

***Physical and Chemical Properties –
Table of Contents***

Division Overview	2
1. The NIST WebBook* and the IUPAC/NIST Chemical Identifier – Standards and Delivery Mechanisms for NIST Chemical Reference Data	9
2. 15 th Symposium on Thermophysical Properties Meets in Boulder	11
3. Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation	13
4. NIST Computational Chemistry Comparison and Benchmark Database	15
5. Collaboratory for Multi-Scale Chemical Science	16
6. Automatic Mass spectral Deconvolution and Identification Software (AMDIS)	17
7. The NIST Retention Index Database	18
8. The NIST Mass Spectral Library - Improving the Evaluation	19
9. Surface Oxygen Chemistry of a Gas Sensing Material: SnO ₂ (101)	21
10. A New Noninvasive Approach to the Measurement of Phase Equilibrium	23
11. Measurement Standards for Thermal Analysis	25
12. Adsorption of Energetic Materials (Explosives) on Surfaces	27
13. The Industrial Fluid Property Simulation Challenge	29
14. Thermophysical Properties and a Data Retrieval System for Ionic Liquids	31
15. Advanced Experimental Capabilities for Fluid Properties Measurements	33
16. Properties of Rocket Propellant (RP-1)	35
17. Structure and Reactivity of the Hydrated Hematite (0001) Surface	37
18. Thermodynamic Interpretation of Low-pressure Ion-molecule Reactions	39
19. Predicting Vibrational Spectra of Dissolved Salts	40
20. Isodesmic reactions for transition states (IRTS)	41
21. Evaluated Molecular Structures and Vibrational Frequencies for C1-C2 Chlorocarbons	42
22. Evaluation of Free Radical Standard Potentials	44
23. Properties and Processes for Cryogenic Refrigeration	45
24. High-Throughput Liquid Transport Properties Measurements in Membranes and Films	47
25. Measurements, Modeling, and Data for Pressure-Driven Membrane Separations	49
26. International Standards for Refrigerant Properties	51
27. Transport Property Models for Refrigerants	53
28. High-Temperature Reference Correlations for the Solubility of Gases in Water	55
29. Chemical Kinetic Database for PAH formation for Heptane Combustion	56
30. OH Kinetics – Evaluation of Data and Experimental Techniques	57
31. Weakly-bound Isomers of the ClOO Free Radical	58
32. New Smart Gel Mechanism Elucidation from Immersive Visualization of Molecular Simulation	59
33. Molecular Electronics Metrology	61

Physical and Chemical Properties Division

Division Overview

Goals:

The Physical and Chemical Properties Division (PCP) seeks to be the world's foremost and best resource for high quality physical and chemical property information. Our **Goals** are to:

- Provide a robust, secure, autonomous information system facilitating access to all high-quality, published physical and chemical property data;
- Provide the evolving experimental infrastructure and expertise as required to ensure the traceability of physical and chemical property data to fundamental standards;
- Provide protocols, reference methods and standards for evaluating the quality of physical and chemical property data;
- Provide methods for obtaining PCP data products that are optimally adapted to the access and application needs of the customer;
- Provide tools for estimation/prediction of physical and chemical property data with reliably known uncertainties;
- Provide the theory, measurement science, and benchmark measurements required to assure the quality of PCP data products and to address and anticipate the needs of the nation for physical and chemical property data;
- Provide leadership and expertise in the development of high quality domestic and international data standards.

The *principal output of the Division is information* that quantitatively specifies physical and chemical properties broadly important to the nation's economy and quality of life. Many of our outputs are included in the Nation's Standard Reference Data system, and an assortment of well known libraries/databases are associated with the Division:

- [NIST Chemistry WebBook](#)
- [NIST/EPA/NIH Mass Spectral Library](#)
- [NIST/TRC Table Database](#)
- [NIST/TRC Vapor Pressure Database](#)
- [NIST/TRC Ideal Gas Database](#)
- [NIST/TRC Thermodynamic Tables](#)
- [NIST Computational Chemistry Comparison and Benchmark Database](#)
- [NIST Chemical Kinetics Database](#)
- [NDRL/NIST Solution Kinetics Database](#)
- [NIST-JANAF Thermochemical Tables](#)
- [NIST Reference Fluid Thermodynamic and Transport Properties Database \(REFPROP\)](#)
- [NIST Thermodynamic and Transport Properties of Pure Fluids Database](#)
- [NIST Thermophysical Properties of Hydrocarbon Mixtures Database](#)
- [NIST Mixture Property Database](#)
- [NIST/ASME Steam Properties Database](#)
- [NIST Cryogenics Materials Properties Database](#)

In addition to these important sources of reference data, in FY2003 Division staff published over 140 papers, made more than 120 scientific presentations, participated in over 60 national and international committees developing nomenclature and information exchange standards, identifying critical data needs, developing consensus standards for the thermophysical properties of reference fluids, and facilitating scientific growth within the thermodynamic research community.

Highlights of the work of the Division are presented in this document. This information is organized according to the program structure of the Chemical Science and Technology Laboratory (CSTL), the organizational unit coordinating our work and that of four other research divisions.

CSTL Program Structure:

The Chemical Science and Technology Laboratory (CSTL) describes its activities in terms of eleven industrial segments that are the *primary customers* for CSTL's products and services; these segments are referred to as **CSTL Programs**:

1. Automotive and Aerospace
2. Biomaterials
3. Pharmaceuticals and Biomanufacturing
4. Chemical and Allied Products
5. Energy/Environmental Systems
6. Health and Medical Technologies
7. Industrial and Analytical Instruments and Services
8. Forensics and Homeland Security
9. Microelectronics
10. Food and Nutrition
11. Technologies for Future Measurements and Standards

CSTL has activities which by their nature are *supportive of all industrial segments* and are best described as *cross-cut* activities. Many of the Division's outputs fall into the CSTL cross-cut category termed **Data and Informatics**. Highlights of the activities associated with these broadly applicable products are described below under the titles:

1. The NIST WebBook and the IUPAC/NIST Chemical Identifier - Standards and Delivery Mechanisms for NIST Chemical Reference Data
2. 15th Symposium on Thermophysical Properties Meets in Boulder
3. Thermodynamics Research Center (TRC) Comprehensive Program on Critical Data Evaluation
4. Computational Chemistry Comparison and Benchmark Database, Version 8.0.
5. Collaboratory for Multi-Scale Chemical Science

Selected accomplishments in Data and Informatics:

The NIST Chemistry WebBook (Highlight 1) has been recognized as the “Best Portal and Information Hub Site in Chemistry” and is second only to Chemical Abstracts in frequency of web-access for chemical information. The site undergoes continuous improvement, with the eighth edition released this year. Usage continues to grow at about 10-20% per year, with access from over 650,000 distinct IP addresses this year.

A major thrust of the research in Data and Informatics is the development of robust, automatable procedures to unequivocally identify molecules according to their chemical structure. NIST, in collaboration with a project under the International Union of Pure and Applied Chemistry, is leading the development of this next generation chemical identifier. (Highlight 1)

The Symposium on Thermophysical Properties hosted triennially by PCP is the premier meeting in this area of science and engineering in the world. This year’s meeting was highly successful with high attendance and numerous sessions highlighting the importance and significance of research developments in this area. (Highlight 2)

NIST’s position in the thermophysical properties area was enhanced in the last few years with the return of the TRC Group as part of the Division. A major accomplishment this year was the initiation of a strategic collaboration with the Journal of Chemical and Engineering Data (JCED) which brings TRC directly into the process of assuring that data approved for publication in JCED simultaneously will be made available on the internet, in an XML format termed ThermoML, and archived in the TRC SOURCE data system. ThermoML, a consensus information exchange standard developed with the leadership of the TRC Group, is designed to assure the capture of the information required to assess data quality. This collaboration with JCED is truly a seminal new paradigm for data collection and dissemination which holds great promise in a wide variety of disciplines. Extension of the collaboration to other primary resources for thermophysical data is planned for the near future. (Highlight 3)

Some Division efforts are a part of the CSTL Program Area of **Industrial and Analytical Instruments and Services**. Highlights of these efforts are described in:

6. Automatic Mass Spectral Deconvolution and Identification Software (AMDIS).
7. The NIST Retention Index Database
8. The NIST Mass Spectral Library - Improving the Evaluation
9. Surface Oxygen Chemistry of a Gas Sensing Material
10. A New Noninvasive Approach to the Measurement of Phase Equilibrium
11. Measurement Standards for Thermal Analysis
12. Adsorption of Energetic Materials (Explosives) on Surfaces

Activities described in highlights 6 and 12 have special application in detection of chemical agents and explosives and directly support the CSTL Program in **Forensics and Homeland Security**.

Selected accomplishments in Industrial and Analytical Instruments and Services:

The NIST/EPA/NIH MS-Library is embedded in over 2000 new instruments each year and is the industry standard for MS analyses. There is a strong emphasis on improving the quality of all the information provided in the library and adding information which will significantly enhance the utility of the MS-Library. The retention index database is an important new step in that direction. (Highlights 7 and 8)

Our research often address long-standing measurement challenges such as how to determine phase co-existence and composition in reactive or unstable chemical systems. The new, non-invasive approach described in Highlight 10 successfully addresses this type of challenge. Our work in Computational Chemistry and Physics continues to reap many benefits: one of the more recent deals with a fundamental advance in our understanding of the mechanisms underlying gas-sensing by widely employed materials such as SnO₂ which respond to changes in oxidative or reducing environments by changes in electrical conductivity. (Highlight 9)

The primary customer for most of our products is the **Chemicals and Allied Products** sector of US industry. The work described in the following is principally in this CSTL Program Area:

13. The First Industrial Fluid Property Simulation Challenge
14. Thermophysical Properties and a Data Retrieval System for Ionic Liquids
15. Advanced Experimental Capabilities for Fluid Properties Measurements
16. Thermophysical Properties for Rocket Propellant RP-1
17. Structure and Reactivity of the Hydrated Hematite (0001) Surface
18. Thermodynamic Interpretation of Low-Pressure Ion-Molecule Reactions
19. Predicting Vibrational Spectra of Dissolved Salts
20. Isodesmic Reactions for Transition States
21. Evaluated Molecular Structures and Vibrational Frequencies for C1-C2 Chlorocarbons
22. Evaluation of Free Radical Standard Potentials
23. Properties and Processes for Cryogenic Refrigeration
24. High-Throughput Liquid Transport Properties Measurements in Membranes and Films
25. Measurements, Modeling and Data for Pressure-Driven Membrane Separations

The work described in highlights 16 and 23 has a special focus in the aerospace sector (CSTL Program 1, **Automotive and Aerospace**).

Selected accomplishments in Chemical and Allied Products:

A major goal for the Division is to provide tools for estimation/prediction of physical and chemical property data with reliably known uncertainties. Industry is increasingly relying on modeling and simulation for enhancement of processes and products and for design and discovery throughout the enterprise. Model-based design relies critically on the availability of an extremely-wide range of data having known uncertainties. Design at the limits of knowledge demands estimation and prediction of information that is currently not available or trustworthy. *Computational Chemistry and Physics* can play a critical role in providing the required information. The First Fluid Property Simulation Challenge is a collaborative program with industry and academia to try to assess and advance the current state-of-the-art in this important area of research. (Highlight 13)

Measurement of key data associated with current or future information gaps requires new measurement techniques and benchmark measurements to facilitate further exploration. Work on ionic liquids and jet fuels falls into this category. Evaluated data, improved models, and test methods also are called for and are exemplified by many of the efforts in this program area. (Highlights 14, 15, and 16)

National goals with regard to energy, environment, and sustainability are of special interest to most CSTL stakeholders. The work described in the following highlights:

26. International Standards for Refrigerant Properties
27. Transport Property Models for Refrigerants
28. High Temperature Reference Correlations for the Solubility of Gases in Water
29. Chemical Kinetic Database for PAH formation for Heptane Combustion
30. OH Kinetics – Evaluation of Data and Experimental Techniques
31. Weakly-bound Isomers of the ClOO Free Radical

is explicitly focused on such issues and is part of the CSTL effort in the **Energy/Environmental Systems** program area.

Selected accomplishments in Energy/Environmental Systems:

The Division has had a long-standing effort in the development of benchmark data for refrigerants in support of National commitments with regard to ozone depleting refrigerants and industrial interests in the development and use of CFC replacements. The results of much of this work has appeared in various releases of databases such as [REFPROP](#). This is a model-based standard reference database, and work to extend the thermodynamic and transport property models and capabilities remains a high priority. An additional significance of this type of effort is that, when successful, this information can become an internationally agreed upon standard which facilitates equity in trade and achievement of world-wide sustainability goals. (Highlights 26 and 27)

The review of OH-kinetic measurement and data defines the current state of the art in this area with a particular emphasis on kinetics important to stratospheric and atmospheric air quality. (Highlight 30) Benchmark chemical reaction mechanism for larger hydrocarbons are critical to advances in model/simulation based design of next generation vehicles and energy systems. The importance of this type of effort was highlighted by the participants of a Workshop on Combustion Simulation Databases for Real Transportation Fuels, held in early September 2003. A full report of the findings of the Workshop will be available in the first quarter of FY2004.

The Division supports industry in its drive to exploit opportunities for reduced environmental impact from current processes and for major innovations in processes and products offered by areas such as ionic liquids, described in Highlight 14, above, and nanotechnology. Efforts related to the latter are described in:

32. New Smart Gel Mechanism Elucidation from Immersive Visualization of Molecular Simulation.
33. Molecular Electronics Metrology

These efforts are part of the CSTL Program on **Technologies for Future Measurements and Standards** in support of the National Nanotechnology Initiative.

Selected accomplishments in Technologies for Future Measurements and Standards:

The research described in Highlights 32 and 33 provides excellent examples of how Computational Chemistry and Physics is enabling otherwise unattainable insights into fundamental processes at the level of molecules, the ultimate in nanotechnology. Previous intuition has in some cases proved wrong; additionally, the predictions of first principle calculations have allowed design for purpose in the forefront of nanotechnology.

Organization:

The work of the Division is distributed over a number of Projects and Groups:

- Computational Chemistry,
- Experimental Kinetics and Thermodynamics,
- Chemical Reference Data and Modeling,

located in Gaithersburg, MD and

- Experimental Properties of Fluids,
- Theory and Modeling of Fluids
- Cryogenic Technologies,
- Thermodynamics Research Center,
- Properties for Process Separations.

located in Boulder, CO. In FY2003 the Division had 56 scientists and engineers on staff, 12 technical and administrative support staff, hosted 44 guest scientists, and worked cooperatively with many students, post doctoral researchers, and outside collaborators.

Staff Recognition:

Carol A. Driver, Division Secretary, was awarded the CSTL Secretarial Achievement Award for exceptional administrative support to NIST, CSTL, and the Division.

Anneke Levelt-Sengers was recipient of the 2003 L'OREAL-UNESCO Award for Women in Science in the field of Sciences of Condensed Matter.

Ray Radebaugh, leader of the Cryogenic Technologies Group, was awarded the Department of Commerce Gold Medal for his outstanding technical contributions, innovations, leadership, and technology transfer in the field of advanced cryocoolers.

