

## **FY 2004 Overview - Physical and Chemical Properties Division**

The Physical and Chemical Properties Division strives to be the foremost and best source of high quality physical and chemical properties information. This vision is driven by the ubiquitous importance of this information to commerce, industry, manufacturing, and national policy objectives. Familiar examples include:

- The vast majority of commodity exchanges in chemicals, energy related fluids, and materials are based on physical and chemical properties. In some cases, national and international standards for these properties are needed, such as AGA-8 for the properties of natural gas, ASME-IAPWS Properties of Water and Steam, ISO-Standard Equations for refrigerants. Generally these standards are presented in the form of high accuracy equations of state which allow determination of a wide range of thermodynamic properties.
- Performance criteria of working fluids, feedstocks, and chemicals are inextricably linked to physical and chemical properties, e.g. viscosity, boiling point, phase behavior, heat capacity, reactivity, rates of reaction, etc. Engineering design for engines, chemicals manufacturing, power generation, heating and air conditioning, distillation, etc. depends critically on knowledge of these properties. Reliable properties data are critical to competitive advantage, sustainability, and innovation.
- In addition to the widespread reliance of industry on properties information, success in setting and achieving national energy, environmental, and security goals often requires an extensive and trustworthy properties information-base.

To meet the broad spectrum of needs, only briefly sketched above, the Division's work is structured along four synergistic themes:

- I. develop and maintain the measurement capabilities, standard materials and reference data needed to underpin a national system of physical and chemical properties measurements;
- II. develop large-scale, readily accessible data resources providing trustworthy physical and chemical properties information meeting high priority needs for a broad range of industries and national agendas;
- III. develop empirical and fundamental predictive capabilities to enable reliable estimation of property values when experimental data are unavailable;
- IV. research experimental techniques and address key data-gaps in support of specific, high priority industrial and national initiatives.

These themes allow effective response to customer needs and are consistent with the Division's operating strategy to maintain a highly synergistic research program that includes an appropriate balance of measurement, theory, and predictive models. The combination of the Division's world class expertise and unrivaled resources in measurement, archiving, and provision of high-quality property data is complemented by its forefront research to develop reliable and highly adaptable methods for estimating property data in cases where measurements are unavailable or extremely difficult and/or costly to obtain.

A key aspect and differentiator of the work of the Division is the provision of properties *information*, i.e. numerical data having clearly specified uncertainties for well characterized substances and conditions. This is the essence of quality for property data, and quality is at the core of all programs at NIST. There is an extensive measurement system – laboratories, institutes, instruments, procedures, quality assurance protocols, and organizations – underlying physical and chemical properties measurement. This measurement system was at one time strongly centered in industry, but increasingly industry relies on universities and associated institutes. The Physical and Chemical Properties Division supports this measurement system in a similar manner as NIST supports other parts of national and international measurement systems, i.e. by developing state of the art measurement capabilities, methodologies, and standards. The standards are often in the form of standard reference data and (to a lesser extent) standard reference materials. Supplying reference data and materials has always been part of NIST's (NBS's) mission and was seen as an essential part of the National Measurement System as first articulated by Huntoon<sup>‡</sup>.

The vast majority of physical and chemical property data is produced and published by institutions other than NIST. These data are widely distributed, typically have ill-defined formats, and often are inadequately specified in terms of quality. The Division produces *information* from these resources through the process of collection, validation, critical evaluation, and creation/distribution of user adapted high quality databases. The value added by creation of such databases is enormous:

- the information is easily located and readily adapted for any application;
- easy access to reliable data eliminates needless measurement or redundant data collection and evaluation both of which are extremely expensive;
- the information can serve a wide variety of user communities on a continuing basis with minimal added investment;
- and, of course, the information itself enables effective, efficient product and process design, supports competitive manufacturing, and facilitates progress in important national programs.

The Division regularly produces and updates a variety of reference data products. Perhaps the most familiar are:

[NIST/EPA/NIH Mass Spectral Library: with Search Software NIST '02](#)  
[NIST REFPROP 7 \(Reference Fluid Thermodynamic and Transport Properties\) Database](#)  
[NIST/ASME Steam Database](#)  
[NIST/TRC Table Database](#)  
[NIST/TRC Vapor Pressure Database](#)  
[NIST/TRC Ideal Gas Database](#)  
[NIST/TRC VLE FloppyBook](#)  
[NIST Chemical Kinetics Database: Version 2Q98](#)  
[NIST Mixture Property Database](#)  
[NIST Thermophysical and Transport Properties of Hydrocarbon Mixtures](#)  
[NIST Thermodynamic and Transport Properties of Pure Fluids](#)

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<sup>‡</sup> Huntoon, R.D., "Concept of a National Measurement System", *Science*, Oct. 1967, pp. 67-71

The Division also provides a wide range of on-line data support, the most well known is:

[NIST Chemistry WebBook](#)

The NIST Chemistry WebBook has been awarded "Best Chemistry Site on the Web - Portals and Information Hubs" by ChemIndustry.com Inc., John Wiley and Sons, Inc. and the Royal Society of Chemistry, UK. The WebBook is second in total use among chemistry database web sites (only the Chemical Abstracts site has higher usage) and over 2,500 sites directly link to the WebBook, including essentially every technical library in the world. This year the Chemistry WebBook has been made available in other language versions, cf. the highlight **The NIST Chemistry WebBook Goes Multilingual.**

Other important resources on-line include:

[NIST Gas Phase Chemical Kinetics](#)

[Computational Chemistry Comparison and Benchmark Database](#)

[Cryogenic Material Properties](#)

[NDRL/NIST Solution Kinetics](#)

[ChemRate: A Calculational Database for Unimolecular Reaction](#)

[CKMech \(Chemical Kinetic Mechanisms\)](#)

In FY2004, the Division reported its work in 125 technical papers. Many papers present new or improved equations of state, high accuracy data correlations, and new experimental data on key systems. Additionally there are regular updates and supplements to reference data collections and series, and numerous book chapters updating the state of the art across a wide spectrum of customer interests. Of particular note this year are chapters titled: "The Development and Application of Cryocoolers Since 1985" and "Refrigeration for Superconductors", see the highlight **Properties and Processes for Cryogenic Refrigeration.** In addition, over 100 presentations to stakeholder groups, international organizations and associations, scientific meetings, and seminars were made by Division Staff in FY2004.

Highlights of the Division's accomplishments in FY2004 can be categorized according to the four themes listed above. (Note that because of the strong synergies and interdependence amongst these themes one might easily associate an accomplishment with more than one area.)

## **I. Measurement System Support**

Currently a project to develop world class density measurement capabilities is coming to fruition with new benchmark measurements for propane. A reference equation of state has been developed that agrees with all high quality experimental determinations to within less than 100 ppm and with the recent NIST measurements to within approximately 20 ppm. A novel and potentially important application of the new density measurement apparatus in determining thermodynamic temperature also was explored this year. This work is described in highlight **Precision Densimetry for Primary Temperature Metrology.**

Reference equations of state developed by the Division have often served as the basis for important international agreements on physical properties. This year the International Standards Organization (ISO) adopted the equations of state used in the NIST REFPROP 7 Database as the basis for a new international standard for the properties of refrigerants. This work, as well as other advances in high accuracy equations of state, is described in highlight **Reference Equations of State**.

## II. Archived and Evaluated Property Data

The Division has a wide spectrum of activities focused on collecting and evaluating published data to produce high quality resources for properties information, such as those listed above. In recent years, the Division's TRC Group has established a truly new paradigm in data collection, data quality specification, and data exchange standards. The new approach in data collection involves direct collaborations with journal editors and submitting authors such that after the acceptance of a manuscript, but prior to its publication, all the contained data are submitted to TRC using the TRC Guided Data Capture tool (<http://www.trc.nist.gov/GDC.html>). TRC subjects the submitted data to checks for specification of all required metadata, the information describing the experiment and the data itself, and for internal consistency. Communication with the authors is used to resolve any consistency or specification issues. Following correction (if necessary) the data are returned to the author and journal editor in ThermoML, the XML standard for exchange of thermodynamic data. At the time of publication, the data are made available on the TRC website (<http://www.trc.nist.gov/ThermoML.html>) and become part of the TRC SOURCE Database\*. In the coming year, collaborations will be established with all 5 major journals publishing thermodynamic data and TRC SOURCE will be maintained current with approximately 80% of all new data appearing in the literature.

The Division has embarked on another collaborative data project this past year, in this case a collaboration to facilitate the collection of data describing the pathways and rates of chemical reactions. In this project, described in the highlight **Combustion Simulation Databases for Real Transportation Fuels: A New Community Collaboration**, the Division has joined with the combustion research community, in an organization called the PrIME Initiative, to create a central repository of all information needed to support the use of combustion models for design and optimization of the next generation of gasoline and diesel engines. As part of this effort, the collaboration is developing specifications and exchange standards for the relevant data, this standard is termed ReactionML.

Data exchange and interoperability infrastructure is required to support widespread and effective use of physical and chemical property information. ThermoML and ReactionML are examples of two of the standards that the Division is helping the community develop and adopt. This year, ThermoML was accepted as the foundation for an IUPAC (International Union of Pure and Applied Chemistry) standard for global communication of thermodynamic data; see the highlight **ThermoML – an Emerging IUPAC Standard for Thermodynamic Data Communications**.

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\*SOURCE is the world's largest collection of experimental data covering thermodynamic, thermochemical, and transport properties for pure compounds and mixtures of well-defined composition. Over 300,000 data points are added to the collection each year.

Another major achievement this year was the release of the beta-version of the IUPAC-NIST Chemical Identifier (INChI). This is a naming system that would allow computers to search for and uniquely identify a chemical based entirely on the connectivity of the molecule – that is what atoms are connected to what other atoms. There is enormous value in this identifier for unambiguous and efficient web searches for chemical data. Its design is discussed in the highlight **The IUPAC NIST Chemical Identifier (INChI)**

In another international collaboration, the Division is working to develop standards for measuring, specifying, and archiving property data for ionic liquids. Some highlights of this work are presented in **IUPAC Partnership Develops Standards and a Data Retrieval System for Ionic Liquids**.

Other important highlights of this year's work in *theme II* deal directly with the provision of property data. A series of papers were published this year describing, for the first time, the transport properties of the heavier linear alkanes commonly present in fuels. The primary approach in this work is the critical assessment of all available experimental data and their representation by models capturing correlations in the properties and incorporating fundamental theory where possible. This work is described in the highlight **Integrated Transport Property Program for Key Systems: Data, Models, and Simulation**. This work complements another project focused on fuels discussed below under *theme IV*, "Measurements for Special Applications".

The highlight **ThermoData Engine: New Generation Expert System for Thermodynamic Data Critical Evaluation** describes an important first, i.e. the realization of expert system software that captures principal elements of the "art of data evaluation". This software/database system, called TDE, is a major step toward the idea of on-demand generation of evaluated property values based on a comprehensive and up-to-date data archive (SOURCE), a process termed "dynamic data evaluation". In addition to relying on all the infrastructure to create and maintain the SOURCE archive, this research includes development of algorithms and computer codes for assessment of the quality of existing data, for selection and application of prediction methods depending on the chemical structure of the compound and nature of the property, for establishing consistency amongst all property values, and for arriving at a recommended value with an uncertainty accurately representing all that is known at the present time.

### **III. Prediction of Property Information**

As the Division continues to increase the information-base in physical and chemical properties, its research creates concomitant gains in understanding these properties and in the science base that allows making reliable estimates of their values. In performing its function, TDE uses much of the current state of the art in estimation. High accuracy equations of state and pure substance correlations also are used as the first step in estimating properties for substances and conditions which have not yet been measured. The Division also maintains a significant effort in computational physics and chemistry to develop practical, first-principles based approaches to understanding and predicting physical and chemical properties.

The major accomplishments in the area of first principles prediction of fluid properties are presented in three highlights. The work reported in **Theory of Non-Bonded Interactions: Molecular Association and Assembly** explores accurate and practical approaches to quantum calculations of intermolecular forces (the basis for describing bulk properties) and methods for reliable and efficient molecular simulation of bulk properties. It has been shown that a computationally efficient approach to calculating intermolecular forces, the Hartree-Fock Dispersion method, developed by the research team provides results in good agreement with experiment and overcomes major short-comings of more conventional computational methods. A very promising result has come from research that addresses efficient methods to calculate bulk properties; in this case mixture phase behavior. An innovative and extremely efficient simulation method, transition matrix Monte-Carlo, has been shown to accurately predict an entire isothermal fluid-phase diagram in a single simulation requiring far less CPU time than currently used techniques. The work discussed in **Transport Coefficients and Molecular Dynamics** is a preliminary, systematic comparison of various approaches to calculating transport properties. The Division in collaboration with scientists from The Dow Chemical Company, BP Amoco Chemical Company, Case Scientific, Mitsubishi Chemical Corporation, 3M Company, and DuPont has conducted the Second Industrial Fluid Properties Simulation Challenge. The goal of the “Challenge” is to evaluate and benchmark available molecular simulation methods and force fields on problems that have significant industrial relevance. The most recent “competition”, described in **Second Industrial Fluid Properties Simulation Challenge**, was very successful and attracted significantly increased interest and industry involvement.

