of hard-to-find spectral errors.

Impact: With over 2,500 new libraries installed on instruments each year, the higher quality and increased coverage of the new version will immediately improve search results in a large number of laboratories.

Future Plans: Progress towards the next release is now underway. This will involve the use of advanced error detection algorithms, new evaluation tools, and further increases in the varieties of substances represented. Emphasis will be placed on the acquisition of simple inorganic compounds and organic derivatives.

Gas Chromatograhy Retention Index Library: A Major New Resource Nears Completion

CSTL Programs: Chemical and Allied Products, Industrial and Analytical Instruments and Services, and Microelectronics
Authors: *J. Klassen, P.J. Linstrom, and S.E. Stein*

Abstract: A comprehensive gas phase retention index library for capillary columns is nearing completion. It contains approximately 70,000 data points for 12,000 compounds. These data are abstracted from the literature and evaluated using structure-based predictive algorithms. The evaluated data collection will be provided along with the NIST Mass Spectral Library to confirm the identity of compounds in chemical analyses. These data will also provide a basis on which to build well-tested predictive methods. These estimates can assist analysts in making identifications of compounds not represented in the Mass Spectral Library. Nonpolar compounds will be added during the next year as will conversions of reported relative retention times to more widely applicable retention index values.

Purpose: To build a reliable, comprehensive collection of gas phase retention indices to confirm the identity of compounds identified with the NIST Mass Spectral Library.

Major Accomplishments: The first version of the collection is nearly complete. It will contain approximately 70,000 retention data points for over 12,000 compounds on widely used nonpolar capillary columns. This is the product of a multiyear data abstraction and evaluation project that has covered all data published in the open literature over a 25-year period. Data entry and evaluation software has been developed specifically for this program, including specialized methods for selecting reference values to convert relative retention data to more useful retention index values. Estimation methods based on these data, along with various data comparison routines have been developed, tested and employed for finding suspect values in the collection.

Impact: This collection will assist in the confirmation of identifications made by matching acquired mass spectra against NIST library spectra library in two ways. First, for those compounds with reference retention data, a check against the measured retention index will either improve the reliability of an identification or exclude a potential false positive result. For compounds not having measured values, this collection provides the basis for a structure-based estimation scheme.

Future Plans: Only nonpolar stationary phases are included in this first version. Polar phases will be added over the next year. Also, all relative retention times will be converted to retention indices by linking selected measurements to retention index values already in the collection. This collection will be regularly updated to reflect the latest values available in the literature. Both these data and estimation algorithms will be made available to users of the NIST Mass Spectral Library.

A Standard Chemical Identifier

CSTL Programs: Chemical and Allied Products, and Microelectronics
Authors: *D. Tchekhovskoi, and S.E. Stein*

Abstract: The objective of this program is to develop a means of generating a unique identifier for a chemical compound from a digital representation of its chemical structure. It is being developed as an IUPAC project with the intention of establishing it as a standard, international means of representing chemical identity. The structure of the Identifer has been established. It has an extensible 'layered' structure in which different structural types appear in separate layers. Within an IUPAC committee, a variety of chemical rules have been developed and are now implemented as algorithms that can reliably treat most features of organic compounds. Extensions are underway for inorganic and organometallic compounds.

Purpose: To develop, test and implement algorithms for extracting a unique chemical identifier from an input connection table representation of a chemical structure.

Major Accomplishments: The basic methods for construction of the Identifier have been finalized. It is expressed as a series of 'layers,' each containing a specific class of structural information. The layers are: chemical formula, connectivity, isotopic, stereochemical, tautomeric, and charge. This modularization increases the robustness of the Identifier, permits the inclusion of all known structural features and, most importantly, enables extensibility. Creation of an Identifier is done in three steps:

1) Normalization, which applies various structural rules to the input structure to extract only that information required for chemical identification. A key simplifying feature is the elimination of all pi-bonds, radicals, and charges. All of the 'chemical' rules are expressed in this step, including definitions of tautomerization (H-atom migration) and stereochemistry.
2) Canonicalization generates a unique label for each unique atom in the normalized structure. This uses well-developed 'graph theoretical' methods. This information can serve as feedback to the chemist for error checking.
3) Serialization transforms the 'canonicalized' structure into strings of characters, one string for each layer. These layers, together, constitute the Identifier.