Jennifer Scott was the recipient of the NIST Boulder "Building Tomorrow's Workplace" Award for her exemplary role in encouraging diversity through understanding, respecting, and valuing physical, cultural, and social differences among individuals.

V. V. Diky, R. D. Chirico, R. C. Wilhoit, Q. Dong, M. Frenkel were nominated for the 2002 CSTL Technical Achievement Award for their publication “Windows-Based Guided Data Capture Software for Mass-Scale Thermophysical and Thermochemical Property Data Collection” which appeared in *Journal of Chemical Information and Computer Sciences*, 2003, **43**, pp.15-24.

Joe Magee was a co-author of "Specific Isochoric Heat Capacity Measurements for Liquid Isobutane," *Trans. JSRAE* 20: 231-237 (2003) which was given the “Best Paper Award” at the Asian Conference on Refrigeration and Air Conditioning (Kobe, Japan, December, 2002).

1. The NIST WebBook* and the IUPAC/NIST Chemical Identifier - Standards and Delivery Mechanisms for NIST Chemical Reference Data

CSTL Program: Data and Informatics

Authors: *P. Linstrom, D. Tchekhovskoi, S. Stein, and 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 10 to 20% per year, currently over 650,000 distinct IP addresses access the WebBook per year. In addition, we continue to see a very high rate of return users indicating a level of satisfaction with the WebBook. Usage continues to grow for all of the components of the WebBook. More effort has gone into acquiring data and a major donation of infrared spectral data from the Dow Chemical Company was received this year. In addition, the work on the IUPAC/NIST Chemical Identifier (INChI) has continued. The work on the INChI along with work on data-exchange standards for chemical data is an essential part of making the WebBook a leading part of the next generation of electronic chemical information.

Purpose: Finding the 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 available to the technical community is time consuming and expensive. A major part of this project is to find and evaluate those data - with a major emphasis in the evaluation process being the deployment of automated tools for that evaluation. The second part is to make this and other data such as infrared (IR), ultraviolet (UV) and mass spectra available and easy to access. In addition, the identification and communication of this information has required the development, testing and implementation of algorithms for extracting a unique chemical identifier from the chemical structure.

Accomplishments: During 2003 the eighth edition of the NIST Chemistry WebBook* was released. In addition to an enhanced profile of prediction tools, a major increase in the infrared spectra was made with the release of the digitized Coblenz Society infrared spectral data. This data had only been available in printed form and the release of the data in fully digitized electronic form represents a major addition to the resources of the WebBook. Perhaps as a result of the increase in IR data, the IR usage increased more than the overall usage. The finalization of the donation of over 50,000 IR spectra by The Dow Chemical Company to NIST culminated a multiyear effort. Historically the large collections of data that are present in the chemical company records have not been available to the public. The decision by Dow to donate the data and the decision to make it available through NIST and the WebBook represent a major vote of confidence for the WebBook. The work on INChI and the web-based standards for chemical information communication have been pursued by committees of IUPAC (of which Steve Stein is the Chairman) and ASTM (of which Peter Linstrom is a pivotal member).

Impact: The WebBook continues to be widely used with over 650,000 distinct internet addresses that accessing the WebBook each year. Growth in usage has been fairly steady with year on year – with same period usage increasing by about 20% in each of the last 4 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%, in 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. It is difficult to overstate the possible impact of the ongoing work on developing standard protocols for transmission of chemical data. The need for such standards has only grown as the use of the Internet in electronic commerce has grown. This need has been acknowledged by the large number of commercial as well as governmental entities participating in the IUPAC and ASTM committee work.

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 FY2004, there will be one release of the NIST WebBook. The digitization of the Dow contribution will begin this year. In addition, ongoing work on making the WebBook an entry point for other kinds of chemical data is continuing. The use of INChI and the ASTM standards will be implemented as soon as they become stable. In addition, the INChI is undergoing extension to the full range of inorganic compounds as well as metal organic compounds.

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

2. 15th Symposium on Thermophysical Properties Meets in Boulder

CSTL Program: Data and Informatics

Authors: *D.G. Friend, G.R. Hardin, and staff of 838; A. Mandelis (U. Toronto)*

Abstract: The Fifteenth Symposium on Thermophysical Properties, organized and co-sponsored by NIST, was held in Boulder, Colo., from June 22-27, 2003. The Symposium on Thermophysical Properties is a well-established series held roughly every three years since 1959, and is recognized as one of the premier international conferences associated with the theoretical, experimental, simulation, and applied aspects of the thermophysical properties of gases, liquids, and solids, including biological systems. The conference attracted about 450 participants from more than 40 countries, with about half from outside the United States. The authorship of more than 660 technical contributions—oral presentations, posters, and software exhibitions—comprised more than 1500 individuals from 49 countries. Many of the 117 sessions were organized by staff in CSTL's Physical and Chemical Properties Division, and others were organized by members of an international community of experts. Planning is underway for the 16th Symposium which will be held in 2006 in conjunction with the International Conference on Chemical Thermodynamics.

Purpose: The community involved in thermophysical properties represents a diverse group of those involved in their measurement, prediction, simulation, and application. The researchers and practitioners in the field comprise physicists, chemists, biologists, materials scientists, chemical engineers, mechanical engineers and others who may seldom have an opportunity to learn of the advances and impediments faced by their colleagues. The triennial Symposium on Thermophysical Properties, now permanently housed in Boulder, CO and organized by NIST, is an attempt to foster communication and focus within this international community. Although the Symposium is largely considered a service to a broad community, it also provides a significant opportunity for the transfer of technologies developed at NIST (including data, models, databases, patents, etc.) and a mechanism for NIST researchers to learn of other problems and needs which should be addressed.

Major Accomplishments: The Fifteenth Symposium on Thermophysical Properties, organized and co-sponsored by NIST, was held in Boulder, Colo., from June 22-27, 2003. The Symposium was the latest in a well-established series held roughly every three years since 1959, and is recognized as one of the premier international conferences associated with the theoretical, experimental, simulation, and applied aspects of the thermophysical properties of gases, liquids, and solids, including biological systems. The conference consisted of 117 sessions including two plenary sessions. Zelda Chapman Bailey, Director of the NIST Boulder Laboratories, gave opening remarks at the first plenary session, and Nobel laureate Eric Cornell was the featured speaker at the second plenary session. There were specialized and more general focus areas devoted to properties of various classes of materials; properties for process design and environmental applications; techniques, including molecular simulation and novel experiments; phenomena; and tools for specialized thermophysical property problems. Many of the sessions were organized by staff in CSTL's Physical and Chemical Properties Division, and others were organized by members of an international community of experts.

Impact: The conference attracted about 450 participants from more than 40 countries, with about half from outside the United States. The authorship of more than 660 technical

contributions—oral presentations, posters, and software exhibitions—comprised more than 1500 individuals from 49 countries.

Future Plans: Work on the Symposium proceedings is in progress, and planning for the 16th Symposium to be held in 2006 as a joint meeting with the International Conference on Chemical Thermodynamics has begun.

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

CSTL Program: Data and Informatics

Authors: *M. Frenkel, R. D. Chirico (838); Q. Dong, X. Yan (Contractor), R. C. Wilhoit[†] (Contractor), X. Hong (Contractor), V. V. Diky (Guest Researcher), R. A. Stevenson, G. R. Hardin.*

Abstract: The TRC concept of “dynamic” data evaluation requires large electronic databases capable of storing essentially all experimental data with detailed descriptions of the relevant metadata and uncertainties. The combination of these electronic databases with artificial intelligence (expert-system) software will allow the dynamic generation of evaluated recommended data as needed. 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 data programs. Significant advances were made in the TRC Data Entry Facility (to support mass-scale data entry), Guided Data Capture (GDC) software (to enhance in-house and external data entry), and ThermoML (an XML-based approach for international data collection and management). It is anticipated that ThermoML will become a prototype of an IUPAC standard under development. Cooperation between the Journal of Chemical and Engineering Data and NIST has been fully established for data communication, quality assurance, processing, and distribution, based on the global use of GDC and ThermoML. Additionally, a Data Quality Assurance Program has been designed and fully implemented in the area of critical constants data. The targeted goal of 300,000 points per year has been achieved at the TRC Data Entry Facility, including strict quality assurance. Algorithms for the implementation of the Dynamic Data Evaluation concept for pure organic compounds were fully developed in 2003.

Purpose: Thermophysical 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 the 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 NIST SOURCE data system has been migrated to an ORACLE 9i database management system residing on a SUN 280R server. The first version of the GDC has been completed and released by NIST. The first (experimental data framework) and the second (uncertainties) versions of ThermoML have been fully developed and released. TRC efforts in the development of new XML-based technology for thermodynamic data communications have been recognized in the establishment of the IUPAC project “XML-based IUPAC Standard for Experimental and Critically Evaluated Thermodynamic Property Data

[†] deceased

Storage and Capture". It is anticipated that ThermoML will become a prototype of this IUPAC standard being developed. Full-scale cooperation between the Journal of Chemical and Engineering Data and NIST has been established in direct data communication, quality assurance, processing, and distribution, based on the global use of GDC and ThermoML. The algorithms for the implementations of the Dynamic Data Evaluation concept for pure organic compounds were fully developed in 2003 and incorporated into the framework of the ThermoData Engine software currently under development at TRC. The third (twelfth) TRC Consortium Annual Workshop has been held to inform the company members about the progress made in FY03.

Impact: Implementation of further improved and newly developed software tools as well as advanced hardware, networking and data management elements in the NIST TRC Data Entry Facility allowed NIST to reach the designed data entry rate of 300,000 data points per year under strict data quality assurance guidance. That, in turn, allowed capture of all relevant experimental data published between 1993 and 2003 in 5 principal journals (Journal of Chemical and Engineering Data, Journal of Chemical Thermodynamics, International Journal of Thermophysics, Fluid Phase Equilibria, and Thermochemica Acta) using the TRC information systems infrastructure.

Future Plans: Complete the development of the second version of the Guided Data Capture software (including uncertainties description). Complete the development of the third version of the ThermoML (critically evaluated and predicted data). Complete the data capture for all relevant data published by the selected journals in the period 1988-1994 and in 2004. Implement the developed algorithms for Dynamic Data Evaluation of pure compounds into C++ subroutines compiled within Visual.net environment. Complete implementation of the data quality assurance program for the melting and solid-to-solid phase transition data. Cooperate with industry in the development of the software 'readers' for ThermoML.

4. NIST Computational Chemistry Comparison and Benchmark Database

CSTL Program: Data Informatics

Author: *Russell D. Johnson III*

Abstract: The NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB) is a website and database which allows users to compare thermochemical properties determined by experiment or by quantum chemical calculations. The database contains experimental data for 640 species, and over 70,000 calculations on those species. It has been online for four years and during 2003 has served an average of 27000 pages per month. It is accessible at <http://srdata.nist.gov/cccbdb>

Purpose: As computers become faster, modeling becomes a more valuable tool. Quantum mechanics can be used to predict thermochemical properties. However there are many approximations in quantum mechanical calculations and the uncertainty in the predictions is not well established. The NIST CCCBDB, by compiling benchmark experimental and theoretical (from quantum mechanics) results, can illustrate the uncertainty in the theory by allowing comparisons between theory and experiment. The CCCBDB also provides developers of new computational methods a set of benchmark experimental data to test the new methods. The experimental and calculated data includes enthalpies of formation, entropies, heat capacities, geometries (bond lengths, angles, rotational constants), vibrational frequencies, and dipole moments.

Accomplishments: Data and calculations for several new species have been added in response to user requests. The species include diborane (B_2H_6), formamide ($CHONH_2$) and a selection of substituted aromatics, $C_6H_5CH_3$ (toluene), $C_6H_5NH_2$ (aniline), C_6H_5OH (phenol), C_6H_5Cl (chlorobenzene), $C_6H_5C_2H_3$ (styrene), and $C_{10}H_8$ (naphthalene). New web pages are being added continuously to allow more comparisons and ease of data retrieval. The number of calculations on all molecules continues to grow.

Impact: The use of the CCCBDB continues to grow. It serves an average of 27000 web pages per month and over 10000 distinct hosts. As well as its stated purpose the CCCBDB is also used just as a source of benchmark experimental data.

Future Plans: Calculated data from the CCCBDB will be used to assess data quality and supplement experimental databases such as the WebBook and the TRC source. The calculations are ongoing. New methods may be added as they are developed. The experimental data is continuously updated. New molecules are added when there is sufficient demand for an individual molecule or for a class of molecules. The CCCBDB will be expanded to include UV/Vis spectra and properties of transition states.

5. Collaboratory for Multi-Scale Chemical Science

CSTL Program: Data and Informatics

Authors: *T. C. Allison (838); L. Rahn, (Sandia National Laboratory)*

Abstract: The Collaboratory for Multi-Scale Chemical Science (CMCS) project is creating a collaborative environment for research in chemical science areas. This environment is centered around a web portal. Goals of the project include creating the infrastructure necessary to realize a collaborative environment on the internet, providing useful tools to create, collect, analyze and share data, providing the means to annotate data, creating new and open formats for various data and its associated pedigree, and establishing a framework in which scientists from different disciplines working on problems with dramatically different length scales can work in a meaningful and productive fashion.

Purpose: This project is part of the DOE's National Collaboratories Program which funds initiatives to create collaborative infrastructure in a variety of scientific fields. The purpose of the CMCS collaboratory is to enable groups of scientists to work together more productively, to collect relevant data and archive it in a searchable manner, to provide an alternate venue for scientific publication, to foster communication between scientists in different disciplines and to reduce the time and effort required to attack large problems. Participation in the project includes members of the academic, industrial, and government research lab communities. It is expected that each of these groups will benefit from being able to quickly and easily exchange data and communicate their needs to their peers.

Major Accomplishments: A SOAP (simple object access protocol) service was established which makes a large database of chemical names, synonyms, formulae, and CAS numbers accessible within the CMCS portal. Critical components of the CMCS infrastructure related to searching were extensively modified to enhance response time and make the infrastructure extensible to larger data collections. A set of recommendations for attaching pedigree information to chemical data was developed.

Future Plans: This project will continue for another one to three years depending on funding. At the present time a great deal of the infrastructure has been created and the focus is shifting toward demonstration of the capability of the CMCS framework in addressing real scientific problems. Near term activities will include the development of more powerful searching techniques, development of "universal" formats for relevant types of data, creating translators for legacy data, and further incorporation of NIST data accessible through the CMCS portal.

6. Automatic Mass spectral Deconvolution and Identification Software (AMDIS)

CSTL Program: Industrial and Analytical Instruments

Authors: Gary Mallard (838.05), Oleg Toropov (Contractor), and Steve Stein (838.05)

Abstract: The Automatic Mass spectral Deconvolution and Identification Software (AMDIS) was originally designed to detect chemical weapons in violation of the Chemical Weapons Convention while at the same time not revealing confidential information not relevant to the convention. The same fundamental algorithms would clearly be of use in automating the analysis of data taken in gas chromatography/mass spectrometry (GC/MS) in an industrial environment. In these cases the role of AMDIS is to provide faster, unbiased and more statistically testable results - thus allowing higher quality analysis. The major efforts over the last year have been focused on assisting the instrument companies in using AMDIS in conjunction with their instrument software.

Purpose: Extend the utility of the AMDIS software and insure that it is available to the widest range of users. This has included incorporating specific features that the instrument manufacturing community as well as the user community has requested.