The highlight **Systematic Validation and Improvement of Quantum Chemistry Methods for the Prediction of Physical, and Chemical Properties** reports new results quantifying uncertainties in properties computed by the most popular levels of theory making use of standard statistical techniques and high quality experimental data. This work is also focused on making available procedures and data that will enable researchers in industry to choose the most reliable quantum chemistry methods for prediction of physical and chemical properties.

Methods developed recently which allow computational chemistry to deal with surface-fluid interface for realistic conditions as encountered in chemical processing or the environment have born fruit in a recent collaborations to understand the surface chemistry of hematite. This work is described in highlight **Computational Chemistry Illuminates Atomistic Processes at Complex Interfaces**.

#### **IV. Measurements for Special Applications**

The Division determined key data for a number of important national agendas this past year. As part of its efforts to support programs to improve the performance of engines which rely on practical (complex) transportation fuels, the Division measured thermophysical properties of RP-1, a rocket fuel. RP-1 is being considered as a fuel for advanced aerospace engines. The work is described in the highlight **Advanced Propulsion Systems Demand Accurate Property Data**.

Concerns in the area of homeland security motivate work related to the detection of explosives which is highlighted in **Explosives on Surfaces: A Sticky Problem**. The most extensive data generation effort in the Division provides a large volume of high quality, evaluated mass spectra

of molecules, known as the NIST/EPA/NIH Mass Spectral Library. This library is included and its associated search capabilities are installed by manufacturers in the vast majority of mass spectrometer systems sold in the world. To assure the quality of these libraries, search and identification algorithms are developed by the Division. This software system, termed AMDIS, is optimized for the analysis of weak features in the spectrum, easily considered “noise”. Recent developments in this area are reported in the highlight **AMDIS – Automatic Mass spectral Deconvolution and Identification Software**. This extremely powerful software is widely employed for highly sensitive and reliable identification of threat agents by mass spectroscopy in the area of homeland security.

AMDIS is based on the Division’s expert knowledge about the paths and probabilities of molecular excitation and fragmentation associated with electron impact ionization. This year the Division embarked on a new research effort to develop a similar high-level of understanding concerning the fragmentation of peptide ions undergoing collisions in MS/MS instruments. The goal is to develop reference peptide fragmentation mass spectra, physically based fragmentation rules which account for differences in instrument design and operating characteristics, and deconvolution/identification software, analogous to AMDIS. MS/MS spectroscopy is a mainstay of the analytical tools employed in the extremely important and challenging national effort in proteomics. This pioneering work is described in the highlight **Mass Spectroscopy in Health and Environmental Science**.

Another research effort in the area of mass spectroscopy seeks to achieve orders of magnitude improvements in the speed and sensitivity achievable with electron impact time of flight mass spectrometry. The approach is based on a Hadamard modulation of the ionizer voltage at very high frequencies; see the highlight **Invention of a New Class of Ultra-fast, Ultra-sensitive Mass Spectrometers for Kinetics, Reference Mass Spectrometry, and Homeland Defense Applications**.

### **Physical and Chemical Properties Accomplishments and the CSTL Program Structure**

The outputs of the four principal themes of the Division’s work are aligned very much with the CSTL cross-cutting themes:

- Measurement Standards
- Data and Informatics
- Technologies for Future Measurements and Standards

with majority of the Division’s work in the area of Data and Informatics.

CSTL organizes its outputs into programs according to principal customers, namely:

1. Automotive and Aerospace
2. Biomaterials
3. Pharmaceuticals and Biomanufacturing
4. Chemical and Allied Products
5. Energy and Environmental Technologies

6. Food and Nutritional Products
7. Forensics and Homeland Security
8. Health and Medical Technologies
9. Industrial and Analytical Instruments and Services
10. Microelectronics

By their very nature, the Division's outputs serve very broad segments of industry and government. The highlights of FY2004 accomplishments can be aligned, to some degree with specific CSTL Programs.

Highlights with a special emphasis in Industrial and Analytical Instruments and Services are:

- **Precision Densimetry for Primary Temperature Metrology**
- **AMDIS – Automatic Mass spectral Deconvolution and Identification Software**
- **Invention of a New Class of Ultra-fast, Ultra-sensitive Mass Spectrometers**

Highlights with a special emphasis in Forensics and Homeland Security are:

- **Explosives on Surfaces: A Sticky Problem**
- **AMDIS – Automatic Mass spectral Deconvolution and Identification Software**

Highlights with a special emphasis in Health and Medical Technologies are:

- **Mass Spectroscopy in Health and Environmental Science**

Highlights with a special emphasis in Automotive and Aerospace are:

- **Advanced Propulsion Systems Demand Accurate Property Data**
- **Combustion Simulation Databases for Real Transportation Fuels: A New Community Collaboration**
- **Properties and Processes for Cryogenic Refrigeration**

Highlights with a special emphasis in Chemical and Allied Products are:

- **Reference Equations of State**
- **Integrated Transport Property Program for Key Systems: Data, Models, and Simulation**
- **ThermoData Engine: New Generation Expert System for Thermodynamic Data Critical Evaluation**
- **Transport Coefficients and Molecular Dynamics**
- **Second Industrial Fluid Properties Simulation Challenge**
- **Systematic Validation and Improvement of Quantum Chemistry Methods for the Prediction of Physical and Chemical Properties**
- **Theory of Non-Bonded Interactions: Molecular Association and Assembly**
- **Computational Chemistry Illuminates Atomistic Processes at Complex Interfaces**
- **IUPAC Partnership Develops Standards and a Data Retrieval System for Ionic Liquids**

The following highlights are so infrastructural that they can best be understood in the cross-cut area of Data and Informatics:

- **The NIST Chemistry WebBook Goes Multilingual**
- **The IUPAC NIST Chemical Identifier (INChI)**
- **ThermoML – an Emerging IUPAC Standard for Thermodynamic Data Communications**

**Organization:**

The Division is composed of 6 groups and 1 project as follows:

<b>Group</b>	<b>Name</b>	<b>Location</b>	<b>Leader</b>
1	TRC Group	Boulder, CO	Dr. Michael L. Frenkel
5	Chemical Reference Data	Gaithersburg, MD	Dr. Gary Mallard
6	Computational Chemistry	Gaithersburg, MD	Dr. Anne M. Chaka
6	Real Fuels Project	Gaithersburg, MD	Dr. Jeffrey Manion
7	Experimental Properties of Fluids	Boulder, CO	Dr. Joseph W. Magee
8	Theory and Modeling of Fluids	Boulder, CO	Dr. Daniel G. Friend
9	Cryogenic Technologies	Boulder, CO	Dr. Ray Radebaugh

About one-half of the Division's staff is located in Boulder, CO.

**Awards:**

The team of Michael Frenkel, Robert Chirico, and Qian Dong received the Department of Commerce Bronze Medal for their pioneering work efforts in developing and promoting wide spread acceptance of an important new communication process for thermodynamic data. The accomplishment is based on the use of XML technology. Termed "ThermoML", this data exchange standard has been broadly endorsed by industry and accepted as the foundation for an IUPAC (International Union of Pure and Applied Chemistry) standard for thermodynamic data communications.

W. Gary Mallard and Peter Linstrom received NIST's French Award for their pioneering development of the NIST Chemistry WebBook leading to revolutionary improvement of the delivery of physical and chemical property data to NIST customers. The French Award is granted for significant improvement in products delivered directly to industry, including new or improved NIST calibration services, Standard Reference Materials, and Standard Reference Databases.

The journal "Measurement Science and Technology" selected for its Best Paper Award 2003 the contribution "Extension of the torsional crystal viscometer to measurements in the time domain," published by Richard Hafer and Arno Laesecke. The award was made at the Annual Meeting of the AIChE in November 2004.

## SELECTED TECHNICAL ACTIVITIES

**Title:** Combustion Simulation Databases for Real Transportation Fuels: A New Community Collaboration

**Authors:** *T. C. Allison, D. R. Burgess, Jr., J. W. Hudgens, W. Tsang, and J. A. Manion.*

**Abstract:** Economic, environmental, and health benefits to the nation from improved combustion processes for real transportation fuels (aviation, diesel, and gasoline) are enormous and well-recognized. Leading expert scientists and engineers from industry, academia, and government met at NIST during the “*Workshop on Combustion Simulation Databases for Real Transportation Fuels*” (<http://kinetics.nist.gov/RealFuels>) to assess needs and opportunities to translate scientific understanding of combustion to technological development. Attendees from industry and academia affirmed the value of predictive models of combustion in the development of more efficient and less polluting engines. Key results of the Workshop were an understanding that a coherent effort within the highly multi-disciplinary combustion research community is required to address the complexities associated with real transportation fuels and that we must create an organized standard infrastructure for the exchange of combustion related data to be successful. As one outcome of the workshop NIST has joined with other members of the combustion community in the PrIME (Process Informatics Model) collaboration. PrIME is utilizing the DoE supported Collaboratory for Multi-Scale Chemical Science (CMCS) project to develop and support the information technology infrastructure required for the effort.



**Purpose:** The goal of this collaborative effort is to generate standard formats for combustion data, together with data libraries, analysis software tools, and the supporting information technology infrastructure that will enable development of predictive models of combustion. NIST’s commitment to the PrIME process envisions the creation of new paradigms for scientific collaboration. The initial phase of the program involves construction of a traceable, comprehensive electronic repository of key data relevant to modeling combustion processes. Development of this library is a community project involving submission and ultimately evaluation of the primary scientific data.

**Accomplishments:** The initial data library consists of data from the NIST Chemical Kinetics Database and GRI-Mech 3.0 (the current “standard” model for combustion of small hydrocarbons). The library includes data collections on atomic properties, chemical species, thermodynamics, elementary kinetics, and transport, as well as bibliographic data. Online data-entry forms for several of the data types have been created and are being integrated into the CMCS portal. XML schema have been created for all of the data formats used in the library. A collaborative workspace for the PrIME project has been created within the CMCS portal.

**Impact:** The facile exchange of data across scientific domains and multiple length scales will overcome one large barrier to progress in the area of combustion processes. Ultimately the PrIME project will facilitate the rapid construction of predictive models for combustion chemistry. This will enable manufacturers to quickly use simulation technologies to explore and

optimize new engine designs [*e.g.* Homogeneous Charged Compression Ignition (HCCI) or pulse detonation] which promise significantly improved efficiency and reduced pollution.

**Future Plans:** Near-term plans include finalizing data formats, improving data entry, enhancing automated checking of input data, creating robust searching tools, and developing additional infrastructure necessary for collaborative research by PrIME team members. Launching of the initial PrIME data repository is anticipated in the first half of 2005. Longer-term plans include the integration of sophisticated tools that reduce human efforts in model creation and reduction.

References:

NISTIR 7155 “Workshop on Combustion Simulation Databases for Real Transportation Fuels” June 2004

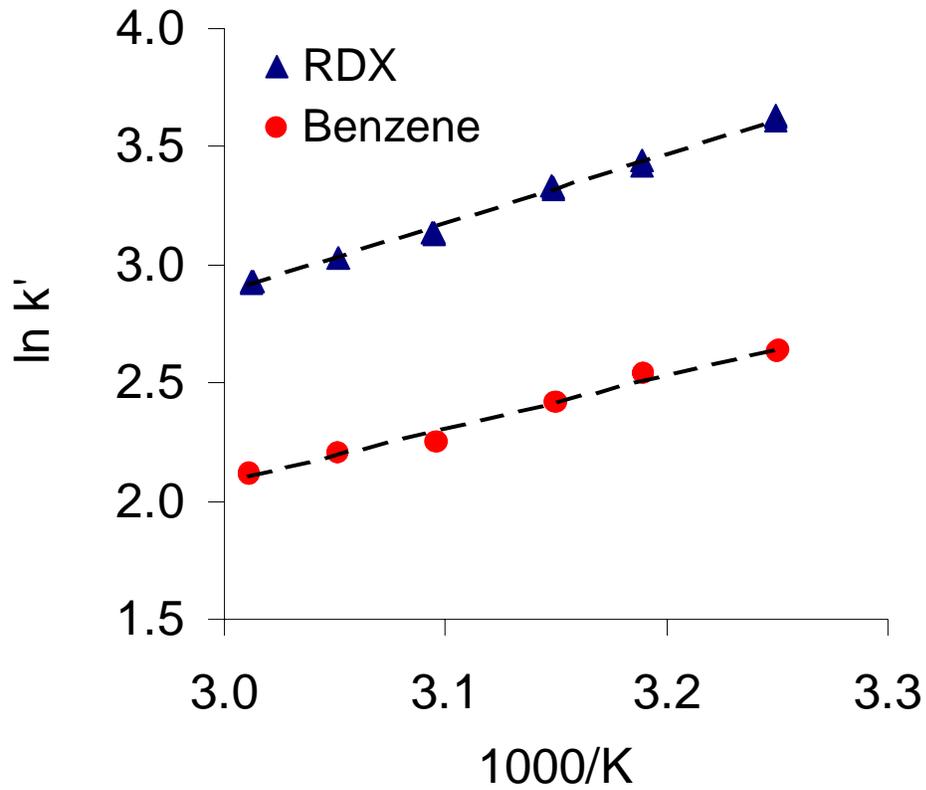
**Title:** Explosives on Surfaces: A Sticky Problem

**Authors:** *Thomas J. Bruno, 838, and Keith E. Miller, University of Denver*

With heightened awareness of homeland security issues the detection of explosive or energetic materials at high sensitivity and with a low error rate has become a pressing priority. Explosive compounds need to be detected on a variety of surfaces - clothing, suitcases, shoes, etc. Every surface will interact with the compounds and the degree of adhesion will vary, surface to surface. By and large, detection of these compounds relies on getting the molecules off the surface and into the gas phase. While there have been significant advances in instrumentation for both laboratory and in-the-field application, a device to be used for airport security will require certification by Federal authorities. Certification will depend upon a sound understanding of device performance and thus, knowing the energetic effects of surfaces, ubiquitous in all measurement scenarios, must be part of the certification process.