The most features involved in the treatment of organic compounds have been implemented and tested. The algorithms were implemented in a test program that was distributed, on request, to well over 60 individuals, who represent a wide range of applications and fields of study. Comments from this testing, along with input from a variety of other source are being used to complete the processing of organic compounds.

Impact: The Identifier provides a standard means of communicating and storing the chemical identity of a substance from a structural drawing. Since no such standard now exists, this could greatly facilitate the digital communication of chemistry in a wide range of applications involving the storage and dissemination of chemical data.

Future Plans: Over the next year, the identifier will be extended to inorganic and organometallic compounds and distributed to a number of organizations for testing. Ultimately, the means for producing the Identifier from a chemical structure will be distributed by IUPAC for integration into chemical processing software.

High-Throughput Liquid Transport Properties Measurements in Membranes and Films

CSTL Program: Chemical and Allied Products
Authors: *C.D. Muzny, S.L. Outcalt, J.L. Scott, and L.A. Watts (838); and B.J. Bauer and R.C. Hedden (854)*

Abstract: Measurements of liquid, vapor, and gas diffusion and sorption in thin layer films are critical for development of techniques to predict membrane transport properties. These measurements provide a means to compile the effects of both chemical and structural subgroups in the material, and ultimately, to delineate rational design criteria for mass separating agents such as membranes and polymeric adsorbents. A high-throughput apparatus for the measurement of the diffusivity and solubility of a variety of test components in a wide variety of membranes is under development. This technique employs an array of sixteen test cells that are individually temperature controlled and that can be loaded with differing solvents, test solutions and membranes under analysis. A critical component of this method is to have easily detectable, standard test compounds that probe different physical and chemical characteristics of the membranes. Toward this end a set of test fluorophores has been identified and produced in large quantities. Automation of the experiment, a key to any high-throughput method, is proceeding using the techniques of robotic sample delivery and fiber-optic sample detection systems.

Purpose: This work is intended to provide critical data for the characterization of membranes and films according to their species-specific transport properties. These data will then be available for use in the rational design of separation processes.

Major Accomplishments: The selection of test fluorophores and their production in quantities large enough for the experiments under design was a major accomplishment. After testing for fluorescence properties and stability, G4 PAMAM dendrimers that have their sizes modified by the attachment of polyethylene glycol surface groups of various molecular weights were chosen as the key test compounds. These were then produced in gram quantities via size-exclusion chromatography (SEC) in a set of four different sizes, each fluorescently labeled with a different color for easy separation and detection. Tests of fluorescent response concentration linearity, solubility in water and ethanol, and size validation were performed. The automation of the high-throughput apparatus has been completed via the use of a robotic injection system. Cells with individual solvent flow control can have small quantities of test fluorophores injected via this robotic injector. Sample detection is then accomplished through fiber-optic connection to a high-sensitivity fluorescence detector. A control system capable of simultaneously controlling the temperature and fluid flow on both sides of the transport cells is in place. Final system tests are currently underway.

Impact: Although polymeric and inorganic materials are used in membrane and adsorptive separation processes, a significant barrier to the optimum use of existing materials and development of new materials is the lack of predictive capabilities for the transport properties of mixtures in any selected material. This data production effort will facilitate the development of the quantitative structure-property relationships necessary for the development of these predictive methods. The availability of both the data and predictive methods will impact all industries that currently use membrane-based separations including the water purification industry, the pharmaceuticals industry, and the chemical industry.

Future Work: Transport data production in the high-throughput apparatus is the next major goal of this project. Data will be produced as a function of temperature, test compounds, and solvent. These data will then go into a membrane transport properties database that will be made broadly available via the Internet. The data will also be used to develop quantitative structure-property methods for the prediction of the transport properties of unknown compounds.