Accomplishments: During 2003 presentations were made to several industrial users at their sites with an emphasis on using AMDIS in solving their problems. In addition, detailed presentations were made to two major instrument manufactures to aid in their integration of AMDIS into the instruments. On going, includes changes in library handling to allow for more records in the libraries and new modes of searching. In all cases these changes have come about from direct requests from the users or the instrument companies.

Impact: AMDIS provides the first broadly available method for automating GC/MS analysis. It offers a tool for finding, with high confidence, components in complex mixtures that would otherwise be impossible. In addition, AMDIS can significantly increase the productivity of analysts in the laboratory by doing the first pass analysis in minutes - without direct intervention, rather than hours - with full involvement of the analyst. AMDIS can also aid in providing statistically valid confidence measures for analysis. There is a growing awareness in the GC/MS community of the utility of AMDIS.

Future Plans: New work on AMDIS will focus on extension to the use for selective ion monitoring, exact mass (as needed by LC and TOF instruments), and better methods for integrating the program into instrument company software. The impact of AMDIS will be greatest if it is adopted by as many of the instrument companies as possible. We continue to work closely with the instrument companies and have a number of presentations to them and their users scheduled in the next year.

7. The NIST Retention Index Database

CSTL Program: Industrial and Analytical Instruments

Authors: *Steve Stein, Peter Linstrom, and Gary Mallard*

Abstract: One of the major problems of the use of gas chromatography combined with mass spectrometry in compound identification is the similarity in mass spectra of homologous series. This problem has traditionally been solved by the use of retention index data (a measure of the time a compound elutes from the chromatographic column), but data and prediction for retention indices has not been widely available. The collection and evaluation of the retention index data will provide a new tool for the identification of organic compounds. The initial release of the database (expected early in FY 2004) will contain data for 9000 chemical compounds along with complete literature references.

Purpose: Develop a reliable, comprehensive collection of gas phase retention indices that can be used both in conjunction with the NIST MS database and as a stand-alone database of retention indices for general use in gas chromatography. An important part of this program is to provide users of the database with some measure of the uncertainty of the measurements.

Accomplishments: During 2003 the first release of the database was prepared. The final checking of the release to confirm that all structures and references are present is being undertaken. In addition, the first stage of the collection of data for the second release has begun. Data for over 14,000 compounds are expected to be present with the second release. In addition, a scheme for using group additivity methods for predicting RI data has been developed. The prediction scheme is used to find outliers in the data and allow for data checking with minimal resources. In addition, the prediction scheme will be available as a part of the WebBook.

Impact: The broad question of confidence in identification using modern analytical methods remains important. The use of retention data - which is an orthogonal set of data to mass spectral data - provides a far greater degree of confidence in the identification than either mass spectra or retention index alone would be capable of providing. This additional confidence is used in NIST deconvolution software to determine a match factor that takes into account all that we know about an identification. Retention data has been used in certain very narrow areas - particularly in natural products or petroleum analysis, but the lack of high quality data sets has made it difficult to use retention data for as broad a scope of problems as it could be.

Future Plans: There is a very substantial body of data that has been identified and is in the process of being digitized and analyzed. Only non-polar stationary phases are included in this first version. Polar phases will be added over the next 2 to 3 years. 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 this data and estimation algorithms will be made available to users of the NIST Mass Spectral Library.

8. The NIST Mass Spectral Library - Improving the Evaluation

CSTL Program: Industrial and Analytical Instruments

Authors: Steve Stein, Anzor Mikaya, Carol Clifton, Yuri Mirokhin (Contractor), and Jane Klassen

Abstract: Since the release of the latest version of the NIST mass spectral database (NIST02) the focus of the effort has been on tools and methods to improve the evaluation of the data in preparation for future releases. The use of ion-thermochemistry data to rank probability of ion occurrence in being developed for both internal use and release to the user community. Work is continuing on both the development of standards for MS/MS libraries and specific specialized MS/MS libraries. As always, we continue to work closely with the instrument manufactures and the user community to define the needs for the MS database.

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 GC/MS and to provide fully validated high quality statistically tested algorithms for searching the data to insure that results are consistent with best practices.

Accomplishments: The new version of the MS Interpreter takes into account experimental and estimated heats of formation for ions, in addition, it finds multiple paths for ion decomposition. As a result of these improvements, a far larger fraction of the peaks in a typical mass spectrum are being identified. While the Interpreter is being developed as a tool for evaluation of NIST MS data, it is also a useful tool for quickly understanding a new mass spectra. A candidate molecule can be drawn and the Interpreter will take the structure and compare it to the data from the unknown. While such analysis does not constitute a proof of the structure, it can reduce the effort of the experimenter considerably. In addition to tools to better evaluate the data currently in the database, some changes in the direction of new data acquired have been made. The NIST mass spectral database has had fewer of the important derivative spectra than it should. These spectra are of compounds that are not easy to analyze by conventional GC/MS and so a derivative is made, with is easier to analyze. The largest group of these derivatives are methyl esters (which are well represented in the database) and trimethylsilyl esters (which are underrepresented in the database). The emphasis on the addition of these derivatives as well as the continuing addition of spectra of newly discovered drugs, drug metabolites and natural products will insure that the NIST MS database meets the needs of the GC/MS community

Impact: The GC/MS instrument is one of the most widely used tools for analysis of organic compounds. The efforts at NIST to provide both the best data and tested methods of accessing that data have lead to a wide acceptance of the NIST MS database and the NIST search software as the best combination of tools for use for analysis. With over 2,500 new libraries installed on instruments each year and a large number of upgrades to the new version of the database, the higher quality and increased coverage of the new version will continue to 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, including new evaluation tools and an ongoing examination of structure and naming of the compounds in the database. The size of the database may not grow

as rapidly as in the past, but more emphasis will be placed on acquiring data that fills in specific holes in the database. This will include the acquisition of simple inorganic compounds, organic derivatives, newly developed drugs, newly observed substances of abuse, and naturally occurring compounds.

9. Surface Oxygen Chemistry of a Gas Sensing Material: SnO₂ (101)

CSTL Program: Chemical and Allied products (should this instead be in INDUSTRIAL AND ANALYTICAL INSTRUMENTS AND SERVICES? --- JMC)

Author: A.M. Chaka (838.06); U. Diebold and M. Batzill (Tulane University)

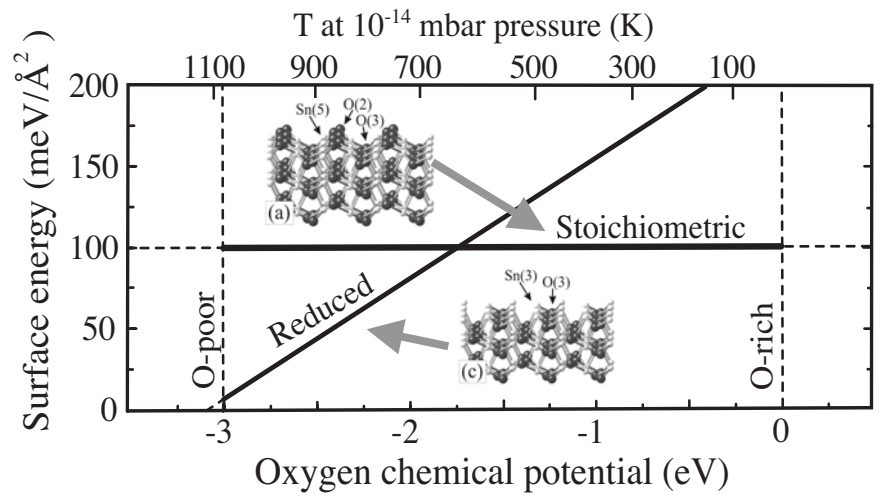
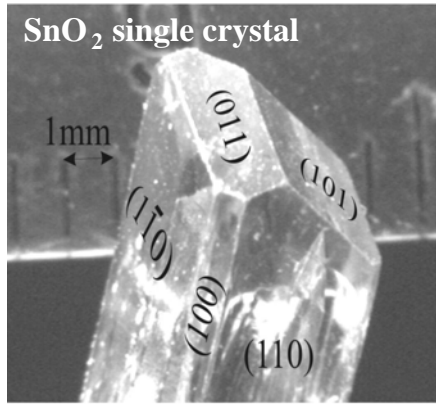
Abstract: Stannic oxide (SnO₂) is used as an oxidation catalyst and is sensitive to the adsorption of oxidizing and reducing gases, which makes it a widely used material for metal-oxide based gas-sensing devices. In gas sensors a change in the electrical resistance of polycrystalline SnO₂ films is detected if the composition of the ambient gas changes. Improving the sensitivity and chemical differentiability of metal oxide sensors has been difficult due to the complexity of the polycrystalline films and poor understanding of the mechanisms responsible for performance. Here the single-crystal SnO₂ (101) surface serves as a model system for gas sensing materials. As the sample is heated, LEIS, STM, ISS, and LEED spectra indicate dramatic changes in the (101) surface from 550-680K @pO₂ 10⁻¹⁴ mbar, which is reversible as pO₂ is varied. Theoretical calculations using density functional theory (DFT) indicate that the stoichiometric Sn⁴⁺O₂²⁻ surface is only stable at high oxygen chemical potential, and as pO₂ is decreased below a threshold pressure a Sn²⁺O²⁻ bulk termination becomes the most thermodynamically favored. These two surfaces interconvert without reconstruction by occupying and vacating bridging oxygen sites. The predicted temperature of ~680K @pO₂ 10⁻¹⁴ mbar is in very good agreement with experimental results. This variability of the surface composition is possible because of the dual valency of Sn (Sn²⁺ or Sn⁴⁺) and is essential for the application of this material in gas sensing devices.

Purpose: The reduced complexity of the single-crystal SnO₂ (101) surface model system allows focusing on the oxygen chemistry and structure under well-defined conditions to identify the mechanisms responsible for conductivity changes in sensors as a function of concentration of environmental gases.

Major Accomplishments: It is not known which crystalline faces are responsible for sensor activity in polycrystalline SnO₂, nor what the mechanisms are. During the past year experimental observations using LEIS, STM, ISS, and LEED on a SnO₂ single crystal have identified the (101) surface as one which undergoes significant changes at elevated temperatures at a pO₂ of 10⁻¹⁴. First principles modeling identified a facile oxidation/reduction reaction as oxygen occupied or vacated bridging sites on the surface. The calculated differences in free energy between these two surfaces predict a temperature threshold at which the interconversion will occur (680 K), which is consistent with the TPISS experiment.

Impact: Understanding the fundamental mechanisms of gas sensors at the atomistic level can lead to design of more sensitive, robust sensors with greater chemical differentiation.

Future Plans: The band structure and density of states at the surface will be calculated to link the differences in surface stoichiometry and oxidation state with observed changes in conductivity as a function of oxygen partial pressure and temperature. Additional surfaces - (110), (100) and (001) - will be investigated, as well as adsorption of other important gases for sensor applications such as CO and NO.



10. A New Noninvasive Approach to the Measurement of Phase Equilibrium

CSTL Program: Industrial and Analytical Instruments

Authors: *Thomas J. Bruno (838); Wendy C. Andersen (Food and Drug Administration)*

Abstract: Accurately describing the phase behavior of mixtures, including those that are reactive, corrosive or toxic (RCT), is crucial for optimizing large and small-scale chemical separations in the chemical and petrochemical industries. We have developed a new non-invasive approach incorporating infrared spectroscopy for composition determination and a vapor entraining magnetic rotor that eliminates the need for recirculation pumps. The new apparatus also permits observation and quantitation of any intermolecular complexation, and the novel metrology eliminates the need to withdraw any mixture samples from the measurement vessel. The instrument has been used for the phase equilibrium measurement of two systems: carbon dioxide + butane (to assess the capabilities of the instrument) and R-134a + polyolester lubricant (required for process optimization in the refrigeration/air conditioning industry). Currently, the apparatus is being used for the measurement of amine containing mixtures, important industrially yet challenging because of intermolecular association. Future work will include a study of alkanolamines in the presence of acid gases, another challenging problem critical to the energy sector.

Purpose: Accurately predicting the phase behavior of mixtures is crucial for optimizing large and small-scale chemical separations in the chemical and petrochemical industries. Many of the important mixtures are reactive, corrosive or toxic (RCT) and therefore difficult to accurately measure with conventional VLE instruments. We have developed a new noninvasive approach to the measurement of this important property.

Major Accomplishments: We have completed the design and construction of a new apparatus that measures phase equilibrium without disturbing the mixture being measured. Two unique and novel features provide the noninvasive approach. First, the composition measurement is based upon mid-range infrared spectroscopy (FTIR), with probes coupled to an equilibrium vessel with fiber optic cables. The compositions of the vapor and liquid phases of a mixture at equilibrium are determined from the spectra, independently and nearly simultaneously, at a particular temperature and pressure. Moreover, any intermolecular complexation can be observed and measured by the spectra. Second, the approach to equilibrium is driven by a new vapor entraining magnetic rotor that eliminates the need for recirculation pumps [1]. The novel metrology eliminates the need to withdraw mixture samples from the measurement vessel for any reason. We have used the new instrument for the phase equilibrium measurement of two systems: carbon dioxide + butane and R-134a + polyolester lubricant. The first was a simple test system that was used to assess the capabilities of the instrument. Measurements on the refrigerant + lubricant mixture were needed by the U.S. Department of Energy, and previous measurements using conventional instruments were unsuccessful. The new approach made the measurement possible.

Impact: The major impact of this work has been to significantly extend our ability to measure a wide variety of mixture classes, and add to our ability with the explicit measurement of intermolecular interaction.

Future Plans: At present, the apparatus is being used for the measurement of amine containing mixtures. These complex yet industrially important materials pose a challenge because of intermolecular association. Subsequently, we will measure alkanolamines in the presence of acid gases, a very challenging problem critical to the energy sector.

Publications:

1. Bruno, T.J., Rybowski, M.C., United States Patent No. 6,585,405, 7/1/03.

11. Measurement Standards for Thermal Analysis

CSTL Program: Measurement Standards (added--JMC)

Authors: *D. G. Archer*

Abstract: Thermal Analysis (TA) is a family of measurement methods in which a characteristic property of a material is followed as temperature is varied. Characteristic properties can be heat, mass, permittivity (dielectric), modulus, or others. Thermal analysis methods are widely used in research and in production analysis in almost all industries including pharmaceutical, polymer, chemical, aerospace, semiconductor and safety engineering. The widespread use of TA methods throughout industry requires a measurement infrastructure that includes calibration methods and standard test methods. This infrastructure requires at least two components: consensus documentary standards and reference materials that can be used, in conjunction with the documentary standards, for calibration of TA instruments and for validation of standard test methods. NIST provides leadership in the development of the measurement infrastructure for TA methods. We make reference materials for calibration and provide leadership in the development of consensus documentary standards. In past years, one of the standards for which NIST led the development and consensus approval was ASTM International's Standard Test Method for Heat of Reaction by Differential Scanning Calorimetry. This year we created and managed an Interlaboratory Test Study to determine the precision of this test method and to explore some of the confounding factors that affect interlaboratory precision. We also completed certification measurements on a new reference material for calibration of differential scanning calorimetry.