The most fundamental measure of the interaction strength with a surface is the enthalpy,  $\Delta H$ . On solids, this describes an adsorption process ( $\Delta H_{\text{ADS}}$ ), while on polymers and liquids, an absorption process ( $\Delta H_{\text{SOL}}$ ). The vapor-phase concentration of explosive compounds is dependent on the enthalpies associated with the surface upon which the explosive residues have sorbed. Surprisingly, there has been very little attention given to this important parameter, primarily due to the experimental difficulties associated with its determination. In earlier work on sorption, we developed a technique to use capillary gas chromatography to measure the surface energetics of organics on soil surrogates. We have extended this work to energetic materials and measured the enthalpy of trinitrobenzene (TNB), trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) sorbed on a polydimethyl siloxane surface. This surface is used as a gas chromatographic stationary phase, and it also is used as a lubricant, release agent, coating, and as a principal component in silicone rubbers. The  $\Delta H_{\text{SOL}}$  for TNB, TNT, and RDX were measured to be  $57.85 \pm 0.2$ ,  $59.48 \pm 0.2$ , and  $62.36 \pm 0.2$  kJ/mole, respectively. We also determined (by measurement of Kováts retention indices) that the energy required to desorb an explosive is similar to that required for  $C_{14}$  to  $C_{16}$  n-alkanes suggesting perhaps a surrogate for instrument calibration. Moreover, we noted that the enthalpy of vaporization for pure TNT and TNB are higher (by  $\sim 20$  kJ/mole) than the  $\Delta H_{\text{SOL}}$  values. This means that it takes less energy to “desorb” an explosive molecule from PDMS or “PDMS-like” material than it would to volatilize (say by heating) a molecule from a solid particle of the pure explosive. One potential application, suggested by this discovery, would be the development of enhanced polymeric release surfaces for wipe testing.

In addition to the vapor phase measurements, we have made similar measurements in the liquid (water) phase. Here, we have used a clay surface as a soil surrogate. These measurements are significant in that residual energetic materials in the environment are a serious threat, especially in live-fire military training venues. Here, for example, we measured  $\Delta H_{\text{ADS}}$  for RDX =  $24.7 \pm 0.7$  kJ/mole, while that for benzene was measured as  $18.9 \pm 1.3$  kJ/mole. These data indicate that while the enthalpies are not especially high, one can expect RDX to persist in the environment longer than benzene.



A retention plot showing the capacity factor of benzene and RDX plotted against temperature, in water as the mobile phase. This illustrates the environmental persistence of energetic materials such as RDX.

**Title:** ThermoML – an Emerging IUPAC Standard for Thermodynamic Data Communications

**Authors:** *M. Frenkel, R. D. Chirico, V. V. Diky (Guest Researcher), Q. Dong, G. R. Hardin.*

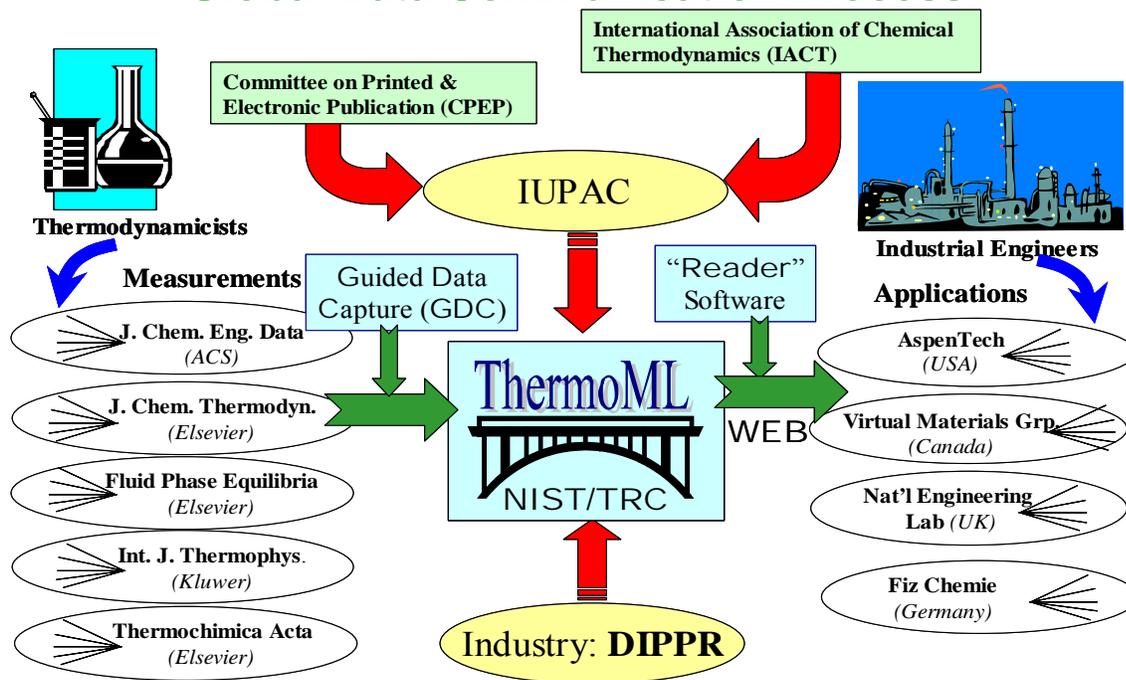
**Abstract:** Establishment of efficient means for thermodynamic data communications is absolutely critical for provision of solutions to such technological challenges as elimination of data processing redundancies and data collection process duplication, creation of comprehensive data storage facilities, and rapid data propagation from the measurement to data management system and from the data management system to engineering applications. Taking into account the diversity of thermodynamic data and numerous methods of their reporting and presentation, standardization of thermodynamic data communications is very complex. The Thermodynamics Research Center (now TRC Group) developed ThermoML, an XML (Extensible Markup Language)-based approach for storage and exchange of thermophysical and thermochemical property data. The ThermoML structure represents a balanced combination of hierarchical and relational elements. The ThermoML schema structure explicitly incorporates structural elements related to basic principles of phenomenological thermodynamics: thermochemical and thermophysical properties (equilibrium and transport), state variables, system constraints, phases, and units. Meta- and numerical data records are grouped into ‘nested blocks’ of information corresponding to data sets. The structural features of the ThermoML metadata records ensure unambiguous interpretation of numerical data and allow data-quality control based on the Gibbs Phase Rule. ThermoML covers essentially all experimentally determined thermodynamic and transport property data (more than 120 properties) for pure compounds, multicomponent mixtures, and chemical reactions (including change-of-state and equilibrium).

Definitions and descriptions of all quantities related to the expression of uncertainty in ThermoML conform to the Guide to the Expression of Uncertainty in Measurement (ISO, 1993). In order to implement this extension of ThermoML, the TRC Group made an interpretation of the U. S. Guide to the Expression of Uncertainty in Measurement for the field of thermodynamics. In 2004, ThermoML was completed with incorporation of extensions for critically evaluated data, predicted data, and equation representations.

In early 2004, ThermoML was accepted as the foundation for the development of the IUPAC (International Union of Pure and Applied Chemistry) standard for thermodynamic data communications.

In order to build an infrastructure for the process of global thermodynamic data communication, Guided Data Capture (GDC) software was developed for mass-scale abstraction from the literature of experimental thermophysical and thermochemical property data for organic chemical systems involving one, two and three components, chemical reactions, and chemical equilibria.

## Global Data Communication Process



Combination of the software tools incorporating GDC and ThermoML allowed establishment of a new data communication process (See figure.), which now includes major journals in the field of thermodynamics, such as the *Journal of Chemical and Engineering Data*, *The Journal of Chemical Thermodynamics*, *Thermochimica Acta*, and *Fluid Phase Equilibria*. As a result of the implementation of this process, hundreds of authors worldwide generate ThermoML files of their reported data at the time of publication. The TRC Group has designed and now supports Web distribution of the ThermoML files in the public domain without restriction. It has also been working with major data-user organizations (Aspentech, U.S.A.; National Engineering Laboratory, U.K.; Fiz Chemie, Germany; Virtual Materials Group, Canada; Korean Institute of Science and Technology Information) to develop software 'readers' of the ThermoML files. In the near future ThermoML will be expanded to provide compound identification using the IUPAC-NIST Chemical Identifier (INChI). Recommendations to IUPAC for a formal approval of ThermoML as a new IUPAC standard will be finalized in FY2005.

**Title:** ThermoData Engine: New Generation Expert System for Thermodynamic Data Critical Evaluation

**Authors:** *M. Frenkel, R. D. Chirico, V. V. Diky (Guest Researcher), Q. Dong, X. Yan (Contractor), C. Muzny*

Traditionally, critical data evaluation is an extremely time- and resource-consuming process, which includes extensive use of labor in data collection, data mining, analysis, fitting, *etc.* Because of this, it must be performed far in advance of a need within an industrial or scientific application. In addition, it is quite common that by the time the critical data-evaluation process for particular chemical system or property group is complete (sometimes after years of data evaluation projects involving highly skilled data experts), it must be reinitiated because significant new data have become available. This type of slow and inflexible critical data evaluation can be defined as ‘static.’ These shortcomings have become magnified dramatically within the last 5 to 10 years due to the significant increase in the rate of publication of experimental and predicted thermodynamic data to be analyzed during the critical data evaluation process.

To address the weaknesses of ‘static’ evaluations, the concept of a dynamic data evaluation system was developed at the Thermodynamics Research Center (now NIST’s TRC Group). This concept requires a large electronic databases capable of storing essentially all experimental data known to date with detailed descriptions of relevant metadata and uncertainties. The combination of these electronic databases with expert-system software, designed to automatically generate recommended data based on available experimental data, leads to the ability to produce critically evaluated data dynamically or ‘to order’ (see figure). This concept contrasts sharply with static critical data evaluation, which must be initiated far in advance of need. The dynamic data evaluation process dramatically reduces the effort and costs associated with anticipating future needs and keeping static evaluations current.

Critically evaluated data produced by the deployment of the dynamic data-evaluation concept can rigorously be characterized with their quality assessments providing the ability to propagate reliable data-quality limits to all aspects of chemical process design. Implementation of the dynamic data evaluation concept consists of the solution of a number of major tasks: (1) design and development of a comprehensive database system structure based on the principles of physical chemistry and capable of supporting a large-scale data entry operation for the complete set of thermophysical, thermochemical, and transport properties for chemical systems including pure compounds, binary mixtures, ternary mixtures, and chemical reactions; (2) development of software tools for automation of the data-entry process with robust and internally-consistent mechanisms for automatic assessments of data uncertainty; (3) design and development of algorithms and software tools to assure quality control at all stages of data entry and analysis; (4) development of algorithms and computer codes to implement the stages of the dynamic data-evaluation concept; (5) development of algorithms to implement, target, and apply prediction methods depending on the nature of the chemical system and property, including automatic chemical structure recognition mechanisms; and (6) development of procedures allowing generation of output in a format suitable for application in major commercial simulation engines for chemical-process design.