Measurements, Modeling and Data for Pressure-Driven Membrane Separations

CSTL Program: Chemical and Allied Products

Authors: *C.D. Muzny, K. Benko, J.L. Scott, and M. Chapman-Wilbert (838); K. Price (U.S. Bureau of Reclamation); and J. Ranville (Colorado School of Mines)*

Abstract: Analysis techniques for the standardization of membrane performance testing in pressure driven separations are under development. These techniques include methods for the characterization of both the membrane and the complex mixture to which the membranes are subjected for separations testing. The membrane is characterized by a novel liquid-liquid porosimetry apparatus for the measurement of pore size distributions, while the standard fouling mixtures are characterized by field flow fractionation. By producing a standard fouling mixture that includes particulates and a range of large organic species, we are able to determine membrane performance under a variety of realistic conditions. These standard test solutions and procedures will provide industry with a uniform method for pressure driven membrane separation performance testing. A reverse osmosis membrane module test bed is under development for the validation of the developed test solutions under realistic conditions.

Purpose: The purpose of this project is to develop standard methods for the determination of membrane performance in pressure driven separations. The ultimate goal is to provide a standard test mixture for testing membrane fouling along with standard procedures for evaluating membrane performance.

Major Accomplishments: As part of this development, it is necessary to have standard techniques for the evaluation of both the membrane and the test solution. The membrane must be evaluated for chemical, physical, and structural characteristics important in the development of rational design criteria for separations. A unique liquid-liquid porosimetry apparatus for physical characterization of membranes that we previously developed has undergone extensive testing during the past year. This testing has included membranes for ultrafiltration, nanofiltration, and reverse osmosis. The final validation of this technique is still underway, but preliminary results indicate it will be useful for membranes with pore sizes from 2 nm to 1000 nm. This includes virtually all membranes of current technological relevance. The characterization of the standard fouling solutions via field flow fractionation has continued. Validation and standardization methods for this technique have been developed in order to provide repeatable and reliable data for standard solution characterization. As a final test of the overall goal of providing standards for pressure driven membrane performance testing, a small-scale membrane module test bed is under development. This will have the capability of testing the performance of spiral wound, reverse osmosis modules under the standard conditions being separately developed and characterized.

Impact: Improved processes for obtaining specialty chemicals, pharmaceuticals, and advanced monomers using environmentally benign processes, and more economic ways to recover, reuse, and supply water are examples of important industrial and municipal uses of membranes. All of these areas will benefit from the development of systematic approaches for matching appropriate membranes to complex mixtures, and from the prediction of the relevant filtration figures-of-merit, species partitioning into the membrane, solvent permeability, and permeability decline over time.

Future Plans: The final production of a membrane test bed for testing the standards being developed will be the major effort of next year. Work will continue on final validation of the liquid-liquid porosimetry technique and on field flow fractionation methods for membrane and solution characterization, but the completion of a membrane test apparatus for module level testing is necessary for the final validation of the standards and methods under development. Finally, the modeling of membrane performance degradation is a key component of this overall program and will see significant development during the next year. Once data are available from the module test bed, the field flow fractionation experiment, and the liquid-liquid porosimetry apparatus, the necessary information needed for the development of predictive modeling techniques will be available.

Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation

CSTL Programs: Chemical and Allied Products, and Energy Systems
Authors: *M. Frenkel, R.D. Chirico, Q. Dong, G.R. Hardin, and R.A. Stevenson (838); X. Yan, and X. Hong (Contractors); and V.V. Diky (Guest Researcher)*

Abstract: The new concept of "dynamic" data evaluation has been developed at TRC. This concept requires the development of large electronic databases capable of storing essentially all the 'raw/observed' experimental data known up-to-date with detailed descriptions of the relevant metadata and uncertainties. The combination of these electronic databases with artificial intellectual (expert-system) software designed to automatically generate recommended data based on available 'raw/observed' experimental data leads to the ability to produce data compilations dynamically or 'to order.' This concept contrasts sharply with static compilations, which must be initiated far in advance of need. Dynamic compilations dramatically reduce the effort and costs associated with anticipating future needs and keeping static evaluations current. The recommended data produced by the deployment of the dynamic data-evaluation concept can rigorously be characterized with their quality assessments providing the ability to propagate reliable data-quality limits to all aspects of chemical process design. The TRC Data Entry Facility was established to support a mass-scale data entry operation for the TRC SOURCE data system. Guided Data Capture software was developed at TRC and released from NIST in 2002 to enhance data entry operation both in-house and from the outside sources. The development of the ThermoML, XML-based standard has been completed, to promote interoperability in experimental thermophysical and thermochemical property data collection and management worldwide. The Data Quality Assurance Program has been designed to control the data quality at various stages of data entry, evaluation, and database management. Implementation of this program in 2002 allowed TRC to establish the most complete and reliable data set of critical parameters of organic compounds. The second (eleventh) TRC Consortium Annual Workshop was held to inform the company members on the progress made during the past year.