Purpose: To provide measurement infrastructure for thermal analysis methods, including reference materials and documentary measurement standards, which benefit wide ranges of NIST's industrial customers. ASTM International's Committee E37 was asked to create a standard test method for heat of reaction by representatives of two industrial groups, polymers and thermal hazard evaluation. In the polymer industry, measurements of heats of reactions can be used to measure the degree of cure of polymers. In the thermal hazard community, heat of reaction and the initiation temperature of a spontaneous reaction are used to assess the risks involved with these thermally unstable materials. In addition, we continued our work to create a set of NIST-certified standard reference materials for differential scanning calorimetry.

Major Accomplishments: 1) An interlaboratory test was created and managed. Volunteer laboratories were enlisted; materials were selected and tested at NIST and then distributed, with directions, to the volunteer laboratories. The study was conducted in two parts. One group was given a sample of 1-phenyl-1H-tetrazole-5-thiol, a thermally unstable mercaptan. The second group was given portions of a commercial sample of 2-butanone peroxide, a thermally unstable free-radical initiator used in the polymer industry. The results from 15 volunteer laboratories have been collected. These results will be analyzed statistically and the appropriate research report will be completed. 2) The temperature and enthalpy of fusion of a sample of bismuth have been completed with high-temperature adiabatic calorimetry. These measurements will be the basis of the certification of SRM 2235, bismuth for calibration of differential scanning calorimetry. 3) ASTM International Standard E967 Standard Practice for Temperature Calibration of Differential Scanning Calorimetry and Differential Thermal Analyzers was revised and led to consensus approval.

Publications this year:

Enthalpy of Fusion of Indium; a Certified Reference Material for Differential Scanning Calorimetry; D. G. Archer and S. Rudtsch. *J. Chem. Eng. Data* **48**, 1157-1163.

New NIST-traceable Standards for Calibration and Validation of DSC; D.G. Archer. Proceedings of the 30th North American Thermal Analysis Society Conference (ed: K. Kociba. B&K Publishing, 2002).

Impact: These accomplishments will provide NIST customers with necessary documentary standards and reference materials with which to better apply thermal analysis methods to their research and manufacturing applications.

Future Plans: In FY2004, we expect to complete certification of SRM 2236. The research report for the Interlaboratory Test Study of ASTM International Standard Test Method E2160-01 will be completed and the Test Method will be revised with the required Precision statements and balloted.

12. Adsorption of Energetic Materials (Explosives) on Surfaces

CSTL Program: Forensics and Homeland Security

Authors: *Thomas J. Bruno (838); Keith E. Miller (University of Denver)*

Abstract: The development of surrogate soil stationary phases for gas chromatography was pioneered at NIST for the evaluation of contaminant adsorptive interactions in the environment. We have now extended our approach to the liquid phase by producing heat treated spray dried soil surrogates, and have applied these surrogates to the study of energetic materials (explosives), residues and taggants. The application of our adsorption metrology to energetic materials is important because of the increased emphasis on homeland security. Several new detectors have been developed for in-the-field detection of explosives, but these devices cannot be used until their performance is certified. Certification cannot be done without an explicit knowledge of the vapor phase concentration of the explosive being measured. Since surfaces play a significant role in determining how much material will exist in the vapor phase, an understanding of the adsorptive interactions is critical. The chromatographic approaches that we have developed are particularly apt in providing that understanding.

Purpose: Because of the critical need to detect the presence of energetic materials (explosives), residues, taggants, etc., in a variety of venues (public places, military installations, hostile locations abroad), several highly sensitive detectors have been developed. Before these devices can be used in most such applications, their performance must be certified. We therefore must develop an understanding of the interaction of these compounds on surfaces in both the vapor and liquid phases.

Major Accomplishments: Following our earlier development of a method to prepare clay soil surrogates (suitable for gas chromatographic adsorption enthalpy measurements), we have now extended the technique to the liquid phase. This was done by preparing a surface by spray-drying a clay suspension to produce 8-10 μm spherical particles that were subsequently heat-treated at 500 $^{\circ}\text{C}$. This material was then slurry- packed in an HPLC column configuration. Measurements were done on a series of substituted benzenes (including hetero-substituted benzenes such as RDX) to determine the partition coefficient, retention factor and enthalpy of adsorption, ΔH_{ads} , in the presence of water. Our measurements led us to a predictive correlation of the interaction on the basis of substituents on the main ring. Our correlation allowed us to conclude that the interaction of substituted benzenes on clay is remarkably similar to that on porous graphitic carbon. At the same time, we noted dramatic differences when the interactions were compared on an organic-like surface such as octadecyl silane. In addition to the development of this predictive correlation, we have measured the enthalpy of adsorption of energetic materials on the clay surface in the presence of water. We found, for example, that the ΔH_{ads} of RDX is 30 percent higher than that of benzene on the clay.

We have also completed measurements of the enthalpy of solution, ΔH_{sol} , of a number of energetic materials in a polymer, polydimethylsiloxane. Thus, the ΔH_{sol} of TNB, TNT, and RDX were measured to be 57.9, 59.5, and 62.4 kJ/mol, respectively. It is interesting to note that these values are approximately 20 kJ/mol lower than the enthalpy of vaporization, ΔH_{vap} , for these compounds.

Impact: This work has demonstrated the importance of surfaces when considering the free concentration of energetic materials that need to be detected in the field, and the need to have a

predictive capability for a variety of compounds. Our observations of the similarity of the clay surface with graphitic carbon, and the enthalpy difference between the bulk solid and absorbed explosives will advance our ability to certify new detection devices.

Future Plans: Future plans include extension of the liquid phase measurements to include modified clays (organo clays). At some point, it will become necessary to explicitly measure the ambient temperature vapor pressures for many of the energetic materials as well.

13. The Industrial Fluid Property Simulation Challenge

CSTL Program: Chemical and Allied Products

Authors: *R. Mountain, A. Chaka, R. Johnson, D. Friend, J. Magee, L. Watts, T. Bruno, R. Chirico, A. Laesecke, E. Lemmon, M. McLinden (838); J. Olson, J. Moore, D. Frurip (Dow Chemical); M. Schiller (Dupont); J. Golab (BP); F. Case (Colgate-Palmolive); R. Ross (3M); P. Kolar (Mitsubishi Chemical)*

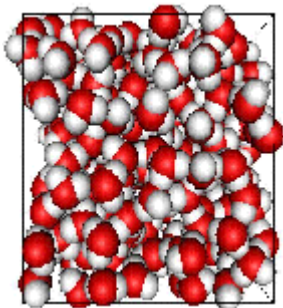
Abstract: Accurate physical property data are critical in product and process design, but the demand for fluid property data far exceeds our capacity to supply it experimentally. This is especially true for unusual, novel, or toxic materials, mixtures, or state points far from ambient conditions where it can be challenging, expensive, or time-consuming to obtain reliable information experimentally in a timely manner. Molecular simulations hold great promise to meet this growing need for property data on demand, but it is not yet clear that this approach is suitably mature for industrial applications. The First Industrial Fluid Properties Simulation Challenge was organized by NIST (together with industrial collaborators) and sponsored by an organ of the American Institute of Chemical Engineers in order to assess the capabilities of these techniques. Successful entrants in this First Challenge were determined, based in part on careful measurement and evaluation of previously unknown property benchmarks, and the interest in this program to further push the frontiers of molecular simulation has led to the initiation of a Second challenge to close in September 2004.

Purpose: Molecular level simulation of dense fluid thermal properties, using molecular dynamics and Monte Carlo methods, has a large potential for predicting thermal and transport properties of industrially important fluids for conditions that are experimentally expensive and/or hazardous. The First Industrial Fluid Properties Simulation Challenge was organized by NIST together with Dow Chemical, DuPont, Colgate-Palmolive, and BP to assess the current capability of simulations to make useful predictions. The challenge was to predict certain liquid properties for specified conditions when the answers were not known.

Major Accomplishments: The First Challenge, sponsored by a committee of the AIChE, was opened to participants in November 2001 and the results of the challenge were announced at the November 2002 AIChE annual meeting. Detailed reports on the challenge, including how the benchmark answers were experimentally determined by NIST and Dow, will be published in a special issue of *Fluid Phase Equilibria*. The Second Challenge (<http://www.cstl.nist.gov/FluidSimulationChallenge>) was opened in September 2003 with challenge problems of predicting vapor pressure and heat of vaporization, solubility of gases in a liquid, and heats of mixing.

Impact: The Challenge brought the current status of simulation methods to the attention of potential industrial users, some of whom are beginning to incorporate molecular level simulation activities within their research and development groups. The First Challenge revealed that existing simulation methods for predicting the shear viscosity may be too inefficient to be of industrial interest, and this has generated interest in improved sampling methods. The challenge has generated interest and support in the academic and industrial research sectors for improving force laws and in improving the efficiency of simulation sampling methods. There currently is no agreement on how to do either of these important tasks. Two additional industrial sponsors, 3M and Mitsubishi Chemical, have signed on to assist with the organization of the Second Challenge.

Future Plans: The Second Challenge will close in September 2004 and the results will be announced at the November 2004 meeting of the AIChE. The Second Challenge will be co-sponsored by the a Divison of the ACS. If the level of interest in the First Challenge is maintained for the Second Challenge, the Challenge will possibly become an annual or biannual event.



14. Thermophysical Properties and a Data Retrieval System for Ionic Liquids

CSTL Program: Data and Informatics

Authors: J. W. Magee, M. Frenkel, R. D. Chirico, Q. Dong, A. Laesecke, M. O. McLinden, R. A. Perkins, J. A. Widegren, D. G. Archer (838); and G. J. 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 US industry with the knowledge base to exploit these solvents, we have begun to study the physical properties of ionic liquids, and to develop both standardized systems and a comprehensive data retrieval system. Thermophysical properties measurements are being compiled and evaluated, and experimental measurements have been initiated on ionic liquids representing broad classes of compounds. CSTL has a key role in recently approved projects under the auspices of the International Union of Pure and Applied Chemistry (IUPAC) that will provide recommendations of standardized systems for data and will develop a comprehensive database for 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 organic or inorganic anion. As such, they are non-volatile and non-flammable. 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 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, a knowledge of standardized systems is needed, and a comprehensive database is needed that could provide US industry with the knowledge base to exploit these solvents.

Major Accomplishments: To achieve the goals outlined above in the shortest time possible and reach an international consensus on the central issues, two IUPAC projects have been initiated with CSTL involvement. The first of these is IUPAC project *Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems* (2002-005-1-100; K. N. Marsh – Task Group Chairman, M. Frenkel, A. Heintz, J. W. Magee – members). This project is addressing the concern that currently there are no internationally adopted standards for reporting thermodynamic data for ionic liquids. This fact in combination with the reality that a significant part of these data are being reported in journals that are not traditionally known for the publication of high-quality thermodynamic data and therefore lack consistent requirements, has led to major barriers to an unambiguous interpretation of the data and a critical evaluation with regard to their uncertainties. In many instances, this could drastically diminish the value of the reported numerical data that could be used in a variety of engineering applications. To address these issues, a standardization in reporting thermodynamic data for ionic liquids could be accomplished by an expansion of the Guided Data Capture (GDC) software developed by the NIST Thermodynamics Research Center. This task group opened a discussion of the issues by conducting the 1st IUPAC Workshop on Ionic Liquids, held at the 17th IUPAC Conference on Chemical Thermodynamics (Rostock, Germany). Outcomes of this workshop were reported in a recent issue of the *Journal of Chemical and Engineering Data*. The second IUPAC project *Ionic Liquids Database* (2003-020-2-100; K. R. Seddon – Task Group Chairman, [A. Burgess](#), [M. Frenkel](#), [M. Gaune-Escard](#), [A. Heintz](#), J. W. Magee, [K. N. Marsh](#), [R. Sheldon](#) – members) is addressing the need for an open-access, public-domain data storage system scoped to cover information pertaining to ionic liquids. The vision for this project is to create a distributed-access data retrieval system for ionic liquids and their mixtures that encompasses chemical

structure, solvent properties, ionic liquids in synthesis, reviews, reactions and catalysis, manufacturer information, benchmark properties and models, and thermophysical and thermochemical data. In addition to the IUPAC projects, a measurement program continues to provide benchmark physical properties data for selected ionic liquids that are liquid-phase at room temperature and stable in both air and with moisture. For 1-butyl-3-methylimidazolium hexafluorophosphate, considered to be the archetypal ionic liquid, we have published the first reports of thermodynamic properties of the ideal state at temperatures to 1500 K and high-accuracy thermodynamic properties in condensed states (crystal, glass and liquid) covering a range of temperatures from 5 to 550 K.

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

Future Plans: The 2nd IUPAC Workshop on Ionic Liquids will be held in 2004, and the IUPAC task group on the database will subdivide the work plan into manageable goals that can be independently achieved. Physical properties studies will continue with new measurements of thermodynamic properties (density, heat capacity, speed of sound, and enthalpy of solution) and also expand to the transport properties (viscosity and thermal conductivity). 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.

Publications: Preface to Special Section: Papers Presented at the Workshop on Ionic Liquids, ICCT, Rostock, Germany, July 28 to August 2, 2002. J. W. Magee, *J. Chem. Eng. Data* **2003**, *48*, 445.

Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Ideal Gas State. Y.U. Paulechka, G.J. Kabo, A.V. Blokhin, O.A. Vydrov, J.W. Magee, and M. Frenkel, *J. Chem. Eng. Data* **2003**, *48*, 457-462.

Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Condensed State. G. J. Kabo, A. V. Blokhin, Y. U. Paulechka, A. G. Kabo, M. P. Shymanovich, J. W. Magee, *J. Chem. Eng. Data* **2004**, in press.

15. Advanced Experimental Capabilities for Fluid Properties Measurements

CSTL Program: Chemical and Allied Products (should this instead be in MEASUREMENT STANDARDS? --- JMC)

Authors: R.A. Perkins, A. Laesecke, J. Magee, M. McLinden, S. Outcalt, J. Scott, S. Altintas (PREP Postdoc), A. Abdulagatov (Russian Academy of Sciences), and C. Lössch (Rubotherm)

Abstract: Advances in measurement technology enable new and improved measurements of the thermophysical properties of gases, liquids, and supercritical fluids. Unique apparatus are under development for improved measurements of density, sound speed, critical points, and phase equilibrium. These apparatus share the common goals of high-accuracy and rapid measurements over a wide range of fluid types and conditions. The sample size is minimized to enable measurements of high-purity, rare, and/or hazardous materials. Materials of construction are selected for maximum resistance to corrosive fluids.

Purpose: These apparatus allow us to provide the data required to extend our knowledge of the thermophysical properties of fluids, to develop *de-facto* and international standards, and to help satisfy the property needs of the chemical, energy, refrigeration, and aerospace industries. In addition, each new experimental capability is well documented to aid industry in the development of its own capability to accurately measure thermophysical properties.