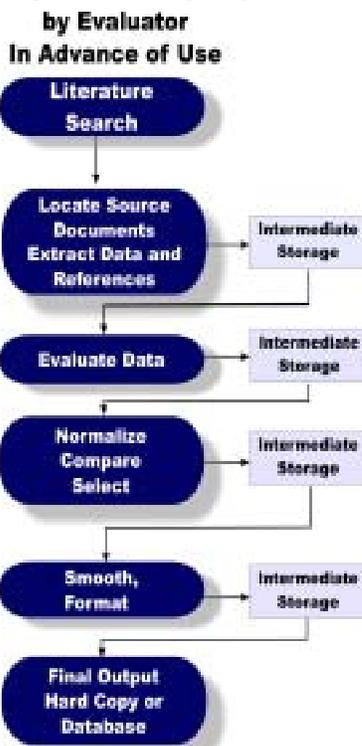
The ThermoData Engine (TDE) software incorporates all major stages of the concept implementation including data retrieval, grouping, normalization, sorting, consistency enforcement, fitting, and prediction. The SOURCE data system is used in conjunction with TDE as the comprehensive storage facility for experimental thermophysical and thermochemical property data. In addition the NIST/TRC Ideal Gas Database is used as a source of thermodynamic property data in the ideal-gas state.

In FY2004, the ‘beta’-version of the first release of the TDE, focused on the thermodynamic properties of pure compounds, was and extensively tested within and NIST. The software architecture

enforcement of consistency between related properties (including those obtained from predictions), assumes an imperfect source of original data, provides for flexibility in selection of default data models depending on the particular data scenario, incorporates a large variety of models for secondary fitting, and allows saving of critically evaluated data in the ThermoML format. The latter assures compatibility of the TDE software with any engineering application equipped with a ThermoML software ‘reader.’

The ‘alpha’ version of the TDE is scheduled for public release in FY05. Further development will include incorporation of the computational tools for generating equations of state on-demand depending on the data ‘scenario.’ Longer-term plans include expansion of the TDE to critical data evaluation for binary mixtures.

### STATIC DATA EVALUATION



### DYNAMIC DATA EVALUATION



Functional comparison of static and dynamic data evaluation concepts.

produced outside emphasizes

**Title:** Systematic Validation and Improvement of Quantum Chemistry Methods for the Prediction of Physical and Chemical Properties

**Authors:** C.A. Gonzalez(838), R. D. Johnson(838), and K.K. Irikura(838)

**Purpose:** This work will lead to the systematic validation and improvements of quantum chemistry techniques for the prediction of physical and chemical properties of a large variety of chemical systems. The primary goal is to provide uncertainties in properties computed by the most popular levels of theory making use of standard statistical techniques and high quality experimental data. This work is also focused in making available procedures and data that will enable researchers in industry to choose the most reliable quantum chemistry methods for prediction of a physical and/or chemical properties. An in-depth understanding of the sources of uncertainties also will lead to improvements of the quantum chemistry methods used in the predictions.

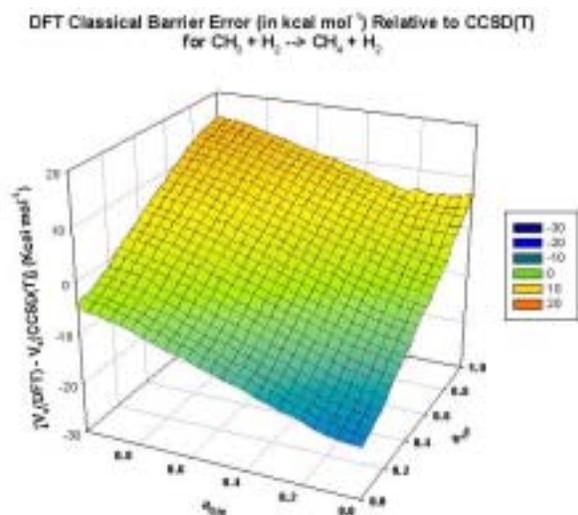
**Scientific Objectives.** The use of modern computational chemistry methodologies in the prediction of molecular properties has become increasingly popular mainly due to significant improvements in the algorithms, the accuracy of the methods, and the advent of powerful computer resources. This is particularly true in the area of thermochemistry, where researchers in industry and academia perform quantum chemistry calculations on a routine basis. Recently, there has been an increased interest in the use of theoretical predictions of physical and chemical properties made by state-of-the-art quantum chemistry methodologies to fill gaps in the available experimental data. This approach could potentially eliminate the cost of experimental measurement and will be particularly useful in cases where extrapolations based on available experimental data are not possible or unreliable. However, despite the aforementioned progress, the predictive power of most of the quantum chemistry methodologies has not been established on solid ground due to the lack of knowledge of their relative uncertainties. To understand these uncertainties an exhaustive and systematic validation of these methodologies involving robust strategies to compare theory and experiment is necessary. In addition, the results of such validations must be widely available to the scientific community so new scientific discoveries could leverage from this knowledge.

A team of researchers in the Computational Chemistry Group is working on an integrated approach that will lead to the systematic validation as well as improvements of popular and new theoretical methods using high quality experimental data. This approach involves the development of state-of-the-art databases in order to disseminate the accuracy, reliability and transferability of the most popular quantum chemistry methodologies in the prediction of physical and chemical properties of a large variety of chemical systems ranging from isolated atoms and molecules to condensed phase. The theoretical methodologies being studied include semi-empirical Hamiltonians, wavefunction-based *ab initio* molecular orbital theory, and Density Functional Theory (DFT) while the experimental data used in the validation include measurements already available in the literature and also made by researchers at NIST.

## Major Accomplishments:

*Assessing the Accuracy and Reliability of Density Functional Theory.* Density Functional Theory (DFT) has become one of the most widely used quantum chemistry methods mainly due to its relatively low computational expense. The electronic energy within the DFT formalism is a functional of the electron density that consists of an “exchange” energy term and a “correlation” energy term. Although in principle there exists a universal DFT functional that can describe the electronic problem exactly, the discovery of such functional has eluded scientists for years. In practice, arbitrary forms for the DFT functionals are parameterized in order to reproduce the experimental energetics of a relatively small set of molecular systems.

Researchers in the Computational Chemistry Group at CSTL have performed a systematic validation of a particular family of DFT functionals, the so-called “hybrid-GGA”, in order to assess their accuracy and transferability to different chemical properties. The performance of these functionals in the prediction of properties such as singlet-triplet gaps, reaction barriers, dipole moments and polarizabilities showed a marked erratic behavior leading to the conclusion that these functionals are not transferable to the computation of different chemical properties. In addition, the results of this work indicate that the major source of error can be traced back to the “exchange” functional, which exhibits significant spurious and uncontrollable electron “correlation” energy due to the empirical parameterization used in the development of these functionals.



*Improvements to the Accuracy of Density Functional Theory.* In order to solve the problems exhibited by the “exchange” functionals we proceeded to develop a rigorous and efficient method (the SC- $\alpha$  method) for the calculation of the exact “exchange” functional<sup>1</sup>. This method has been implemented in various popular quantum chemistry software packages and it has been tested in more than 40 molecules and the results have shown the possibility of computing the exact “exchange” functional in complicated polyatomic systems at the computational cost comparable to the inexpensive Hartree-Fock

formalism. Encouraged by these results, we focused in procedures that could improve the “exchange-correlation” functional as a whole. One of the most difficult steps in the generation of “exchange-correlation” functionals (XC) that do not require empirical parameters (and therefore, making it more general than the semi-empirical “hybrid-GGA” functionals) is the development of closed forms for the derivatives of these functionals with respect to the electron density. These derivatives (or potentials as they are known) are critical in the calculation of molecular properties in a “variational” manner and are difficult if not impossible to implement for reliable XC functionals such as the Meta-GGA DFT due to their complicated mathematical

forms. In this work, we have developed a general and simple methodology called the “Approximate Self-Consistent Potential” (ASCP) that allows scientists compute the corresponding derivatives without the knowledge of a closed form. The method has been implemented in two of the most popular quantum chemistry packages and tested in the calculations of absolute energies and atomization energies of 20 different molecules. The results indicate that the method is robust and sufficiently general.

*Quantifying Uncertainty in Prediction of Enthalpies of Formation and Vibrational Frequencies.* It is well recognized that a complete expression of experimental measurement includes both the central value and its associated uncertainty. The central value alone is incomplete. Throughout computational science, the results of models are usually reported without their associated uncertainties, making them incomplete. The term *virtual measurement* refers to a prediction from a computational model together with its associated uncertainty, and emphasizes the analogy with experimental (physical) measurement. Our investigation of the uncertainties associated with predictions from quantum chemistry models are intended to help “virtual measurements” supplant “calculated results.” The results from *ab initio* calculations differ from experiment by systematic biases, not random errors. For a given *ab initio* calculation corrections can be applied to compensate for this bias and an uncertainty can be determined from the distribution of corrections for a class of molecules. We use the experimental and *ab initio* data contained in the NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB), which contains data for over 600 molecules, over 100 calculations for each molecule, and over 4000 vibrational frequencies. We combine this data with analysis based upon the *Guide to the Expression of Uncertainty in Measurement*, published by the International Organization for Standardization (ISO), to determine biases and uncertainties. We have applied this to enthalpies of formation and vibrational frequencies<sup>2</sup>. This allows us to upgrade these “calculated values” into “virtual measurements”. For the enthalpies of formation we found the class of molecules to be critical in determining the bias and uncertainties. For the vibrational frequencies we found the uncertainties to be orders of magnitude larger than previously believed. We plan to continue extracting such information from the CCCBDB to determine the uncertainties for other calculated properties as well.

**Future Plans:** In the near future, this work will be extended to validate other quantum chemistry methodologies including DFT, wavefunction-based *ab initio* molecular orbital theory, and semi-empirical Hamiltonians. In addition to thermochemical and spectroscopic properties, the performance of these methods in the description of physical and chemical properties of metals and organometallic systems (important in material science, biochemical processes as well as in catalysis) will also be assessed.

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<sup>2</sup> Irikura, K. K.; Johnson, R. D., III; Kacker, R. N. *Metrologia* **41**, 369-375, 2004.

**Title:** Theory of Non-Bonded Interactions: Molecular Association and Assembly

**Authors:** C.A. Gonzalez(838), V.K. Shen(838), K.K. Irikura(838) and J.R. Errington (State University of New York at Buffalo)

**Purpose:** To develop and validate efficient theoretical and computational methodologies for the description of long-range interactions in gas-phase and solution and thereby enable prediction of thermodynamic and transport properties of fluids.

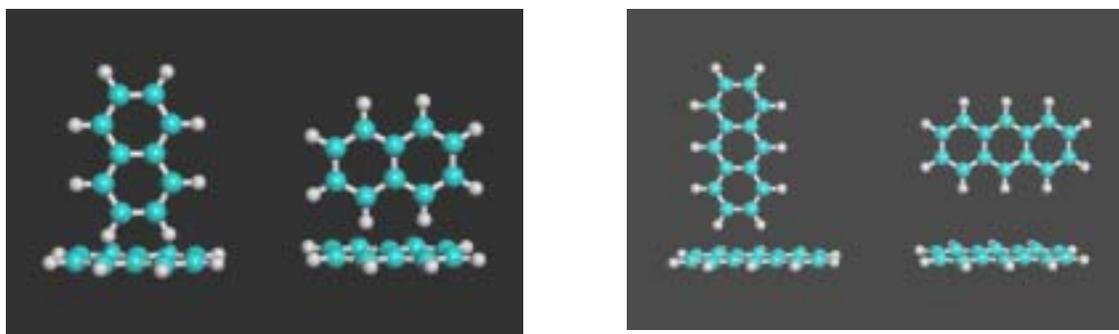
**Scientific Objectives.** Long-range inter-molecular forces play important roles in many chemical and biological systems. They control, among others, the base-base interactions leading to the double helical structure of DNA, the function of the special pair in photosynthetic reaction centers, the packing of aromatic crystals, the formation of aggregates, the conformational preferences of polyaromatic macrocycles and chain molecules as well important bulk fluid properties. It has also been found that weak interactions can be important in atmospheric chemistry. For example, the molecule ClOO (chloroperoxy radical, formed by the collisions of the chlorine atoms with oxygen molecules) is critical in the catalytic, homogeneous destruction of ozone in the stratosphere. Most Cl-O<sub>2</sub> collisions lead to excited states of ClOO and we have found that many of these excited states surprisingly support weakly bound but stable vdW complexes which must be considered to accurately predict the rates of ozone destruction.