Purpose: Thermophysical property data evaluation is currently one of the most time- and resource-consuming stages of process design in a number of industries (chemical, petroleum, pharmaceutical, *etc*.). It has also very significant implications in the analysis of mutual relations of various properties within particular classes or groups of chemical substances, which is traditionally a subject of fundamental research. However, unprecedented growth of the thermophysical data becoming available at present (almost doubling every 10 years) makes it practically impossible to employ traditional (static) methods of data evaluation used over the last 50 years. The main objective of this project is to create new efficient methods and computer tools for the thermophysical, thermochemical, and transport property data collection, critical evaluation, mining, quality control, management, and dissemination and to provide high quality recommended data in the forms directly suitable for industrial and scientific applications.

Major Accomplishments: The TRC Data Entry Facility was established to support a mass-scale data entry operation for the TRC SOURCE data system. Guided Data Capture (GDC) software was developed at TRC and released from NIST in 2002 to enhance data entry operation both in-house and from outside sources. The development of the ThermoML, XML-based standard has been completed to promote interoperability in experimental thermophysical and thermochemical property data collection and management worldwide. The Data Quality Assurance Program has been designed to control the data quality at various stages of data entry, evaluation, and database management. Implementation of this program in 2002 allowed TRC to establish the most complete and reliable data set of critical parameters of organic compounds. The second (eleventh) TRC Consortium Annual Workshop was held to inform the company members on the progress made during the past year.

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Impact: The establishment of the TRC Data Entry Facility and TRC Data Quality Assurance Program has dramatically increased TRC capabilities in volume and quality of the 'raw' experimental data collecting, forming the necessary data management foundation for the implementation of the dynamic data evaluation concept. The use of the GDC at the TRC Data Entry Facility made it possible to establish a rate of data entry at 200,000 data points per year.

Future Plans: Future plans include the establishment of a framework of direct data communication, quality assurance, processing and distribution between major journals in the field and NIST, and the development of the software prototype to implement the Dynamic Data Evaluation Concept for phase equilibrium property groups.

Chemistry and Properties of Trace Components of Fuel Gas

CSTL Program: Energy Systems
Authors: *T.J. Bruno, and W.C. Andersen (838); and A. Abdulagatov (Dagestan Scientific Center of Russian Academy of Sciences)*

Abstract: The United States consumes approximately 23 trillion cubic feet of fuel gas each year. Natural gas consists primarily of methane, but 400 additional compounds may be present at varying levels. Most of these materials are naturally occurring (heavier hydrocarbons, sulfur compounds, water, carbon dioxide, etc.), and some are added during processing. Liquefied petroleum gas (LPG) consists primarily of propane, but many other compounds are present. The efficient, safe design of equipment operated with fuel gases critically depends upon the properties and chemistry of individual components of natural gas and LPG. Moreover, it has become very clear that the components present at minor levels (or even at trace quantities) can have a significant impact on the overall properties of the fuel gas mixture.

Purpose: To provide the natural gas industry with chemical characterization and properties that are critically needed for the efficient operation of fuel gas processing, transmission and distribution. This is required for custody transfer, calorific value, quality control, safety and environmental compliance.

Major Accomplishments: Recent work has included (1) completion of work on carbonyl sulfide (COS) hydrolysis in propane, (2) the relationship of COS hydrolysis on the Copper Strip Corrosion Test (CSCT), and (3) a comprehensive evaluation of the applicability of the CSCT. Our kinetics measurements revealed that the hydrolysis reaction of COS is too slow to be of consequence for the propane industry. We made measurements at several temperatures, and in the presence of nine catalysts. An Arrhenius plot was developed to provide a predictive approach to the hydrolysis kinetics. In addition, we studied the effect of hydrocarbon diluents in this multiphase reaction system. We determined that the hydrocarbon imposes a diffusion barrier to the reaction, and that a correlation exists between the diffusion coefficient of the hydrocarbon and the reaction rate constant. Our kinetics measurements were confirmed with CSCT measurements done on COS mixtures in propane. Our evaluation of the CSCT revealed significant operational problems with the test, and we have taken steps to improve the test. Finally, we completed a major review of the chemistry of COS, and the patent on our COS removal technology was issued.