Major Accomplishments: The two-sinker densimeter has demonstrated a reproducibility of 0.0002 kg/m^3 , which represents sub-ppm resolution for liquids and of the order of 20 ppm for gases at 1 MPa. The uncertainty in density is 25 ppm at 293 K and increases at the extremes of temperature, i.e. 90 K and 520 K. A complementary isochoric PVT cell is under development to cover the high temperature region up to 1000 K with pressures up to 20 MPa. This isochoric PVT cell has a greater uncertainty (0.02-0.03 % in density) but is very robust and corrosion resistant as required for fluids at high temperatures. A short-residence-time flow apparatus is under development to rapidly measure the critical temperature (up to 1000 K) and pressure (up to 10 MPa) of small samples of fluids with an uncertainty of 0.08 K and 0.01 MPa. A new apparatus to measure phase equilibrium for systems where multiple liquid phases coexist with the vapor phase has been demonstrated with initial test measurements of propane. This apparatus operates at temperatures from 200 to 400 K and utilizes a moveable capillary line to sample each phase since the volume of each phase can vary significantly. Finally, a cylindrical sound speed apparatus, based on the pulse-echo technique, has been developed for liquid measurements from 90 K to 310 K. Tests on liquid propane verified that the uncertainty in sound speed is less than 0.05 %.

Impact: Apparatus developed under this program have been used to establish several *de-facto* standards for the thermophysical properties of fluids. These standards allow the calibration and performance verification of apparatus used to measure the thermophysical properties of fluids. Data measured with these apparatus, along with available literature data, forms the basis of correlations and models in NIST databases, such as REFPROP, so that industry has convenient access to the most accurate properties available.

Future Plans: It is necessary to continue to develop our experimental capabilities to meet the evolving needs of U.S. industry, while taking advantage of technological advances in

micromachining and electronics. In this regard, work has begun on apparatus and procedures to characterize the thermophysical properties of ionic liquids.

16. Properties of Rocket Propellant (RP-1)

CSTL Program: Data and Informatics (should this instead be Automotive and Aerospace? --- JMC)

Authors: *J. W. Magee, D. G. Friend, T. J Bruno, M. L. Huber, E. W. Lemmon, A. Laesecke, R. A. Perkins, J. A. Widegren (838); and I. M. Abdulagatov (Russian Academy of Sciences)*

Abstract: Thermophysical properties of rocket propellant (RP-1) are being measured, and new models for this fuel are under development. Prior to this work, published data were limited to near atmospheric pressure and temperatures to less than about 100 °C. NASA requires validated property information at higher temperatures and pressures for the development of a Rocket Engine Prototype planned for future launch vehicles. A measurement program is underway that is intended to provide high quality data in order to support the advanced model development. Measurements of chemical composition, stability, density, heat capacity, viscosity and thermal conductivity are being conducted in a range of temperatures up to 700 K and pressures to 60 MPa. The first compositional studies, based largely on a GC-MS method, have identified key components and classes of chemicals found in a sample of RP-1. Initial measurements of density and viscosity have been completed, and advanced models, based on both published data and these new measurements, are under development.

Purpose: The National Aeronautics and Space Administration (NASA) has, for decades, used a kerosene blend, designated RP-1, as a rocket propellant. Presently, NASA and its contractors are designing advanced rocket engines that will combust RP-1 fuel. While reliable thermophysical properties are essential for this purpose, present-day models are either based on a pure component surrogate compound (dodecane) or on estimation methods that are grounded in very limited data. To address the issues surrounding the accuracy of thermophysical properties of RP-1, new measurements and models were needed.

Major Accomplishments: A gas chromatography - mass spectrometry method was used to chemically characterize a sample of RP-1 supplied by NASA. As expected, the ion chromatogram showed that RP-1 is a complex liquid fuel that consists of significantly more than 100 components. When the best resolved chromatogram peaks were individually integrated and interpreted, a report was prepared that identifies the key constituents of this mixture. From this report, an initial slate of compounds has been selected for a surrogate mixture to be used for modeling thermophysical properties. The selection was based on the predominance in RP-1 and the variety of chemical structures to represent key classes of compounds identified in the complex fuel. An experimental program was initiated to measure important thermodynamic (density and heat capacity) and transport (viscosity and thermal conductivity) properties of RP-1 in ranges of temperature from 300 to 700 K and pressure from 0.1 to 60 MPa. The first measurements reported were the density and viscosity. Modeling studies have concentrated on the pure compounds comprising the surrogate mixture. Short equations of state and models for the transport properties have been developed for each of these constituents of RP-1, and a preliminary Helmholtz energy mixture model has been developed that is based using a set of predicted interaction parameters. Similarly, a preliminary mixture model has been nearly completed for the transport properties of RP-1.

Impact: The properties information developed under this project will be used by NASA, under its Space Launch Initiative's Next Generation Launch Technology Program. The feasibility of developing a "Rocket Engine Prototype" as a highly reliable long-life liquid oxygen/kerosene

engine for future launch vehicles depends, in part, on the thermodynamic and transport properties of RP-1, at the high pressure and temperature conditions required for the high performance propulsion system. The techniques for characterizing complex fuels, the measurement protocols, and the modeling algorithms will increase our ability to describe a variety of fuels used for aerospace and ground transportation.

Future Plans: Measurements of the heat capacity and the thermal conductivity of RP-1 will be completed in wide ranges of state conditions. A pseudo-pure fluid Helmholtz energy formulation will be developed to accurately represent the thermodynamic properties of the RP-1 mixture. In this formulation, the dew and bubble point pressures will be calculated from the Helmholtz mixture model. Transport properties models for dodecane will be formulated based on published data. When the new experimental data are available, the models for the transport properties of RP-1 will be updated. To disseminate these results to design engineers, the updated thermodynamic and transport properties models for RP-1 will be incorporated into a special version of the NIST REFPROP database. This project is seen as part of a more comprehensive program to develop evaluated and standardized property information for a series of complex fuels.

17. Structure and Reactivity of the Hydrated Hematite (0001) Surface

CSTL Program: Energy and Environmental Technologies, Chemical and Allied products

Authors: A.M. Chaka (838); T. Trainor, P. Eng, and M. Newville (U. Chicago), G. Waychunas (Lawrence Berkeley National Lab), J. Catalano and G.E. Brown (Stanford)

Abstract: Reactions at metal-oxide surfaces are of great significance in environmental chemistry of contaminants in aquifers and soils, as well as industrial/technological processes such as catalysis, microelectronics, and passivation of metals. Hematite (α - Fe_2O_3) and the isostructural corundum (α - Al_2O_3) are among the most common metal oxides in industry and in soils, but exhibit drastically different chemistry for reasons that are not understood. Using crystal truncation rod diffraction (CTR) and *ab initio* thermodynamics (first principles density functional theory (DFT) electronic structure calculations linked to finite temperature and pressure thermodynamics), it was determined that the stable hydrated hematite (0001) surface consists of two domains – one with Fe-rich regions terminated by singly coordinated hydroxyls, and one with oxygen-rich regions terminated by doubly and triply coordinated hydroxyls. The presence of singly coordinated hydroxyls on hydrated α - Fe_2O_3 (0001) and their absence on hydrated α - Al_2O_3 (0001) explain the higher reactivity of the former. DFT calculations indicate that water reacts with hematite both heterolytically and homolytically at a threshold water pressure orders of magnitude lower on α - Fe_2O_3 (0001) than on α - Al_2O_3 (0001). The electronic structure of corundum does not support the homolytic dissociation mechanism of water.

Purpose: To obtain a molecular and nanoscale understanding of metal oxide structure and chemistry in a realistic environment to order to develop robust, predictive models for development of catalysts, coatings, sensors, microelectronic components, corrosion inhibitors, as well as mediation of ground and surface water pollutants.

Major Accomplishments: Investigating surface phenomena under realistic conditions has been a long standing challenge due to the limitations of traditional ultrahigh vacuum spectroscopic instrumentation and 0K first principle electronic structure calculations. The types of surface functional groups exposed at metal-oxide/water interfaces are likely to differ substantially from models based on ideal surface terminations of the bulk crystal and should result in dramatic differences in reactivity compared with clean or dehydroxylated surfaces. The combination of theoretical and experimental work performed in a wet environment has provided the first evidence for the fundamental mechanisms involved in the early stages of hydrolysis of iron atoms in iron oxide. Phase diagrams of the surface free energies calculated as a function of water vapor pressure and in equilibrium with liquid water, as well as surface relaxations, were used to identify the structure of the two domains observed in the CTR experiment on the hydrated hematite surface and to account for the difference in reactivity between Fe and Al oxide.

Impact: In the environmental arena, this work will lead to improved predictive models used for assessment of contaminant risk and the design of contaminant remediation strategies in soil and groundwater. In technological applications, knowing how the structure and reactivity of a metal oxide surface changes upon exposure to water enables better design and control of surface properties for industrial conditions. The theoretical techniques developed in this work can be extended to sensor and thin film growth applications.

Future Plans: Investigate the structure/reactivity relationship of iron oxide surfaces under chemical conditions likely to be encountered in environmental and biogeochemical settings. Of

particular interest is the interaction of the iron oxide surface with priority contaminant metals (Pb(II), Zn(II), Cd(II) and Hg(II)), as well as the impact of common aqueous reductants, such as Fe(II), and low molecular weight organic acids on surface structure and reactivity.

18. Thermodynamic Interpretation of Low-pressure Ion-molecule Reactions

CSTL Program: Chemicals and Allied Products

Author: *Karl K. Irikura*

Abstract: Thermochemical data is used throughout chemistry to determine the feasibility and the thermal requirements of chemical reactions. Its fundamental importance justifies prominence in standard compilations such as the NIST Chemistry WebBook. Part of the quality control for such data compilations involves understanding the proper procedures for analyzing experimental data. In most cases, the original publications follow standard procedures and data interpretation is not a serious issue. However, an important exception is the interpretation of low-pressure reactions between ions and neutral gases. Two incompatible procedures have been in use since the beginning of that field of research, ensuring that a large fraction of the experiments have been analyzed incorrectly. Although the resulting errors are usually small, they are large in some situations. We are working to resolve the controversy, which will lead to improved data quality and the avoidance of future errors.

Purpose: Gas-phase studies of reactions between ions and molecules have been a rich source of thermochemical data for more than 30 years. Surprisingly, there are two competing procedures for extracting thermodynamic data from the experimental observations. Only one of these procedures can be correct. In practice, the two procedures usually give similar results, so the fundamental confusion in interpretation has been neglected. However, for some types of reaction (those with large entropy changes) the two methods of analysis give widely different results. Consequently, the debate over interpretations has been revived. The goal of this project is to settle the debate.

Major Accomplishments: This work has stimulated at least one additional experimental study and an opposing opinion. In reply, an additional publication has been prepared, which offers additional evidence and arguments in favor of one interpretation.

Impact: A large amount of thermochemistry in the standard databases is incorrect because of mistakes in the data analysis. Once consensus is reached about the correct procedure, past errors can be corrected and future errors avoided.

Future Plans: A list of high-entropy reactions should be extracted from the published literature. Comparison of the observed reaction rates with the corresponding reaction thermochemistry, either from independent experiments or from theory, will accelerate the resolution of the controversy.

19. Predicting Vibrational Spectra of Dissolved Salts

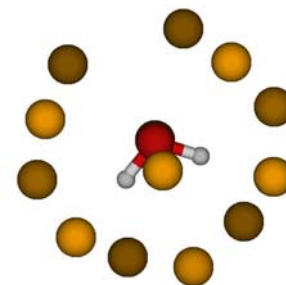
CSTL Program: Chemicals and Allied Products

Author: *Karl K. Irikura*

Abstract: Vibrational spectroscopy is an important technique in analytical chemistry. Compounds are identified by comparing observed spectra with those of candidate compounds, which must be previously known or predicted by theory. Despite the ubiquity of ions throughout chemistry, there are no reliable theoretical procedures for predicting their vibrational spectra in solution. The goal of this project is to produce a reliable, practical procedure to fill this need. This would have widespread impact for the analysis of organic and inorganic compounds. To date, the most popular, cheapest models have been found useless, and better models are being investigated.

Purpose: Aqueous ions are commonplace and important in biology, geochemistry, many manufacturing processes, and elsewhere. Vibrational spectroscopies (infrared, Raman, and near-infrared) are often used to analyze or monitor such systems. For example, most biological molecules are ions, and vibrational spectroscopy is important for identifying their structures and interactions. For chemical analysis, molecules can only be identified by spectroscopy if the spectra of candidate molecules can be predicted in some way, for comparison. Modern theoretical methods can now predict gas-phase spectra with useful precision, but predicting condensed-phase spectra is more challenging. Ions are especially difficult because they interact strongly with the solvent or matrix, often causing dramatic changes in the spectrum. Although significant progress has been achieved in modeling solvation, the primary emphasis has been on energetics, with a secondary emphasis on molecular structure. The performance of solvation models in predicting vibrational spectra using quantum chemistry has received little attention.

Major Accomplishments: The inexpensive continuum models tested have failed. Consequently, computations with explicit solvent molecules are now underway. Two reasonable electronic-structure models have been identified and compared for the prototype ion H_2O^+ solvated by neon, which was chosen as the initial, simple case for which benchmark experimental data are available. Increasingly large computations still have not reached the bulk limit. A sample structure for $\text{H}_2\text{O}^+(\text{Ne})_{13}$ is illustrated.



Impact: Reliable theory will permit observed spectra to be assigned with confidence, thus providing the necessary interpretation of the experimental data.

Future Plans: Ion-solvent clusters are mechanically “soft”, with multiple, competing structures. The corresponding effect upon the vibrational spectrum remains to be investigated. Simulated-annealing approaches will also be applied to find the most stable structure for each cluster. Both procedures will help in reaching the bulk limit, a major goal of this project.

20. Isodesmic reactions for transition states (IRTS)

CSTL Program: Chemical and Allied Products

Authors: V.D. Knyazev

Abstract: The technique of isodesmic reactions for transition states (IRTS) has been developed and validated for calculation of reaction barriers and rate constants. This computational approach is based on combining accurate experimental knowledge of reactivity in one or several reactions of the same class with computational information based on quantum chemistry. The IRTS technique has been shown to yield the energy barriers and rate constants for abstraction reactions of two classes (H + chloroalkanes and Cl + halomethanes) with a high degree of accuracy. For example, average deviations between calculated and experimental rate constants for seven H + chloroalkane reactions considered are 17 – 24%, depending on the quantum chemical method used. Accuracy in reaction barrier calculations at the level of a few kJ mol⁻¹ has been demonstrated for the Cl + halomethanes reaction.

Purpose: To provide computational tools for accurate prediction of reactivity (calculation of reaction barriers and rate constants) for series of chemical reactions of the same type.

Major Accomplishments: The technique of isodesmic reactions for transition states (IRTS) for accurate calculation of reaction barriers and rate constants has been developed and validated. For the two classes of reactions considered (H + chloroalkanes and Cl + halomethanes), accuracy of the reaction barriers obtained using this technique significantly exceeds that achieved with even much more expensive high-level quantum chemical methods without the use of the IRTS technique. At the same time, the IRTS technique can be used in combination with relatively computationally inexpensive quantum chemical methods without loss of accuracy. Two articles have been published in *J. Phys. Chem. A*.

Impact: The results will have an impact on the field of chemical kinetics by providing a predictive computational tool suitable for quantitative evaluation of reactivity in a wide range of chemical reactive systems. This tool is expected to find application in several fields of chemistry beyond gas phase kinetics, such as materials chemistry, nanotechnology, polymer chemistry, biochemistry, organic synthesis, studies of soot and pollutant formation, etc.