The molecular systems ideally suited for a detailed study of the intermolecular potentials are van der Waals (vdW) dimers and higher clusters of aromatic hydrocarbons formed as a direct consequence of intermolecular interactions. Given the maturity reached by quantum chemistry and the improvement in the algorithms used in quantum chemical calculations, it is logical to expect that highly correlated *ab initio* electronic structure methodologies could be a valuable tool to predict the structures and energetics of these clusters. We must assess the validity of these methodologies in the case of larger clusters of different aromatic molecules and possibly determine if alternative methodologies that incur lower computational expenses can be devised for these larger systems. Once the reliability and accuracy of these theoretical models are properly validated for gas-phase clusters they can be used for the generation of efficient and reliable empirical force-fields to be used in large-scale simulations of molecular systems in condensed phase such as liquids. This task of course, also requires robust and efficient simulation methods that predict the different physical properties of bulk fluids in a reliable manner.

### **Major Accomplishments:**

*Fundamentals of van der Waals Interactions in Aromatic Clusters.* The first phase of the project consisted of the use of second order Møeller-Plesset perturbation theory, MP2, with different basis sets in order to optimize the geometries and compute the relative binding energies of the lowest energy conformers for the dimers, trimers and tetramers of benzene, naphthalene, and anthracene. These systems are a prototype for vdW clusters containing large aromatic molecules dominated by a delicate balance between electrostatic and dispersion forces. They were chosen on the basis of the availability of reliable experimental data. Overall, the results obtained in this project indicate that the combination of molecular dynamics simulations using the MM3 force field, followed by full geometry optimizations at the MP2/6-31G level of theory appear to

provide a reliable tool for the study of van der Waals aromatic clusters. One significant outcome of this research has been the realization that the use of a small basis sets such as 6-31G with the *ab initio* MP2 methodology predicts binding energies closer to the experimental results than the corresponding binding energies computed with larger basis sets. This surprising result is very important given that calculations of vdW clusters with larger basis sets are highly prohibitive due to the computational resources needed. Careful analysis of the data led to the conclusion that the source for this interesting behavior is rooted at a fortuitous but systematic cancellation of errors between the lack of convergence of the perturbation method MP2 and deficiencies in the 6-31G basis set. Given that the study of larger vdW clusters involving more than four aromatic molecules is almost impossible even at the MP2/6-31G level, we have performed a systematic comparison of the results obtained with the very efficient methodology Hartree-Fock Dispersion (HFD)<sup>1,2</sup> previously developed in our group and the results computed at the MP2/6-31G level of theory. It was found that HFD predicts structures (see figures) and binding energies in very good agreement with the MP2/6-31G results<sup>3</sup>.



Computed structures of  $(C_{10}H_8)_2$  and  $(C_{14}H_{10})_2$

*Prediction of Mixture Phase Behavior Using Transition-Matrix Monte Carlo Simulation.* The fluid-phase behavior of mixtures is a subject of immense industrial and technical importance. For example, in multi-component systems, it is the fact that different coexisting phases often have different chemical compositions that serves as the basis for fundamental unit operations, such as, absorption, distillation, and liquid extraction. Thus, knowledge of the phase coexistence properties of mixtures is crucial to the design of effective separation processes. Because laboratory determination of mixture phase equilibria can be potentially expensive and time-consuming, it is highly desirable to have a computational means for this purpose. While molecular simulation is ideally suited for this, only within the last twenty years have advances in simulation methodologies made this goal a realistic one. Current state-of-the-art simulation methods directly simulate phase coexistence and only yield a single equilibrium point per simulation. Therefore, a large number of these simulations are required to obtain phase equilibria data over a range of thermodynamic conditions, which can take a substantial amount of time.

Building upon recently developed transition-matrix Monte Carlo methods, we have developed a new simulation methodology capable of precisely predicting an entire isothermal fluid-phase diagram in a single simulation in a significantly shorter amount of CPU time relative to existing methods. To validate the mixture transition-matrix Monte Carlo method (M-TMMC)<sup>4,5</sup>, we have investigated a number of binary mixtures whose phase behavior is well known, and also mixtures that are known to pose problems for conventional methods. M-TMMC produced results in

excellent agreement with literature data in **all** cases. Additionally, we found that the relative uncertainties of the predictions were at most 0.2%, an order of magnitude improvement over current methods. Because the method determines the system's free energy as a function of density and composition, the utility of the information yielded by this approach goes far beyond that for use in determining phase equilibria, and it should therefore serve as a highly efficient computational tool for studying a wide range of phenomena at the molecular level.

We are currently extending this work in order to study vdW interactions between polar molecules, where dispersion forces and electrostatics interactions might be competitive with other forces such as hydrogen bonding. In addition, our HFD method will be used to probe the dynamics of cluster formation by means of Carr-Parinello simulations.

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- (4) V. K. Shen and J. R. Errington, *The Journal of Physical Chemistry B*, (in press).
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**Title:** Integrated Transport Property Program for Key Systems: Data, Models, and Simulation

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

Efficient design of chemical processing equipment for various industrial sectors such as transportation, petroleum refining, energy, and refrigeration requires reliable values for the transport properties viscosity and thermal conductivity. To meet these data needs, we pursue an integrated strategy that combines experiment, theory and simulation in the development of advanced models for transport properties, leading to predictions of reliable information even when experimental data may be lacking. The primary approach is the critical assessment of all available experimental data and their representation by correlations, incorporating theory when possible. Here we have extended the model base to the viscosity and thermal conductivity of the linear alkanes *n*-octane, *n*-nonane, *n*-decane and *n*-dodecane. These are the first such models for the heavier alkanes commonly present in liquid-phase fuels. The development of these transport properties formulations was driven in part by the industrial need/demand for accurate knowledge of the properties of hydrocarbon mixtures, including economically important fluids such as natural gas and jet fuels.

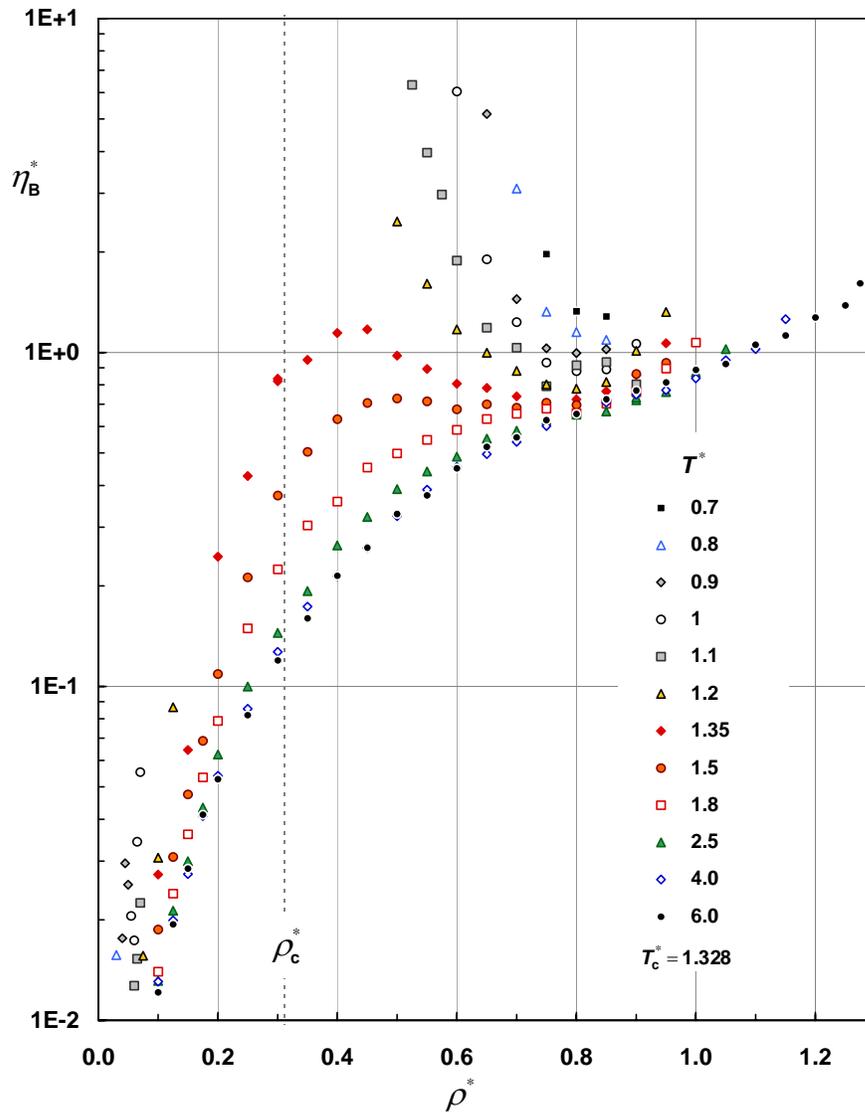
The new models represent the viscosity and thermal conductivity surfaces of these compounds over their entire fluid region, encompassing the dilute gas to the dense fluid and supercritical regions, at temperatures down to the triple point. They represent the available experimental data to within their experimental uncertainties and extrapolate in a physically meaningful manner. Our models for *n*-octane, *n*-nonane, *n*-decane and *n*-dodecane have been presented in three manuscripts and at the Properties and Phase Equilibria for Product and Process Design (PPEPPD) conference in Snowbird, Utah (May 16-21, 2004).

Complementing our experiment-based approach are computational studies of the properties of systems with model potentials. Such studies can improve fundamental understanding for conditions where measurements are not feasible. Results of high computational accuracy have been published for the shear viscosity, the self-diffusion coefficient, and the bulk viscosity. With comprehensive simulation data at over 350 state points, the temperature and density dependences of these properties of the Lennard-Jones potential are characterized for the first time over a wide range of fluid states. The simulation data for the bulk viscosity has revealed a large critical enhancement similar to that known for the thermal conductivity, but extending much farther into the supercritical region (it can be observed even at 4.5 times the critical temperature). From our simulations, the bulk viscosity is now known in a wider range of states for the Lennard-Jones model fluid than for any real fluid.

The integrated program on transport properties represents a portion of our coordinated efforts on thermophysical properties. These are important to both our infrastructural work (information will be disseminated through such standard reference databases as NIST REFPROP), and to the immediate needs of customers, such as a project on rocket propellant RP-1. The ongoing program will continue to focus on both immediate and specific demands for transport property information and on longer-term efforts to improve our predictive capabilities in these areas.

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Computer simulation results of the first comprehensive characterization of the bulk viscosity of the Lennard-Jones model potential. Shown is the density dependence of the bulk viscosity along twelve isotherms. The corresponding temperature range for argon is 84 K to 720 K. The simulations reveal a critical enhancement of the bulk viscosity that is more pronounced and wider ranging than those of other properties. With these results, the bulk viscosities of real fluids can be estimated with much reduced uncertainties

**Title:** Invention of a New Class of Ultra-fast, Ultra-sensitive Mass Spectrometers for Kinetics, Reference Mass Spectrometry, and Homeland Defense Applications

**Author:** *J. W. Hudgens*

**Purpose:** The project will demonstrate the feasibility for improved mass spectrometers based on Hadamard-transform data acquisition. Hadamard mathematics describes the most accurate procedures for measuring properties of any ensemble. To the chemist, its most familiar form includes a digital representation of the fast-Fourier transform used in modern infrared spectrometers. The project involves building a prototype Hadamard time-of-flight mass spectrometer (HT-TOFMS), measuring its performance, and using test data to model a Hadamard-transform MS-MS instrument. A goal is to show that Hadamard MS-MS instruments are feasible and can rapidly resolve the chemical structures of components in a complex mixture. Hadamard mathematics suggests that such instruments can acquire comprehensive structure determination data of chemical unknowns as much as 3,000-600,000 times faster than current art.

**Major Accomplishments:** The first Hadamard TOF mass spectrometer incorporating an electron-impact ionizer has been invented, designed, and constructed at NIST. The instrument appears similar to a commercial Reflection TOF mass spectrometer; however, it contains a specialized electron gun, ion optics, and high voltage electronics that are optimized for high frequency modulation. Laboratory tests have demonstrated that this ionizer can switch ion streams on and off with a 5 ns rise-fall time when modulated at 13 MHz. These performance specifications will permit Hadamard operation. Integration of this hardware with the necessary software is in progress.

Conventional TOFMS ion optics accelerate individual ion bunches down a flight tube to a detector. The detector signal is sent to a 1 GHz multi-channel scalar that counts the ions and measures their arrival times. The TOF spectrum is simply the graph of ion counts vs. time. Because a conventional TOFMS instrument flies each ion bunch individually, it has a duty cycle of only ~ 2 %. When operating in Hadamard mode, the ionizer modulates the ion stream with a simplex code sequence that is derived from a Hadamard matrix. The simplex matrix is composed of rows of 1's and 0's that instruct the ionizer to switch the ion current on and off. With a Hadamard modulation frequency of 13 MHz, ~ 500 distinct ion packets are simultaneously in flight. The signal from an HT-TOFMS initially looks like random noise. The mass spectrum is obtained by multiplying this "noise" by the inverse of the simplex matrix. The duty cycle of the HT-TOFMS is 50 %. Hence, the HT-TOFMS obtains a 25x-50x sensitivity improvement from its higher duty-cycle. Other features of Hadamard mathematics further enhance sensitivity and reduce measurement uncertainties.