Impact: Our work on COS hydrolysis and its relation to the CSCT will change the way the propane industry deals with this sulfur contaminant. Moreover, the CSCT itself will now have to be reevaluated in terms of applicability. Our comprehensive review of COS chemistry will replace the earlier 1957 review, and the technology developed during this project will be used in industry and the laboratory.

Future Plans: We will complete our improvements to the copper strip corrosion test, and implement other approaches, including near infrared analysis and eddy current evaluation of the test strips.

Publications:

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Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes

CSTL Program: Environmental Technologies and Services
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Abstract: Clays are used in a broad array of applications ranging from pollution prevention and remediation, enhanced oil recovery, the treatment of petroleum liquids, the manufacture of cosmetics and pharmaceuticals, and the synthesis of polymer nanocomposite materials. They are also a critical part of the land environment, and as such, must be considered in any pollutant-soil interaction. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a critical issue for future developments in the environment and in clay applications. In order to understand the physical chemistry (both thermodynamics and kinetics) of the clay-solute interaction, we have advanced the application of physicochemical gas chromatography by devising stable clay- and organoclay-coated capillary columns. The capillary column approach we have developed is more efficient, requires lower temperatures, and produces enthalpy of adsorption (ΔH_{ads}) results with a much lower uncertainty than the conventional techniques.

Purpose: Our goal is to exploit the unique characteristics of clay platelets in the production of organic-inorganic composite materials with revolutionary material properties and in the development of novel chemical separation, and also to use clays as a platform to study the pollutant-soil interaction.

Major Accomplishments: We have completed the production and characterization of the first successful organo-clay coatings for capillary column gas chromatography. We used them to measure the enthalpy of adsorption (ΔH_{ads}) for a family of hydrocarbons on Laponite complexed with CTAB, and also Laponite coated with octadecane. These substrates are especially significant as surrogate soil systems that can be used to model the interaction of pollutants on soils. In this work, we demonstrated that the ΔH_{ads} is uniformly lower for organoclay than it is for the pure clay surface, and concluded that the organic component "ties up" the most active sites on the clay. As an application of the work with clay and organoclay substrates, we studied the ΔH_{ads} of fuel gas odorants on soil surrogates. This was motivated by the observation of odorant fading in fuel gas, a suspected cause of which is soil adsorption. We have derived the ΔH_{ads} difference ($\delta\Delta H_{ads}$) between fuel gas components and their respective odorants, and have used this value to predict fading. Our values of ΔH_{ads} complement breakthrough values that have been measured on real soil samples. A significant result is the observation of a high ΔH_{ads} for THT, and a relatively low ΔH_{ads} for TBM. We extended the work to hydrated clay surfaces and found that the ΔH_{ads} is reduced for thiol odorants, an observation confirmed by breakthrough experiments.

Impact: An immediate impact of this work has been the recognition of differential adsorption of the various fuel gas odorants. The (very common) presence of clay in a pipeline or the leak of a pipe up through a clay soil can have devastating consequences. Our results will allow avoidance of unfavorable odorants, and thereby improve safety.

Future Plans: Future work in this area includes development of particles with a higher porosity, and thus greater surface area. In addition, near-term measurements are planned for aqueous phase)H measurements of environmentally important classes of compounds including polar pesticides and nitro-aromatics, including explosive components and their degradation products.

Publications:

Bruno, T.J., Lewandowska, A, Tsvetkov, F., Hanley, H.,J.M., and Miller, K., **"*Wall Coated Open Tubular Column Chromatography on an Organo-clay Stationary Phase,*"** J. Chromatogr. A (in press).

Miller, K. E. and Bruno, T.J., **"*Enthalpy of Fuel Gas Odorants on Surrogate Soil Surfaces by Gas Chromatography*,"** J. Chromatogr. A (in press).