Future Plans: We plan to extend the field of application of the IRTS technique to reactions involving large molecules relevant to polymer chemistry, nanotechnology, and biochemistry. Also, we intend to develop a tool for reactivity extrapolation from small to large molecular systems via isodesmic reactions for transition states.

21. Evaluated Molecular Structures and Vibrational Frequencies for C1-C2 Chlorocarbons

CSTL Program: Chemicals and Allied Products

Authors: *D.R. Burgess Jr. and J.A. Manion*

Abstract: Chlorinated hydrocarbons are used throughout the chemical industry, both as end products and as base chemicals in the production of refrigerants, plastics, pesticides, solvents, and other products. Reliable molecular property data are needed to derive accurate thermodynamic information for use in models of industrial production, to better understand the fates of chlorinated compounds in the environment, and to improve waste destruction methodologies. We have recently reviewed the experimental information on the enthalpies of formation of the stable C₁ and C₂ closed-shell chlorinated hydrocarbons. The present work is a related effort, where we have compiled and recommended gas-phase molecular geometry and vibrational frequency data (including torsion and inversion modes) for all C₁ and C₂ chlorocarbons, including radicals. The intent is to provide a reliable self-consistent set of data, which will enable the accurate modeling of chemical systems containing these molecules. The closed shell species considered herein generally have complete or near-complete structural and vibrational frequency data determined by experimental methods. This is not the case for the radicals which, because of their transient nature, are much more difficult to study experimentally.

Purpose: To provide reliable molecular property data for deriving accurate thermodynamic functions for use in models in industrial production and waste destruction technologies where chlorinated compounds are involved. To provide a systematic assessment of the current state of our ability to accurately compute molecular properties for this important class of compounds.

Major Accomplishments: Molecular geometry and vibrational frequency data for C₁ and C₂ chlorocarbons have been compiled and evaluated. The available experimental data were supplemented with *ab initio* and density functional theory calculations both from the literature and from our own work. Comparisons between experimental and calculated data were made to verify the experimental data, to validate the calculated values, and to provide theoretical values in the absence of experimental data. We have attempted to correct the theoretical geometrical parameters and vibrational frequencies for systematic differences by benchmarking the calculations using similar molecules with reliable experimental data. Based on the evaluated experimental data, supplemented with those from calculations, recommended values for the molecular structure and vibrational frequencies (including torsion and inversion modes) are given for each of the molecules. The C₁ chlorocarbons include the chlorine-substituted methanes, methyl radicals, methylenes, and the chloromethylidyne radical. The C₂ chlorocarbons include the chlorine-substituted ethanes, ethyl radicals, ethenes, ethenyl radicals, ethynes, and the chloroethynyl radical. We include data for the unsubstituted, reference compounds (*e.g.*, methane, methyl radical, ethane, ethyl radical).

Impact: These reliable molecular property data will allow NIST customers to derive accurate thermodynamic information for use in models of industrial production, to better understand the fates of chlorinated compounds in the environment, and to improve waste destruction methodologies. Additionally, this systematic assessment of the current state of our ability to accurately compute molecular properties for this and similar classes of compounds is very important as the chemical industry requires an ever-increasing amount of information on a wider variety of compounds. The pace of change has far outstripped our ability to provide this

information on a purely experimental basis. Species of interest frequently have highly polar substituents, including chlorine, and these compounds have proved to be among the most difficult to calculate accurately. The work thus provides a reliable database with which to compare alternate predictive strategies and computational methods, as well as provide guidance on the best methods to extend available information to related compounds.

Future Plans: In FY2003, we expect to provide a measure of comparison between enthalpies of formation for these molecules computed through ab initio methods and those recommended in our recent review based on experimental data in the literature. We also expect to extend the evaluation of molecular property data to small-to-moderate (C1-C5) hydrocarbons, both stable molecules and radicals, important in hydrocarbon combustion.

22. Evaluation of Free Radical Standard Potentials

CSTL Program: Chemicals and Allied Products (should this be in MEASUREMENT STANDARDS? -- JMC)

Authors: *P. Neta and R. E. Huie*

Abstract: Standard potentials for a broad set of organic and inorganic free radicals are being compiled and evaluated as part of an international collaboration under the auspices of IUPAC.

Purpose: The standard electrode potential of a substance is a fundamental thermodynamic quantity that represents the tendency for a molecule to gain or lose electrons. They are widely used by the scientific community since they provide predictive power about the course of chemical reactions. Although these have been extensively evaluated and tabulated for stable species, the situation is much less satisfactory for reactive intermediates such as free radicals. The explosive growth in biochemical articles in which one-electron oxidations and reductions are explored has highlighted the need for an updated evaluation of these standard potentials. To do this work, an IUPAC Task Group was formed, with CSTL participation, with the objective of updating the earlier compilations, published in 1989, and developing a consistent set of recommended standard potentials for a wide range of organic and inorganic radicals in aqueous solutions.

Major Accomplishments: The first major phase of this activity, data compilation and evaluation for the major organic and inorganic radicals, has been mostly completed. At CSTL, a number of organic radicals derived from phenols, anilines, indols, and related antioxidants were evaluated based on various equilibrium studies and recommendations presented to the Task Group. Also, standard potentials were derived for the solvated electron and the hydrogen atom. These are particularly important as they form an anchor point for the reducing end of the potential scale. Other members of the Task Group have dealt with a range of other organic and inorganic free radicals, including the important hydroxyl radical, which anchors the oxidizing end of the potential scale.

Impact: This activity is expected to have an immediate impact in the field of physiological free radical chemistry, which is increasingly recognized as a critical component of the life process. It is also expected to have an impact in such areas as advanced oxidation technologies, which are usually based on free radical chemistry, and in the development of antioxidants for use in stabilizing organic systems such as polymers. This effort will also form a logical framework for further research to clear up problems that are being uncovered.

Future Plans: The planned CSTL contribution to this IUPAC effort for the future includes an extension to aromatic organochalcogens and organoradicals derived by oxidation and the inorganic P, As, Sb, Bi radicals. We will also work with the Task Group in carrying out the optimization of the standard potential scale and would like to establish a public web site at NIST for the dissemination of these results.

23. Properties and Processes for Cryogenic Refrigeration

CSTL Program: Auto and Aerospace

Authors: *R. Radebaugh, P. Bradley, M. Lewis, (J. Gary and A. O'Gallagher, Applied and Computational Mathematics Division), (Dr. E. Luo, Chinese Academy of Sciences).*

Abstract: This research aims to develop measurement and modeling techniques for evaluating and improving performance of cryocoolers and their components; to develop new and improved refrigeration and heat transfer processes below about 230 K; and to provide an electronic database on cryogenic material properties. Models were developed and measurements made for the behavior of inertance tubes in pulse tube refrigerators. The models are also used to optimize the geometry of inertance tubes. Technology related to a pulse tube neon liquefier was transferred to industry, and a 15 K two-stage pulse tube refrigerator was developed for use with both thermoacoustic and mechanical pressure oscillators with an ultimate goal of liquefying and subcooling hydrogen. A low temperature of 17 K was achieved in the prototype after additional fabrication, testing, and development of measurement procedures. A two-stage pulse tube refrigerator was developed for cooling superconducting motors and for comparisons with our models. We have also modeled, designed, fabricated, and tested a prototype pulse tube cryocooler for higher-than-normal temperatures for possible dermatology applications. Comparisons with the model show reasonable agreement, but an improved pressure oscillator with position sensors is required for more accurate comparisons. Our web-based electronic database on the properties of materials at cryogenic temperatures is being redesigned to handle additional data and more extensive references.

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 industrial gas, and many other existing and potential applications. The use of these technologies has been hampered because of problems with existing cryocoolers, including short lifetimes, inefficiency, high cost, and excessive vibration. Metrology needs to be developed to characterize losses, and models are needed to optimize the design of such systems. Material properties at cryogenic temperatures are required for the design of cryogenic equipment.

Major Accomplishments: We have carried out measurements of the complex fluid dynamic impedance of small inertance tubes and compared them with two types of models. Our measurements revealed that typical laminar flow elements have large errors in the measurement of oscillating flows, whereas hot-wire anemometers do not. Papers were presented at the Cryogenic Engineering Conference on the results of our measurements and modeling of inertance tube behavior. A large (500 W at 30 K) prototype pulse tube neon liquefier was developed last year, and extensive tests have now been completed to measure losses in both the regenerator and the pulse tube. The pulse tube effectiveness was found to be even better than expected, but losses in the regenerator were higher than expected. Measurements indicated that temperature non-uniformities exist which may be a result of non-uniform flow; we have not yet been able to pinpoint the reason for such behavior. Solving this problem is very important for large pulse tube refrigerators being considered for cooling of power applications of superconductors (motors, generators, transformers, and fault current limiters). Under a CRADA, we assisted another sponsor in developing test measurements that led to obtaining temperatures

of about 17 K in a small two-stage pulse tube refrigerator that we designed to achieve 15 K. The sponsor plans to use this prototype 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. We began tests on another two-stage pulse tube refrigerator for use in cooling large superconducting motors. As part of a fourth CRADA (with a medical device company), we completed measurements on the performance of a simple pulse tube refrigerator for the cooling of dermatological pens to about –90 °C. Such temperatures are higher than typical operating temperature of pulse tube refrigerators, and although our models predicted the performance quite well, problems with the compressor have hampered some necessary measurements. An invited book chapter on “Refrigeration for Superconductors” has been developed for a special IEEE Proceedings on *Electronic and Large Scale Applications of Superconductivity*. The chapter is about 75% completed; it is expected to be about 30 pages in length and cover the fundamentals of refrigeration for both small and large superconducting systems. The layout of our existing group web site is currently being redesigned to handle additional data that we expect to include in the database on the properties of cryogenic materials.

Impact: Our accomplishments during this past year have provided industry with new tools to improve the performance of cryocoolers, particularly those operating at temperatures below about 50 K and above 150 K. Our model for inertance tubes led to the publishing of design curves for their optimization, and the model results in more efficient cryocoolers. Our work on two-stage pulse tubes at 30 K and below will aid the superconductor industry in the development of superconducting systems that can be marketed to a larger customer base and improve the electrical infrastructure of the U.S. Our materials properties database is now receiving considerable 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 by various parameters.

24. High-Throughput Liquid Transport Properties Measurements in Membranes and Films

CSTL Programs: Chemicals and Allied Products

Authors: *C. Muzny, S. Outcalt, J. Scott, L. Watts, and R. 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 separations processes.

Major Accomplishments: The testing of this instrument using standard test fluorophores has continued. The characterization via fluorescence correlation spectroscopy of the molecular diffusivity of the G4 PAMAM dendrimers that are used as test fluorophores in this experiment was performed. This novel technique provides the fundamental measurement needed for membrane transport characterization of a molecular species. With the instrument operating in a continuous test and data production mode, numerous operational problems were identified including a lack of fluorescence stability, robotic liquid handling problems, and a large number of program and control problems. The issue of fluorescence stability was largely addressed by testing a range of buffer solutions in order to control the pH. Automation issues have also been solved, and the instrument has now been operating stably for periods of up to one month with only standard maintenance needed. A web-based database of membrane transport data being produced has been developed and is currently undergoing internal testing. While fluorescence detection is the current standard for this instrument, it is designed to be capable of other remote optical detection methods. Because of the limitations imposed on the experiment by the fluorescence technique, a study of other techniques including Raman spectroscopy and UV-Vis absorption spectroscopy was made.

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: Final launch of the web-based database for membrane transport data produced by this instrument is the next major goal. The continued production of data by the instrument is also key to its the ultimate usefulness

25. Measurements, Modeling, and Data for Pressure-Driven Membrane Separations

CSTL Program: Chemicals and Allied Products

Authors: *C. Muzny, H. Sun, J. Moon, J. Cho (University of Colorado), M. Chapman (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 physical membranes and the complex mixture to which the membranes are subjected for separations testing. Membranes are 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. Membrane fouling experiments are also being conducted as part of membrane performance testing under standard 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. 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.

Major Accomplishments: The standard physical property used industrially to characterize membranes is the pore size distribution or a molecular weight cutoff. Since the concept of a pore size distribution has no industrial standard, we have developed a set of standard membranes with highly regular pore structures for use in development of standard membrane characterization methods. These are inorganic membranes with pores in the 10 nm -100 nm size range with very narrow pore diameter distributions. The liquid-liquid porosimetry apparatus for physical characterization of membranes that we previously developed has been used as the principle characterization method for these standard membranes, although FESEM has also been used for pore size verification. Membrane testing has also included a fouling study using uniformly sized polystyrene beads as a model foulant. By looking at both monodisperse and polydisperse foulant solutions, we have been able to test the validity of a standard fouling model on particles in the 10 nm – 100 nm size range. Characterization of these fouling solutions has also included field flow fractionation, and correlations between field flow fractionation results and flux reduction continue to be developed. 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 now in service and being used to test the performance of spiral wound, reverse osmosis modules under the standard conditions .

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 membrane module test bed will continue to be used to generate membrane performance data. The liquid-liquid porosimetry apparatus will continue to be used for characterization of various membranes. Modeling of the degradation of membrane performance is a key component of this overall program and will continue to be developed.

26. International Standards for Refrigerant Properties

CSTL Program: Physical Property Data

Authors: *M.O. McLinden and E.W. Lemmon*

Abstract: A new ISO standard for the thermodynamic properties of 14 key refrigerants (10 pure fluids and four refrigerant blends) has been completed and is currently in review as a Draft International Standard. This Standard is based on the same equations of state implemented in the NIST REFPROP database, and NIST staff were lead authors of the Standard. Assuming its acceptance, it will define the properties used by the air-conditioning and refrigeration industry for the performance rating of their equipment.

Purpose: To evaluate the energy efficiency, capacity, etc. of any fluid in a thermodynamic cycle, knowledge of the thermophysical properties is required. Standards exist for determining and reporting the performance of air-conditioning systems at standard ratings conditions. But differences among multiple property formulations lead to differing performance ratings. This is especially a problem in international trade and was the prime motivation for ISO to develop a standard for refrigerant properties.

Major Accomplishments: The new ISO Standard, entitled “Refrigerant Properties,” has progressed from a blank sheet to the status of a Draft International Standard in just over three years. The ISO Working Group first had to decide on the scope of the Standard (including which properties and which fluids to include) and how to define the properties (*e.g.* in terms of experimental data, published equations of state or other models, or some sanctioned computer package). NIST staff were the lead authors of the Standard as well as key technical experts in the Working Group (WG) discussions.

The properties for the refrigerants R12, R22, R32, R123, R125, R134a, R143a, R152a, R717 (ammonia), and R744 (carbon dioxide) and the refrigerant blends R404A, R407C, R410A, and R507A were felt to be sufficiently well-known to be included. Older refrigerants, such as the CFC R12, were included for comparison with the newer HFCs, such as R134a. All of the key thermodynamic properties, in single-phase states and along the saturation boundary, are included. The Standard defines the properties with tables and by defining the equations used to generate those tables. The equations of state and mixture model are from the published literature, and, for completeness, all numerical coefficients are also given. The widespread use of the NIST REFPROP database was acknowledged in the WG discussions, and some members suggested that the Standard simply adopt REFPROP. We argued against this, but did defend the models implemented in REFPROP as being the best available.