Preliminary numeric simulations have been conducted and suggest that useful Hadamard MS-MS instruments are possible. The incorporation of test results from the present HT-TOFMS will help us optimize trial instrument designs and data acquisition procedures.

**Impact:** The demonstration that any conventional TOFMS can be converted into a more sensitive Hadamard instrument may accelerate adoption of this superior technology. Hadamard technology is expected to find application in fields of chemistry such as the study of the rates of chemical reaction or forensic analyses where high sensitivity, sample conservation, and high

operational speed are essential. If Hadamard principles could be adapted to other variations of MS-MS, say those used in the drug discovery process, it would enable the acquisition of complete MS-MS data sets within the duration of a single HPLC peak. Currently, such data campaigns take days to execute and can require use of an expensive (~\$1M) ion cyclotron resonance MS in order to conserve sparse samples.

**Future Plans:** This project will continue along practical avenues. The present Hadamard mass spectrometer will be used to obtain feasibility data for an MS-MS instrument. The design target is an instrument that can measure the kinetics of complex hydrocarbon mixtures.

Algorithms that reduce the effects of mask errors (which in mass spectrometers arise from non-ideal ion current modulation) on the measurement quality are an active research area in mathematics. The community needs data from a well-characterized experiment to verify assumptions about the nature of Hadamard measurements. Since we plan to incorporate error correction algorithms into the NIST HT-TOFMS, we can generate this benchmark reference data. This data may facilitate improvements in other Hadamard application fields including microscopy, NMR, and medical MRI.

**Title:** Ab Initio Mass Spectrometry

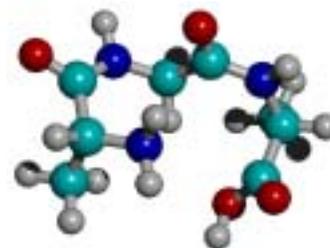
**Author:** *Karl K. Irikura*

**Vision:** Develop predictive theory for analytical mass spectrometry.

**Purpose:** Traditional electron-impact (EI) mass spectrometry (MS) is used for detecting and identifying compounds in the vapor phase. Important applications include detecting toxic compounds, verifying compliance with international chemical weapons treaties, detecting chemical explosives, detecting illegal drugs, and laboratory analysis of organic compounds. Compounds are identified by comparing observed spectra with those of candidate compounds, which must be previously known (e.g., in the NIST Mass Spectral Database). Spectra cannot currently be predicted theoretically. However, theoretical developments at NIST (in CSTL and PL) over the past several years offer new opportunities for developing theoretical means for predicting EIMS. We would like to develop a predictive theory, which would make it possible to positively identify compounds not found in the standard databases.

Another type of mass spectrometry, tandem mass spectrometry (MS/MS) is the ionic equivalent of gas-phase pyrolysis. MS/MS has gained prominence recently as a key technology of proteomics. The standard procedure involves protein digestion followed by MS/MS analysis of the resulting peptide fragments. Sequence information is obtained from the spectra by using a few simple, empirical rules. However, about half the information in the spectra is discarded because it does not conform to the known rules. Recent computational chemistry techniques, developed in CSTL under an earlier Exploratory Research project, suggest how additional rules might be discovered theoretically. We will use these and other strategies to seek new rules, which will increase the power of MS/MS for proteomics applications. This will increase the speed and reduce the cost of protein sequencing.

**Accomplishments and Future Plans:** After consultations with Steve Stein, the director of the NIST Mass Spectral Database, it was concluded that MS/MS is a higher priority than EIMS. Fortunately, MS/MS is also the simpler chemical process from a theoretical perspective. A new NRC postdoctoral associate, Christopher Kinsinger, has joined this project full-time. His entry point into the peptide fragmentation problem is to examine certain general trends (e.g., the “glycine effect”) that have been observed in large data sets. Again after consultations with Dr. Stein, tripeptides have been chosen as the most appropriate model for the fragmentation of tryptic peptides. The goal is to understand the trends and to make them both quantitative and predictive, thus defining new fragmentation rules. Experimental measurements will be done to support the calculations.



**Protonated Ala-Gly-Ala**

**Title:** Thermodynamic Reference Data

**Authors:** *E.W. Lemmon, M.O. McLinden, A.H. Harvey, R.A. Perkins*

**Context:** Databases are the primary technology transfer vehicle by which we deliver our collective expertise in fluid properties to our customers. Much of our theoretical, modeling, and experimental efforts are directed towards improving and extending the databases to meet customer needs.

**Accomplishments:** We have expanded the NIST REFPROP (Reference Properties) database to include over 20 new fluids of industrial importance including hydrogen sulfide, carbon monoxide, nitrous oxide, toluene, xenon, and R227ea. New “short-form” equations of state (EOS) for these fluids describe all of the thermodynamic properties using a fixed functional form based on the Helmholtz energy. The short fixed form allows us to calculate properties for fluids with limited data sets but with higher accuracies (typically 0.1 to 0.5% in density, 1 to 3% in liquid heat capacities and sound speeds) than previously attained for these fluids. REFPROP has also been improved by the addition of equations for the dielectric constant of both pure fluids and mixtures.

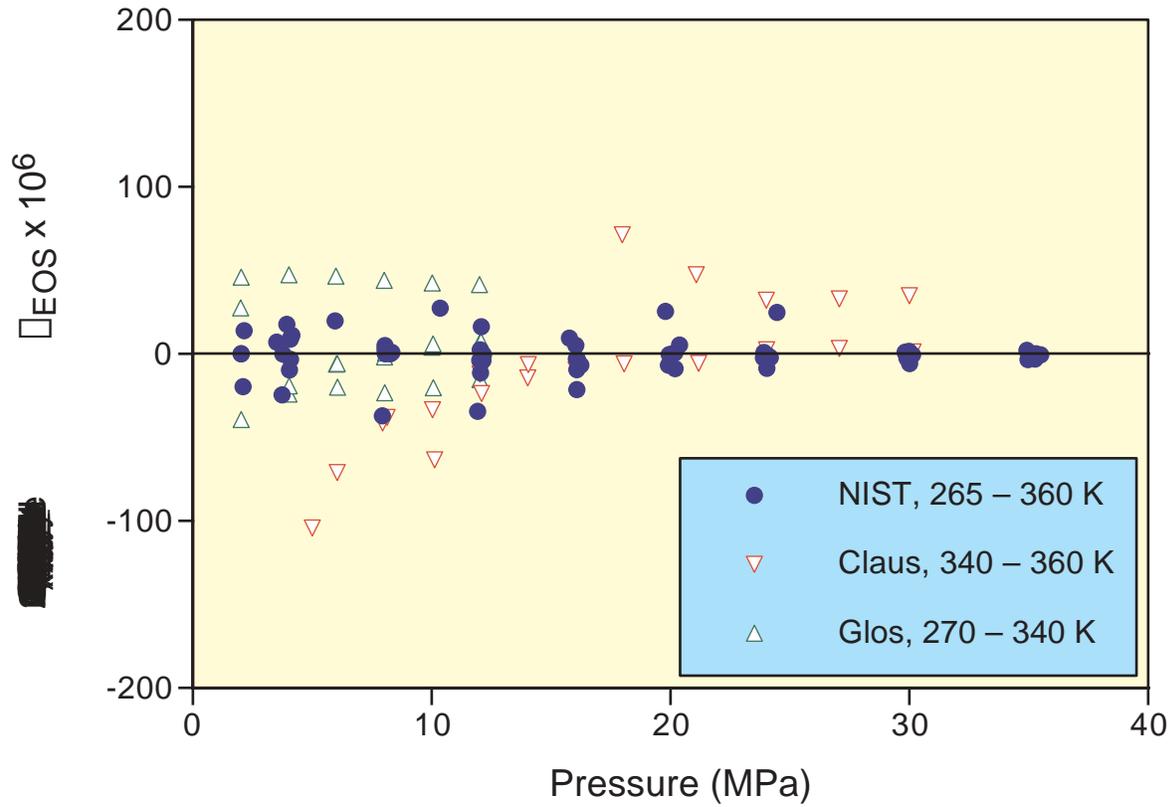
These new short-form equations of state are based on state-of-the-art EOS for reference fluids. We have advanced the state-of-the-art for EOS with new formulations for R125 and propane containing new terms and using new fitting techniques designed to make the equations more fundamentally sound. (Traditional high-accuracy EOS were highly empirical and did not have the proper behavior beyond the range of the data, while theoretically based EOS had proper qualitative behavior but were not of high accuracy.) The new functional form eliminates certain nonphysical behavior in the two phase region. The addition of nonlinear fitting constraints has yielded an equation which achieves proper phase stability, *i.e.*, only one solution exists for phase equilibrium at a given state. We have developed new fitting techniques to ensure proper extrapolation of the EOS at low temperatures, in the vapor phase at low densities, and at very high temperatures and pressures.

Development and validation of these high-accuracy equations of state require extensive, high-accuracy experimental data, and our recent measurements include the heat capacity ( $C_V$ ) and density ( $p$ - $\rho$ - $T$ ) of propane. Between  $C_V$  and  $p$ - $\rho$ - $T$ , our measurements cover the entire fluid range from the triple point to 500 K, including low-density gas states and compressed liquid states up to 36 MPa. The  $p$ - $\rho$ - $T$  data include extensive measurements near the gas-liquid critical point. These data, combined with new terms in the EOS, allow us to determine (using only single-phase data) the critical point at least as accurately as the available literature values.

**Impact:** The REFPROP database has been the *de facto* standard in the refrigeration industry for many years. In 2004, a new ISO standard for refrigerant properties was approved which adopts the same formulations as those used in REFPROP, making REFPROP compliant with the international standard. We were key members of the working group which developed this standard. As REFPROP expands, it is used increasingly beyond the refrigeration industry.

**Future Plans:** Future work will include porting the computational engine of REFPROP to the Thermo-Data Engine (TDE), giving TDE the advantage of the inherent thermodynamic consistency of representing properties with EOS versus the present approach of representing

different properties with discrete correlations. Models for aqueous (water-based) systems and hydrocarbon mixtures containing hydrogen and helium will also be developed.



*Comparison of the new NIST  $p$ - $\rho$ - $T$  data for liquid propane and two literature sources with the equation of state.*

**Title:** The NIST Chemistry WebBook Goes Multilingual

**Authors:** *Peter Linstrom and Gary Mallard*

The role of international trade is growing more important in the US economy each year. There is a natural market for US goods in the Western Hemisphere that has been hampered by a number of factors, but one of them is the limited ability to communicate in the non-English languages of the hemisphere. This has been addressed by the Standard Reference Materials group by an active effort to make information available in Spanish. The NIST Chemistry WebBook is a widely used tool for both teaching chemistry and the practice of chemistry. And while the majority of scientist have some English ability, there is a clear need to make our data and tools available in more languages. To this end we have been cooperating with a project funded by the European Commission to make the WebBook available in more languages.

The need for as much information to be available in as many EU languages as possible has been a driving force for a number of projects in the EU. The use of the WebBook in Europe is very extensive and so when the suggestion was made to work together on this effort we welcomed it. NIST's role has been to provide the basic text in marked up format so that it can be translated. The entire cost of the translation has been born by the EU. The first results of this are a set of web pages allowing the basic search to be done with instructions and some help in French, Spanish, Czech and Portuguese.

W3C (the World Wide Web Consortium) has had standards for multilingual sites for some time. These standards are supported by most of the new browsers but must be used by the web site. The WebBook had not been delivering alternative language pages, but with this new effort a user with Spanish as the native language will be greeted with:

**Libro del Web de Química del NIST**

***Base de Datos de Referencia Estándar del NIST Número 69 – Publicada en  
Noviembre, 2004***

Where a user from Brazil will be greeted with:

**NIST Livro de Química na Web**

***Base de dados de Referência padrão do NIST número 69 – Publicada em  
Novembro, 2004***

With these additions, as well as French, all of the major Western Hemisphere languages are available. The addition of other languages will be done as the EU provides the translated pages.

While it is not possible to translate every section of the WebBook, there are major portions of the opening screens that allow the users in other languages to more readily use the more complex search features of the WebBook. The final stages of this initial effort included a two week visit by Rui Pinto from Departamento de Quimica, Universidade de Aveiro (the Department of Chemistry, University of Aveiro, Portugal) who has been active in the Portuguese, Spanish and French translations.

Because the WebBook has been conforming in its design to the most rigorous standards of W3C, the use of multiple languages with full support of the language specific character sets was relatively straightforward to implement.