The Draft ISO Standard differs from some analogous ASTM documents in allowing the use of “alternative implementations,” *i.e.*, simpler correlations fitted to the standard values but valid over limited ranges. This concession accommodates the simpler models which are often used in the industry, either by tradition or from a need for very rapid calculations. Any “alternative implementation” must match the standard values within prescribed tolerances, and the definition of these tolerances was a major point of controversy in the WG. NIST carried out an analysis to investigate the sensitivity of refrigeration cycle performance to deviations in the thermodynamic properties; this analysis was a key factor in setting the tolerances.

Impact: Assuming acceptance of the Draft International Standard, this Standard will define the properties used by the air-conditioning and refrigeration industry for the performance rating of their equipment. It will remove the long-standing potential for contention and confusion arising from different manufacturers using different property formulations.

Although the Standard does not specify any particular computer package, the models specified in the Standard are the same ones used in REFPROP. Thus, REFPROP will be compliant with the new standard; this will elevate the current status of REFPROP as a *de facto* standard to one with a true international sanction. This is a fitting acknowledgment of the 15 years of effort which NIST has devoted to the properties of the “alternative” refrigerants.

Future Plans: The Standard anticipates regular updates to include additional properties and additional fluids and to update the properties of the present fluids as better data become available. In particular, adding the hydrocarbons propane and isobutane and the properties of viscosity and thermal conductivity for all of the fluids are high priorities. We intend to keep REFPROP compliant with the Standard, and if different models are specified in future revisions of the Standard, we will include those models in future updates of REFPROP.

27. Transport Property Models for Refrigerants

CSTL Program: Energy and Environment (should this instead be Chemical and Allied Products? --- JMC)

Authors: *M.L. Huber, A. Laesecke, and R. Perkins*

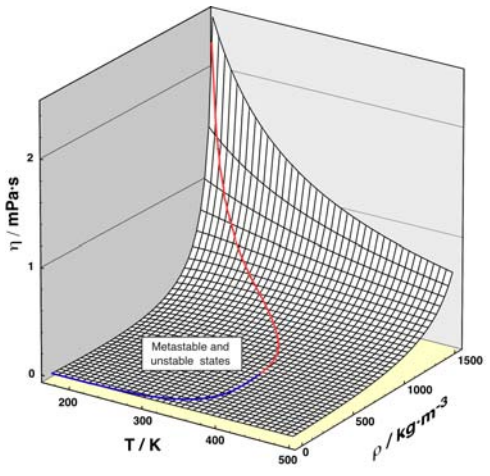
Abstract: Transport properties, such as viscosity and thermal conductivity, are important in the design of chemical processing equipment for various industrial areas including the petroleum refining, transportation, energy and refrigeration industries. The NIST computer program REFPROP (NIST REference fluid PROPERTIES) is widely used and has become a global *de-facto* standard for refrigerant properties. We have developed new models and correlations that improve the representation of the viscosity and thermal conductivity surfaces for refrigerant fluids and have implemented them into the NIST REFPROP software package for quick dissemination to industry.

Purpose: The purpose of this work is to develop and disseminate the best available knowledge of the transport properties of refrigerant fluids. When there are available wide-ranging data of high quality, we develop fluid-specific correlations for viscosity and thermal conductivity that represent these fluid properties to within the experimental uncertainty of the best data. We use a combined correlational/predictive model for the many fluids of industrial importance that lack wide-ranging data. We develop these models using both NIST data and literature data and incorporate these correlations and models into NIST Standard Reference Databases, such as REFPROP, that are used for technology transfer to end-users in industry and academia.

Major Accomplishments: The method of extended corresponding states (ECS) has been used successfully to provide viscosity and thermal conductivities for fluids that lack wide-ranging and accurate data. This method applies a technique in which one obtains estimates of the properties of a fluid of interest by mapping onto the properties of a well-characterized fluid known as the “reference fluid”. We developed a high accuracy correlation for the viscosity surface of R134a, an important fluid used in many applications including automobile air conditioning units, supermarket display cases, and in health care, as a propellant for asthma inhalers. R134a is also important as a reference fluid for ECS models to predict properties of similar, but less well-characterized halocarbon fluids. The new surface represents the viscosity to within 2% along the liquid saturation boundary and 0.5% in the dilute vapor region. We also developed a high accuracy correlation for the viscosity surface of R125, another important refrigerant fluid that is a component of refrigerant blends such as R407C and R410A that may be used as replacements for R22. We then applied the ECS model to 17 additional pure halocarbon fluids, and developed improved surfaces for calculating the viscosity and the thermal conductivity of these fluids.

Impact: We implement our improved models and correlations into the computer program REFPROP, which is widely used in industry. It offers US industry rapid access to the best available models and correlations for viscosity and thermal conductivity.

Future Plans: Future plans involve the addition of mixture properties of cryogenic and natural gas mixtures and the development of high accuracy transport surfaces for natural gas constituent fluids.



28. High-Temperature Reference Correlations for the Solubility of Gases in Water

CSTL Program: Energy and Environment

Authors: A.H. Harvey (838), R. Fernández-Prini (CNEA, Argentina), J.L. Alvarez (CNEA)

Abstract: The solubility of gases in water is important in many industrial, environmental, and geochemical applications. The distribution of solutes between liquid water and steam is of great importance for the steam power industry. Especially at high temperatures, good data are scarce. We have evaluated high-temperature data for 14 solutes in ordinary water and 7 in heavy water, making use of the best scientific knowledge to produce reliable values of the Henry's constant (which describes gas solubility) and the vapor-liquid distribution constant. These are fitted to theory-based expressions that allow reliable extrapolation to high temperatures.

Purpose: In the steam power industry, it is important to know the distribution of solutes such as O₂ and CO₂ between liquid water and steam at high temperatures. The solubility of gases in water is an important parameter in the design of many industrial and environmental processes. These quantities are also important in geochemical modeling, particularly for common geologic gases such as CH₄, CO₂, and H₂S. For all of these applications, it is useful to have reliable, evaluated data in the form of a correlation covering the entire temperature range of interest (which extends to near the critical temperature of water).

We took advantage of two relatively recent advances to produce state-of-the-art correlations. First, our collaborators in Argentina have developed improved methods for reducing experimental data to the thermodynamic quantities of interest (the Henry's constant and the vapor-liquid distribution constant). Second, previous work at NIST has produced theoretical constraints on the high-temperature behavior of these properties as the solvent critical point is approached. This leads to improved functional forms that better describe the high-temperature data and have superior extrapolation behavior for systems where the range of high-temperature data is limited.

Major Accomplishments: We conducted a thorough literature search and found usable high-temperature data for 14 solutes in ordinary water and 7 solutes in heavy water. We evaluated the data, converted them to the appropriate thermodynamic quantities, and produced correlations for the Henry's constant and vapor-liquid distribution constant, with both correlations based on the same final data set. Our new reference correlations have been published (Fernández-Prini, Alvarez and Harvey, *J. Phys. Chem. Ref. Data* 32, 903-916 (2003)).

Impact: This work provides reference correlations for solubility of important gases in water at high temperatures. These standards will find use in numerous areas of high-temperature aqueous physical chemistry, particularly in the steam power industry and in geochemical applications.

Future Plans: The correlations developed in this work have been incorporated into an official guideline that will be adopted by the International Association for the Properties of Water and Steam at its 2004 meeting. The project at this point is complete and there are not any near-term plans for additional work. It may be updated at some point in the future if new data become available.

29. Chemical Kinetic Database for PAH formation for Heptane Combustion

CST: Program: Energy and Environment

Authors: *V. Babushok and W. Tsang*

Abstract:

Purpose: New computer tools make it increasingly possible to simulate real devices. This offers an alternative to expensive and uncertain physical testing. In the combustion area the complexity of the fuel and their reactions have been a severe barrier towards the deployment of this tool. The key to the fidelity of these simulations is the accuracy of the database. The purpose of the work is to build a kinetic database for heptane combustion that can be used to simulate both the oxidative properties (ignition delay, flame velocities) as well as the PAH/Soot forming propensities of the system.

Major Accomplishments: Existing mechanisms for the combustion of heptane have been extended to include the reactions involved in the formation of the precursors of PAH/Soot. It involves including the cracking reactions of heptane. Particular emphasis was placed on the beta C-C bond scission reaction and isomerization of the radical intermediates in the decomposition. These include, the four heptyl and 2 pentyl radicals as well as all the 1-olefinyl radicals, 1-butenyl-3, 1-butenyl-4, 1-pentenyl-3, 1-pentenyl-4, 1-pentenyl-5, 1-hexenyl-3, 1-hexenyl-4, 1-hexenyl-5 and 1-hexenyl-6

The effects of energy transfer leading to pressure dependencies have also been considered. These reactions lead to the small, unsaturated compounds and radicals that are the inputs to existing PAH/Soot models. The model was validated against existing data on ignition delays (from OH) and flame velocities. Some problems on existing databases for the latter have been identified and modifications have been made to fit results under rich conditions.

Impact: The new mechanism that has been developed extends the possible use of simulations to include PAH/Soot formation processes. In combination with the capability of existing databases to cover oxidations, this represents at least in principle the **complete picture** for the combustion with heptane as a fuel. This mechanism is presently being utilized by engineers at Wright-Patterson AFB to model the impact of the use of nitromethane additives on soot formation.

Future Plans: The future plans are two fold. First a large extension of the present work to cover an assortment of the components of a real fuel mixture that can serve as a surrogate. A workshop dealing with these issues was held seven weeks ago and a report is being prepared. Second optimization and extension of existing databases so that more modern data and concepts are included.

30. OH Kinetics – Evaluation of Data and Experimental Techniques

CSTL Program: Energy and Environment

Authors: *V. Orkin and M.J. Kurylo*

Abstract: The determination of lifetimes for chemicals emitted into the atmosphere has been critically reviewed, with particular reference to measurement methods and techniques for hydroxyl radical kinetics and procedures for estimating the ODP and GWP.

Purpose: Reactions of the hydroxyl radical in the gas phase are central to atmospheric chemistry and combustion processes. We have been engaged for a number of years in carrying out accurate and precise kinetic determinations, and also in developing computational procedures for estimating these values. One of the major reasons for carrying out these studies is the important role of OH in establishing the atmospheric lifetime of chemical compounds, which is the key parameter in estimating environmental impact due to their emission to the atmosphere, ozone depletion potentials and global warming potentials.

Major Accomplishments: Over the past several years, we have improved the flash photolysis-resonance fluorescence technique sufficiently to be able to obtain a precision of better than 3% in measurements of the kinetics of OH reactions over the temperature interval of atmospheric interest, and have applied this capability to determine more accurate and reliable atmospheric lifetimes. In the past year, we carried out an extensive review of the determination of atmospheric lifetimes, with particular reference to measurement methods and techniques for hydroxyl radical kinetics and procedures for estimating the ODP and GWP. The review covered all aspects of atmospheric lifetimes, from the basic concept of an atmospheric loading, removal processes, sources and estimates of OH, and how atmospheric lifetimes are determined and used. The major part involved a critical review of the accuracy and precision of all commonly utilized techniques and a thorough analysis of uncertainties and its proper treatment. Finally, the evaluation of OH reaction rate constant data was discussed in detail.

Impact: This work has provided an important overview of a critical area in the application of free radical kinetics. It has gone into great detail in areas often glossed over, such as uncertainty analysis. It is thus likely to be heavily relied upon in subsequent data analysis efforts. Although the discussion was particularly aimed at OH kinetics, it is clearly applicable to kinetic measurements of other radicals and will have impact well beyond its immediate target.

Future Plans: The accurate measurements of OH rate constant over the wide temperature range using FP-RF technique will be continued for selected reactions. Firstly, reliable data are needed for particular compounds of industrial interest. Secondly, a number of new studies of OH reactions are being done using a relative rate techniques at room temperature, which require reliable and accurate absolute data for the rate constants of reference reactions. Thirdly, accurate measurements of temperature dependences when being combined with the higher temperature measurements create an experimental basis to support developing calculation tools for predicting the reactivity of new chemicals.

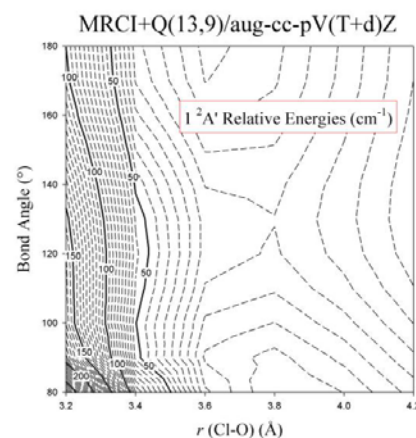
31. Weakly-bound Isomers of the ClOO Free Radical

CSTL Program: Energy and Environment

Author: K.K. Irikura

Abstract: The principal gas-phase cycle for the catalytic destruction of stratospheric ozone involves the chloroperoxy radical, ClOO. Surprisingly little is known about this important molecule. For example, its structure has not been determined experimentally. One recent experiment, however, suggests the existence of an isomer of ClOO that is very weakly bound. Recent theoretical work here at NIST has confirmed the experimental result and determined that the Cl-O bond in this isomer is 20 times weaker than in the stable form of ClOO. Further calculations are underway to characterize the weakly-bound states sufficiently well for their implications in atmospheric chemistry to be determined and for the experimental spectrum to be assigned.

Purpose: A recent experiment provided evidence for the existence of a weakly-bound form of the ClOO radical, which is important in the stratospheric destruction of ozone. The atmospheric implications of this finding, and even its veracity, were unknown. The primary goal of the present project was to verify or deny the existence of such an isomer. It has been confirmed (plot of potential energy function at right). The secondary goal is to characterize the new states for spectroscopic identification. In addition to the potential environmental impact, these results are theoretically important for two reasons. (1) This may be representative of a more general feature of the gas-phase chemistry of oxygen. (2) This type of electronic structure is especially challenging for popular methods of quantum chemistry, thus providing a good test case for the development of better methods.



Major Accomplishments: The potential energy functions of three (of five) valence-excited states of ClOO have been mapped. The experimental inference of weak binding has been corroborated, but for two states (so far), not only one.

Impact: These results provide important data for global ozone models that can be used to determine the impact of the ClOO radical chemistry in the atmosphere.

Future Plans: Detailed dynamics calculations must be done to determine whether the new forms of ClOO are important in atmospheric chemistry. Spectroscopic simulations should be done for comparison with the experimental observation. Related systems, such as ONOO, should also be investigated to learn if weakly-bound isomers are a general feature of the gas-phase chemistry of oxygen.

32. New Smart Gel Mechanism Elucidation from Immersive Visualization of Molecular Simulation

CSTL Program: Technologies for Future Measurements and Standards

Authors: C.A. Gonzalez (838), S. Satterfield (ITL), Y. Simon-Manso (Universidad de Chile), Y. Aray (Instituto Venezolano de Investigaciones Cientificas), and Manuel Marquez-Sanchez (KRAFT Foods, Inc.)

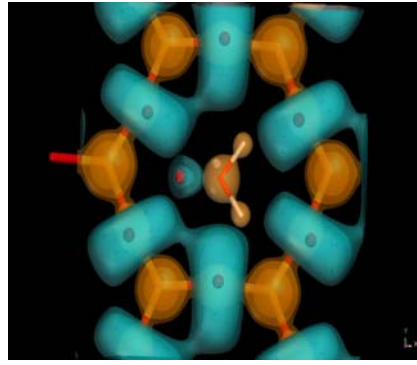
Abstract: “Shake gels” are a class of materials resulting from an aqueous solution of a clay (Laponite) and an associative polymer such as poly-ethylene oxide (PEO). Through some complex and as yet unknown process, these watery mixtures of clays and polymers firm up into gels when shaken, and then relax again to the liquid phase after some time has passed. Scientists in Industry are currently working on the application of these materials in the manufacture of novel biological fluids, food thickening agents, drug delivery materials, cosmetics, and sensors. The main objective of this work is to elucidate the mechanisms governing the gelling processes in “shake gels”. In particular, we are interested in understanding the nature of the interactions between the different components of the “shake gel” (water, laponite and PEO) and the effects of the shaking in the gelling process. To achieve this goal the information obtained from theoretical calculations were analyzed with a 3-D immersive visualization engine available at ITL, which allows scientists to immerse themselves among giant-sized molecules whose behavior can be seen and understood in minutes instead of the weeks required using traditional techniques.

Purpose: This work will develop the necessary theoretical infrastructure to aid in the elucidation of the complicated mechanisms involved in the formation of “shake gels”. The overall goal is to provide reliable predictive tools to guide experimentalists in the rational design of novel “shake gel” systems tailored to different industrial applications.

Major Accomplishments: Making use of a novel algorithm developed by Dr. Yosslen Aray’s group to determine the topology of the electrostatic potential of molecules interacting with surfaces, we were able to determine the mechanisms by which PEO interacts with the clay surface and water in order to produce the gel. According to this mechanism, it is the polymer’s oxygen atoms, instead of its hydrogen atoms as previously thought, that attach to the clay. In addition, electrical charges affect the binding process, resulting in water binding to clay surfaces in a perpendicular arrangement, which is believed to help create the firmness of the gel. Our results also indicate that the polymer size is important. Thus, our calculations predict that larger or smaller polymers cannot undergo the conformational changes necessary to optimize the binding to the clay. These predictions are in very good agreement with experimental findings that “shake gels” have only been observed with solutions of PEO.

Impact: This project is providing important mechanistic details about the electrostatic interactions between water, PEO and Laponite not previously known. For the first time, detailed quantum chemical calculations and atomistic simulations are integrated in order to gain a more complete picture of the physical and chemical properties of these gels.

Future Plans: The next step of this program will involve a systematic study of the role of the “shaking” and temperature in the gelling process. Once a better picture of the role of these two factors is obtained, the models will be used to guide experiments in the synthesis of other “shake gels” with different chemical and physical properties that might be useful for industrial applications (for example: optical properties, viscosity, etc.).



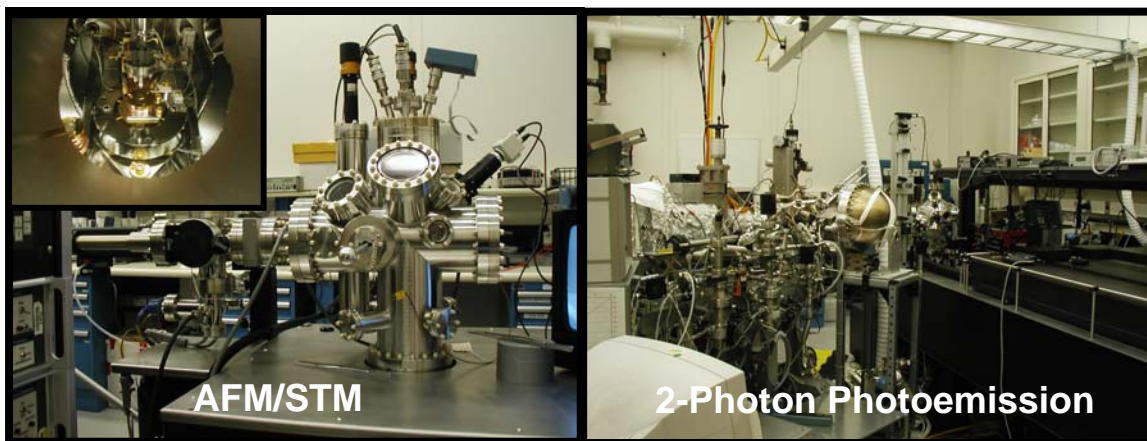
33. Molecular Electronics Metrology

CSTL Program: Technologies for Future Measurements and Standards

Authors: *J. D Batteas, C.A. Gonzalez, J.C. Garno, C.A. Hacker, L.J. Richter, S. W. Robey, C. D. Zangmeister, and R. D. van Zee*

Scientific Objectives. Molecular Electronics (“moletronics”) is a field that many predict will have important technological impacts on the computational and communication systems of the future. In these systems, molecules perform the functions of electronic components. Our objectives are to characterize the structural properties of, and the conduction mechanisms through, molecules and to develop methods that reliably and reproducibly measure the electrical properties of molecular ensembles in test structures.

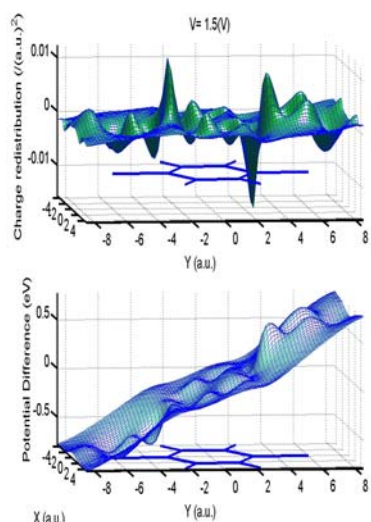
The drive to increase electronic device performance, with the associated push to ever smaller device dimensions, has lead industry observers to conclude that silicon-based technology will reach a point of diminishing gains in the near future. This, in turn, has generated interest in alternative technologies based, for instance, on single-electron devices and molecular components. It is hoped that the tremendous flexibility available with organic synthetic chemistry and self-assembly techniques can be harnessed to produce non-linear devices analogous to silicon-based diodes and transistors, but comprised of single or small numbers of molecules. The CSTL team of researchers in molecular electronics is integrating a range of techniques that will provide key information on electronic structure and electron transport in candidate molecular electronic systems. The methodologies being employed include two-photon



photoemission, which accesses unoccupied electronic levels and tracks electron relaxation effects, scanned probed microscopies, which can characterize electron transport down to the single molecule level and afford means of manipulating matter on the nanometer scale, as well as theoretical modeling of electronic states and transport properties to better elucidate the mechanisms involved in such transport function.

Purpose: This work will develop measurement techniques and expertise necessary to understand electronic structure and transport found in molecular systems comprised of organic thin films and small ensembles. The overall goal is to reliably provide experimental details which, when coupled with theoretical input, will help to elucidate the physical mechanisms that produce device function in molecular based systems. This work is also aimed at providing the requisite measurement protocols for such systems.

Major Accomplishments: *Theoretical Studies of Electron Transport in Molecular Wires.* We have continued our study of the possible mechanisms governing electron transport in molecular wires. Particular attention has been focused to the electrostatics at the molecule-metal interface, which has been found to affect significantly the transport properties of the system. In order to properly describe the electrostatics at the interface, a novel algorithm has been developed that efficiently computes the electrostatic potential by solving the Poisson equation at each cycle of the self-consistent field iteration based on *ab initio* electronic structure calculations. This algorithm has been used to study the possible sources that lead to asymmetric current-voltage (I-V) curves in atomic wires as well as in a series of organic thiolates connected to gold electrodes. In order to develop efficient and robust models to gather a qualitative picture of electron

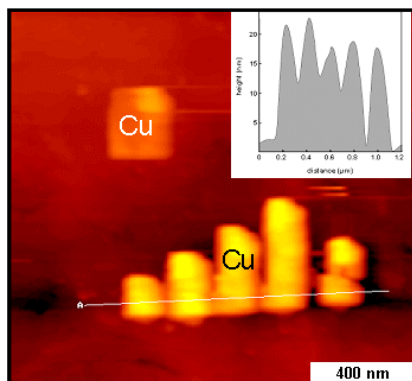


Charge Distribution and Electrostatic Potential profiles for benzene di-thiolate attached to gold electrodes.

conductance through molecular bridges, a simple algorithm to compute the first-order expansion of the system's Green function projected only onto fragments of the isolated molecule (no electrodes are included) has been implemented. This simple model, called the Green Function Condensed to Fragments model (GFCF) was found to be very useful in studying electronic transport properties of molecular bridges where the contact to the electrodes does not seem to play an important role in determining the shape of I-V curve. This approach has been used to compute I-V characteristics of the molecule 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate

(NH₂-NO₂-OPE), found to exhibit "Negative Differential Resistance" (NDR) behavior at 60 K. The results of the calculations are in good agreement with the experimental I-V curves. Calculations based on the same model predicted that the fluorinated derivative 4,4'-di(ethynylphenyl)-2'-fluoro-1-benzenethiolate (F-OPE) was also a good candidate for NDR behavior. Chemists in the Nanotechnology Group at Kraft

Foods worked on the synthesis of the molecule and very recently, scientists at the Surface and Microanalysis Sciences Division, have made I-V measurements that qualitatively agree with the predictions of this model. This is the first time that a theoretical prediction of the behavior of molecular bridges upon electrification has prompted experimental work leading to its validation. These results indicate the potential of theoretical tools in the rational design of electronic devices at the nano-scale.



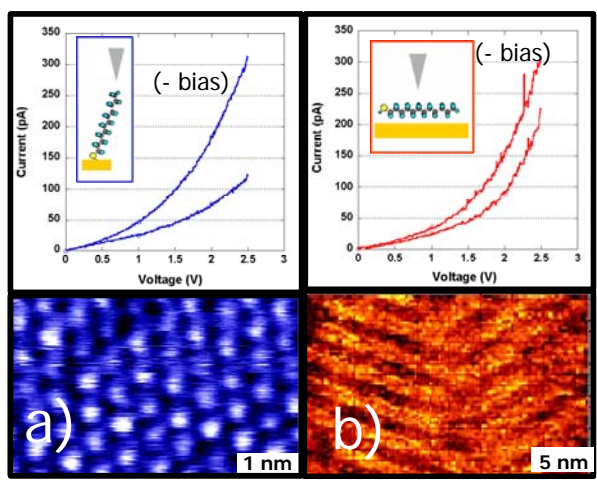
Nanopatterned Cu contacts on the SAM surface. Patterns range from 150 – 400 nm and are ~ 20 nm thick.

SPM Directed Device Fabrication. Precisely engineered nanostructures provide a means for the exploration of chemical reactions under spatially well-defined and controlled environments. Although not yet practical for high throughput applications and manufacturing, scanning probe lithography studies provide fundamental information on tip-surface interactions, structures, and properties at the level of nanometers. Under the support of ATP, nanopatterns of copper were constructed at dimensions ranging from 100-400 nm via AFM-based lithography. The writing density and size of the nanopatterns affect copper growth. Varying solution chemistry parameters, such as the immersion intervals and the concentration of metal salts, can control

pattern sizes. Copper grows beyond the edges of the nanopattern boundaries. An effective resist was found using mercaptoundecanol, with very high selectivity observed, even at the nanometer scale. Longer chain length alcohols (C_{11} vs C_6) were more effective as resists. Preliminary results using silanized tip coatings are promising for inhibiting copper deposition on AFM tips during *in situ* experiments. Future work will investigate charge transport with copper overlayers on SAMS using conductive probe AFM measurements at a metal-molecule-metal interface.

Orientational Effects on Electron Tunneling in Dodecanethiol. Obtaining a detailed understanding of electronic transport properties in molecules requires the ability to correlate structure and transport mechanisms. Here we are utilizing dodecanethiol as a “standard” test molecule to provide reference I-V measurements. This molecule affords means of probing the impact of molecular orientation on tunneling behavior. Self-assembled monolayers of dodecanethiol have been prepared with regions of densely packed molecules whose molecular axis is oriented $\sim 30^\circ$ from the surface normal right next to regions of lower density molecules which are arranged with the molecular axis parallel to the surface. Asymmetry in tunneling I-V curves show that in the

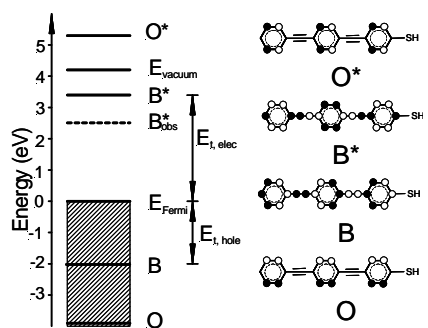
of the standing up phase the tunneling behavior is rectified by the asymmetry of the transport junctions, while in the laying down molecule, this asymmetry almost completely removed and may be explained by differences in metal surface potentials of the tip and sample surface. Future work will be aimed at correlating compression effects on the tunneling properties as investigated by conducting probe atomic force microscopy. Theoretical modeling of the transport properties is also underway.



Orientation dependence on tunneling behavior in dodecanethiol showing asymmetric I-V behavior in molecules standing up on the surface (a) vs. more symmetric behavior in molecules laying down (b).

Spectroscopic Measurements. The configuration of molecules within and the electronic structure of electrically-active molecules are believed to be governing factors in molecular conductance. To investigate whether these molecular properties are related to the test-structure measurements, ultrafast spectroscopies have been used to study the geometry and electronic structure of molecular films. The electronic structure of these films was studied using one- and two-photon photoemission.

Specifically, oligo(para-phenylene-ethynylene) thiolate chemisorbed on gold surfaces was studied. Within 5 eV of the Fermi level, four states were observed, two occupied (2.0 eV and 4.0 eV below Fermi level–B/B*) and two and two unoccupied (3.2 eV and 5.3 eV above the Fermi level). This



Energy-level diagram for OPE chemisorbed on Au.

information is shown schematically in the energy level diagram. The two states closest to the Fermi level are assigned to pi-conjugated molecular orbital along the backbone of the molecule, and the other two are assigned to molecular orbitals formed by the “ortho” carbons. (See schematic representation of these orbital above.) From this assignment, the hole- and electron-barriers can be determined. These are, respectively, 2.0 eV and 3.4 eV. The charge transport gap is can also be estimated. It is between 3.7 eV and 5.4 eV, depending on the criteria used to determine the onset of transport.

Impact: This project is providing detailed insight into the complex behavior of electronic transport through molecules. The program combines for the first time detailed theory and molecular scale measurements that can provide a basis for the complete understanding of electronic structure and transport effects in molecular electronic systems. The foundation that these results provide not only benefits the development of molecular electronics applications, but also affords a groundwork for the investigation of molecular based optoelectronic device applications.

Future Plans: On the horizon are experiments aimed at probing the electrical behavior of ensembles of molecules based on nanopatterning to afford a means of assessing molecular function in device level measurements, as well as scaling conductance properties in molecular ensembles. The results from these experiments will be compared to theoretical models and to the performance of device-prototypes fabricated and tested by our collaborators in the Semiconductor Electronics Division. The photoemission work will systematically investigate the effects of chemical substitute on the molecular orbitals.