This meant that this language:

The National Institute of Standards and Technology (NIST) uses its best efforts to deliver a high quality copy of the Database and to verify that the data contained therein have been selected on the basis of sound scientific judgment. However, NIST makes no warranties to that effect, and NIST shall not be liable for any damage that may result from errors or omissions in the Database.

could become this:

Národní Institut pro standardy a technologii (NIST) vynakládá maximální úsilí, aby zpřístupnil vysoce kvalitní databázi a mohl potvrdit, že zde obsažená data byla vybrána na základě řádného vědeckého posouzení. Přesto však NIST v této věci nedává žádné záruky a NIST nebude zodpovědný za jakoukoliv škodu, která může vzniknout v důsledku chyb nebo opominutí v Databázi.

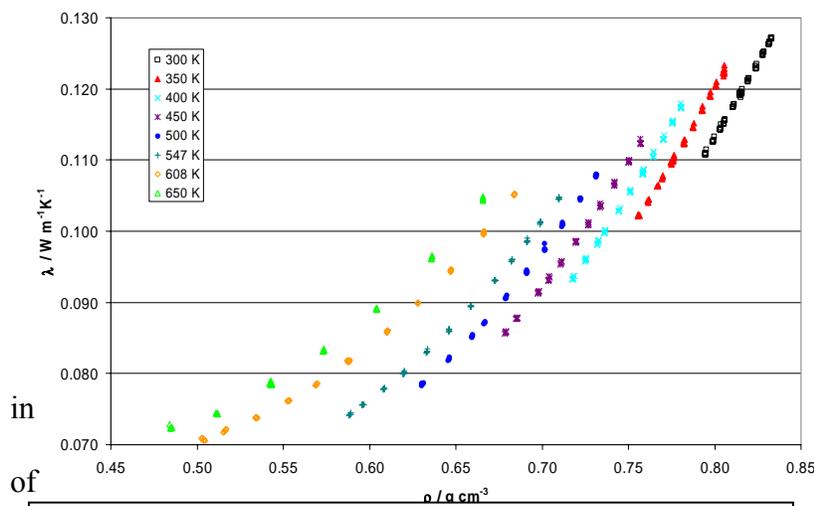
for the Czech version. Future changes will only require that the text be made available in standard formatted files.

## Title: Advanced Propulsion Systems Demand Accurate Property Data

**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), I. M. Abdulgatov (Russian Academy of Sciences), P. C. Andersen (2B Technologies)

As part of the NASA Space Launch Initiative's Next Generation Launch Technology Program NASA and engine manufacturers 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 single pure component surrogate compound (with measurements limited to less than 100°C) or on estimation methods that are grounded in very limited data. NASA representatives cite a study which concluded that property uncertainties account for 70% of the uncertainty in a portion of the propulsion system design, and that the differences in RP-1 properties from different sources can amount to 5% to 60%. To address the concerns surrounding the accuracy of available thermophysical properties of RP-1, new measurements and models were needed.

A gas chromatography - mass spectrometry – infrared spectrophotometry method was used to chemically characterize a sample of RP-1 supplied by NASA. As expected, our analysis showed that RP-1 is a complex liquid fuel that consists of significantly more than 100 components.



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Accurate experimental results for thermal conductivity of RP-1 have replaced estimated values NASA had relied since the 1950's

present in this fuel. A study of thermal decomposition kinetics for RP-1 as a function of temperature was made, so that property measurements could be avoided at temperatures where decomposition was excessive. Measurements of chemical composition, boiling temperature, density, heat capacity, viscosity and thermal conductivity were conducted in a range of temperatures up to 700 K and pressures to 60 MPa. Short equations of state and models for the transport properties were developed for each of the 20 key constituents in RP-1. A Helmholtz energy mixture model was developed that is based on the 20 short equations and estimated/predicted interaction parameters. Similarly, a mixture model was developed for the transport properties of RP-1. Both models were implemented in a single program that features a user-friendly REFPROP interface.

These accomplishments were presented to specialists in rocket fuels (from NASA, the Air Force, commercial rocket engine manufacturers, and academia) at a CSTL hosted workshop at the Boulder campus of NIST in December 2003. A software implementation of the preliminary models was delivered to NASA engineers and their contractors for testing and to assist in the resolution of current engine design problems. Participants in the workshop were eager to use the new results, and were very interested in continued NIST efforts to explore the effects of sample-to-sample variation and refined processing methods on fuel properties, to help establish new protocols for fuel characterization, and to expand the range of conditions and properties. Efforts in this regard will await further funding from the interested agencies and organizations.

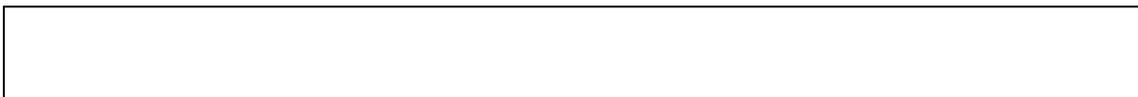
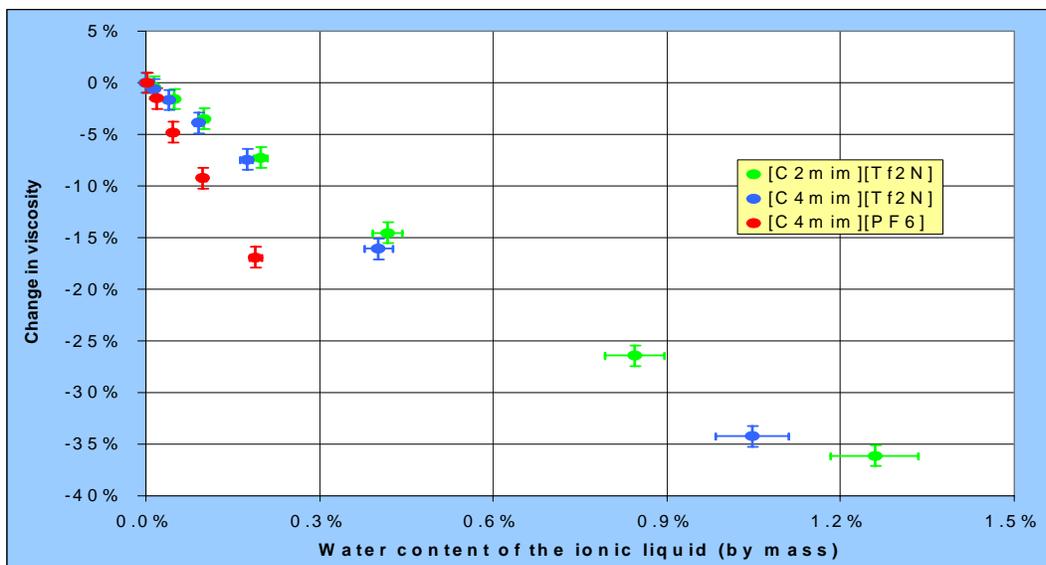
**Title:** IUPAC Partnership Develops Standards and a Data Retrieval System for Ionic Liquids

**Authors:** J. W. Magee, J. A. Widegren, D. G. Archer, S. L. Outcalt, M. Frenkel, R. D. Chirico, Q. Dong, A. Laesecke, M. O. McLinden, R. A. Perkins (838), K. N. Marsh (University of Canterbury, New Zealand), B.-C. Lee (Hannam University, Korea), E. M. Saurer (University of Notre Dame)

Ionic liquids, a class of organic salts that are liquid at or near room temperature, have been proposed as solvents for *Green Processing*, cf C&E News, November 8, 2004, p.44, “Ionic Liquids in Organic Synthesis” and Chemical Engineering Progress, September 2004, p. 7, “Ionic Liquids make an Environmental Splash”. In spite of the many advantages that these fluids are predicted to offer, fundamental data on their physical and chemical properties, property measurement methodology, high quality data on reference systems, standards for reporting thermodynamic data, and creation of a comprehensive database infrastructure for ionic liquids are needed to provide US industry with a knowledge base to exploit these solvents.

To achieve these goals 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 (2002-005-1-100) *Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems* (K. N. Marsh – Task Group Chair, M. Frenkel, A. Heintz, J. W. Magee, L. Rebelo, J. Brennecke – members). This lack consistent requirements for the publication of thermodynamic data for ionic liquids, has lead to major barriers to an unambiguous interpretation of the data and a critical evaluation with regard to their uncertainties. This drastically diminishes the value of the reported numerical data for use 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 TRC Group. This IUPAC task group has convened international discussion of the issues by conducting two IUPAC workshops on ionic liquids, held at the 17<sup>th</sup> IUPAC Conference on Chemical Thermodynamics (Rostock, Germany) at the 18<sup>th</sup> IUPAC Conference on Chemical Thermodynamics (Beijing, China) and a 3<sup>rd</sup> Workshop will be convened in Boulder as part of the 19<sup>th</sup> IUPAC Conference on Chemical Thermodynamics in 2006.

Outcomes of the first workshop were reported in a special section of the *Journal of Chemical and Engineering Data* (see reference section). In Beijing, the IUPAC Task Group planned an international round robin study of a reference substance, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, abbreviated as [hmim][Tf<sub>2</sub>N]. Using NIST supplied reagents, 1.5 kg of [hmim][Tf<sub>2</sub>N] was synthesized at the University of Notre Dame and then was shipped to NIST. After drying and chemical characterization at NIST, samples were packaged under an inert atmosphere and were shipped to the participating laboratories. NIST will coordinate round robin studies of density, heat capacity and viscosity, and will participate in measurements of those properties plus thermal conductivity, electrolytic conductivity and industrial gas solubility.



The second IUPAC project (2003-020-2-100) *Ionic Liquids Database* (K. R. Seddon – Task Group Chair, [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 use in synthesis, reviews, reactions and catalysis, manufacturer information, benchmark properties and models, and thermophysical and thermochemical data. During FY2004, the task group met to share a common vision and to divide the data collection effort amongst the participants.

The NIST measurement program continues to provide benchmark physical properties data for selected ionic liquids that are liquid-phase at room temperature and both air and moisture stable. 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 gas 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. A study of the viscosity, cf. Figure, of three hydrophobic ionic liquids and the effect of a dilute water impurity has been completed.

In the future, properties studies will continue with new measurements of thermodynamic density, heat capacity, enthalpy of solution, gas solubility and also expanded transport property measurements - thermal conductivity and electrolytic conductivity, a key electrical characteristic. Structure-property relationships for physical properties will be explored by analyzing evaluated

data in our database. Modifications that support ionic materials will be applied to the TRC Group's Source Database and to the Guided Data Capture application to facilitate the storage and retrieval of ionic liquids property data.

**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. Blohkin, Y. U. Paulechka, A. G. Kabo, M. P. Shymanovich, and J. W. Magee, *J. Chem. Eng. Data* 2004, 49, 453-461.

Physical Property Measurements and a Comprehensive Data Retrieval System for Ionic Liquids. J. W. Magee, G. J. Kabo, and M. Frenkel, *ACS Symposium Series*, 2004 (in press).

The Effect of Dissolved Water on the Viscosities of Hydrophobic Ionic Liquids. J. A. Widegren, A. Laesecke, and J. W. Magee, prepared for *Chem. Comm.*

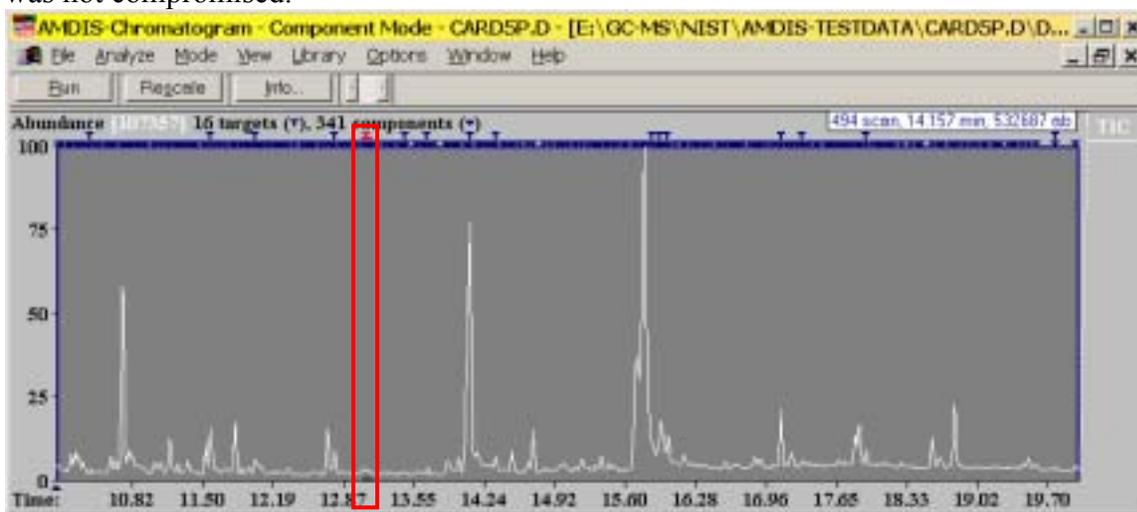
Enthalpy of Solution of Potassium Tetrafluoroborate in Water and in Aqueous Sodium Fluoride. Thermodynamic Properties of the Aqueous Tetrafluoroborate Anion and Potassium Tetrafluoroborate. D. G. Archer, prepared for *J. Chem. Eng. Data*.

**Title:** AMDIS – Automatic Mass spectral Deconvolution and Identification Software

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

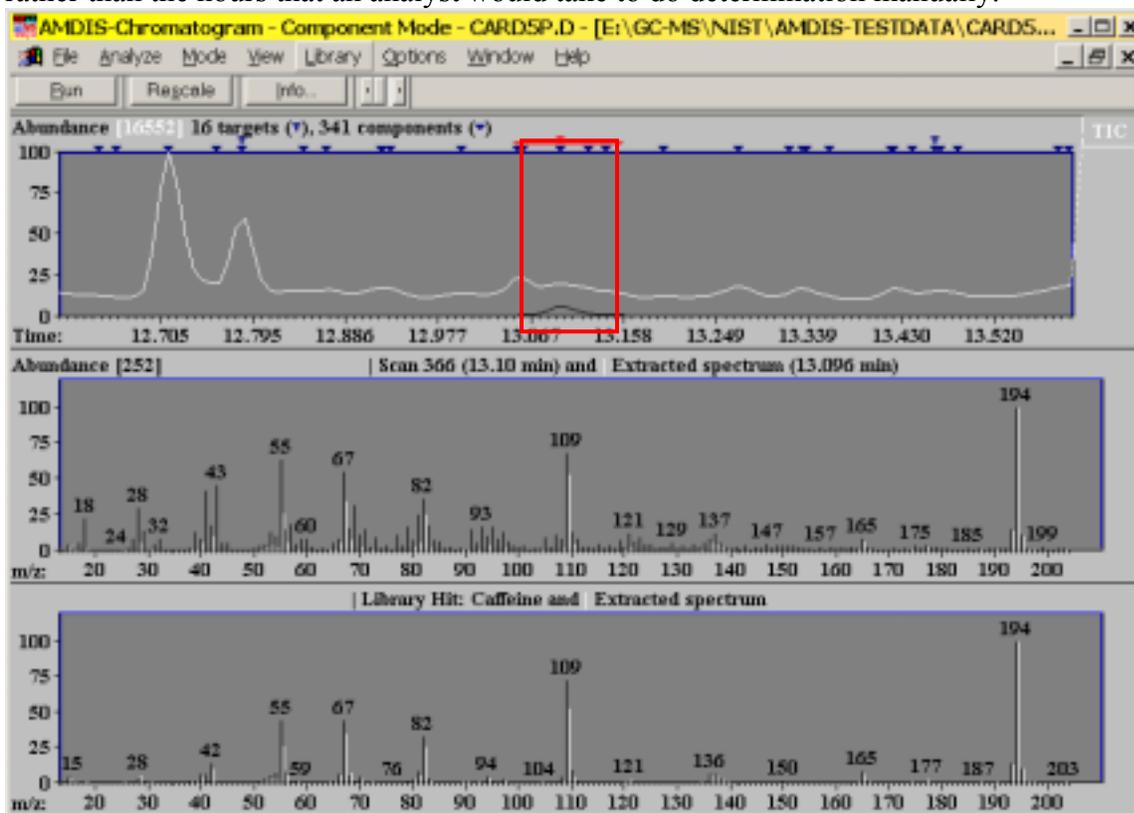
One of the most powerful tools for the analysis of complex mixtures is the combination of the gas chromatograph (GC) to separate the mixture into component parts, followed by the mass spectrometer (MS) to identify each component as it is eluted. This combination GC/MS is the most widely used analytical tool for low concentration analysis for food safety and environmental monitoring. In addition it is widely used in general organic analysis, the development of new flavoring agents, the analysis of fragrances and in many medical applications.

At extremely low concentrations, it can be difficult to extract the signal from the data file due to the very complex background that is present. The time spent by an analyst trying to analyze the data file can be many hours. AMDIS is a solution to this problem. AMDIS was originally developed for detection of chemical weapons in complex mixtures such as might be found in the environment or in chemical process streams. It was designed to work without analyst input as a method of insuring that sensitive business information that could be present in a process stream was not compromised.



The data that AMDIS analyzes, such as that shown above (which is a plot of total MS ion current as a function of elution time from a GC) is not typically the large obvious peaks, rather it is the very small components that are not obvious to the user. In this case, AMDIS extracted 341 distinct components from this data file (information provided by the components label in the figure). Typical software provided with the instruments might have found 50, and the analyst would have still had more work to do to identify the large majority of peaks. AMDIS can of course analyze the larger peaks, but the time spent by the analyst on these is small and in most cases the answer is known before the analysis is done. It is the small components that can change the flavor, can be the toxic residues, can be the indicator of disease. It is in extracting these small components that AMDIS excels. In the above example (which is cardamom oil with very low levels of pesticides) AMDIS found the pesticides, but also found low levels of caffeine. Shown below (in the top window) is a blow up of the region indicated by the red rectangle in the figure above. This is the location of the caffeine found in the data file. In the second window is a mass spectrum from the region (in red box the elution time plot) where the caffeine was found. The signal in this region is very small, as indicated by the full scale abundance in each window.

Here the white lines (displayed next to the extracted peaks) indicate the portion of the data that was used for identification the caffeine. The bottom panel shows the extracted data (again in white) compared to the library spectrum of caffeine. The entire process takes a few minutes rather than the hours that an analyst would take to do determination manually.



In the last year the growth in the use of AMDIS by the organic analytical community has been very strong. One of the most exciting developments has been the incorporation of AMDIS into a new set of tools for automatic analysis developed by Agilent Technologies. The tools have been given the general name of Deconvolution Reporting Software (DRS) and incorporate Agilent Technologies run time locking technology, the NIST search software, and AMDIS in a combined tool to allow users to identify pesticides more confidently and at lower concentrations and with more confidence than had been possible with the Agilent system alone.

The use of AMDIS with the DRS is discussed in three Agilent technical notes:

P. Wylie, M. Szelewski, and C.K. Meng "Comprehensive Pesticide Screening by GC/MSD using Deconvolution Reporting Software", Agilent Technologies publication 5989-1157EN.

<http://www.chem.agilent.com/scripts/LiteraturePDF.asp?iWHID=37589>

M. Szelewski and B. Quimby, "New Tools for Rapid Pesticide Analysis in High Matrix Samples", Agilent Technologies publication 5989-1716EN.

<http://www.chem.agilent.com/scripts/LiteraturePDF.asp?iWHID=38704>

C.P. Sandy, "A Blind Study of Pesticide Residues in Spiked and Unspiked Fruit Extracts Using Deconvolution Reporting Software", Agilent Technologies publication 5989-1654EN.

<http://www.chem.agilent.com/scripts/LiteraturePDF.asp?iWHID=38636>

**Title:** Precision Densimetry for Primary Temperature Metrology

**Author:** *M.O. McLinden*

**Context:** Temperature is among the most important quantities in a vast array of applications, yet recent work at NIST and other NMLs provides strong evidence that the currently accepted temperature scale, known as ITS-90, differs from the true thermodynamic temperature (i.e. is wrong) by about 11 mK at 505 K. This work has been done with acoustic resonators which are the leading alternative to the traditional constant volume gas thermometer for the determination of thermodynamic temperatures. The present work explores a third, independent method and so would provide a consistency check on the acoustic results—important for any redefinition of the temperature scale. The new method is related to gas thermometry but avoids many of the practical difficulties which have led to its virtual abandonment by the NMLs.

With a constant volume gas thermometer, the temperature is derived from the pressure ratio of a fixed quantity of gas at some temperature  $T$  and a reference temperature, usually the SI defining temperature of 273.16 K. With the densimeter, the pressure is held constant, and the density ratio measured at several pressures and extrapolated to zero pressure to yield the temperature:

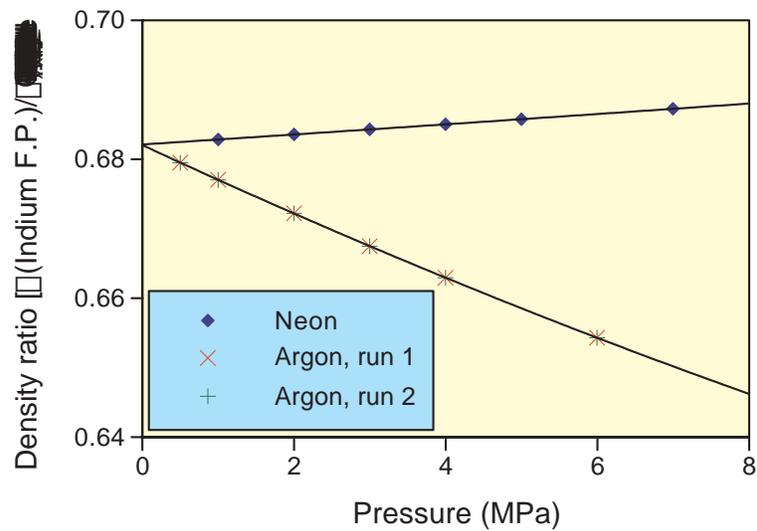
$$\frac{T}{273.16} = \frac{\rho(273.16 \text{ K})}{\rho(T)}$$

**Accomplishments:** This exploratory research has included numerical studies to determine the optimum working gas and the measurement uncertainties needed to obtain a thermometer with an uncertainty of a few thousandths of a kelvin. Argon is the best gas with neon a close second. The most challenging problems would be determining the sinker volumes to a few parts in  $10^6$  over a wide range of temperature and weighing sinkers of a few hundred grams mass with uncertainties of  $10^{-6}$  g. These uncertainties represent 5- to 10-fold improvements over current state-of-the-art densimeters, but they should be achievable with available technology.

This work is enabled by a new apparatus recently put into operation in the Division which is proving to be more accurate than older methods by factor of ten. This densimeter operates on the familiar Archimedes (buoyancy) principle and provides an absolute determination of density. Several twists on the conventional Archimedes experiment—including a differential weighing with two sinkers and a magnetic suspension coupling to separate the balance from the fluid being measured—reduce the uncertainties and allow operation over a wide range of temperature and pressure. For this exploratory project, experiments over the range of 234 K to 505 K with argon, nitrogen, and neon as the working gas have been carried out. Experimental protocols and data analysis have been demonstrated. Systematic errors in the magnetic suspension coupling were found, but, while not small enough to ignore, they were reproducible at the ppm level. While these experiments have demonstrated the feasibility of the method, the present densimeter has uncertainties which are too high for temperature metrology—in particular, the uncertainty in the sinker volumes is large. The method was inverted and used with the measured data to determine, in-situ, the sinker volumes as a function of temperature. This reduced the uncertainties in the sinker volumes, and thus the uncertainties of fluid densities measured with this apparatus, by a factor of four compared to values computed using literature values of thermal expansivity.

**Future Plans:** A manuscript presenting these results is in preparation. Further development of this method into a temperature standard would require a significant effort involving temperature,

pressure, density, length, and mass metrologists, but no insurmountable obstacles are foreseen. We are currently assessing the priority of an independent determination of thermodynamic temperature.



*The ratio of gas densities measured at two temperatures converge to a gas-independent value at zero pressure; this intercept is the ratio of the thermodynamic temperatures.*

**Title:** Second Industrial Fluid Properties Simulation Challenge

**Authors:** *Ray Mountain, Daniel Friend, Russell Johnson, Anne Chaka, Fiona Case, Case Scientific, Dave Frurip, Jonathan Moore, Jim Olson, The Dow Chemical Co., Joseph Golab, BP Amoco Chemical Company, Peter Gordon, ExxonMobil, Petr Kolar, Mitsubishi Chemical Corporation, Rick Ross, 3M Company, Martin Schiller, DuPont*

The Physical and Chemical Properties Division, in collaboration with scientists at The Dow Chemical Company, BP Amoco Chemical Company, Case Scientific, Mitsubishi Chemical Corporation, 3M Company, and DuPont have staffed the organizing committee of the Second Industrial Fluid Properties Simulation Challenge. The Challenge is an opportunity for the molecular simulation community to predict fluid properties that are not available in the open literature. This competition is an open, biannual program that is sponsored by the Computational Molecular Science and Engineering Forum (CoMSEF) of the American Institute of Chemical Engineers (AIChE) and by the Theoretical Subdivision of the American Chemical Society (ACS) Physical Chemistry Division.

The goal of the Second Industrial Fluid Properties Simulation Challenge was to evaluate and benchmark the available molecular simulation methods and force fields on problems that have significant industrial relevance. This process will encourage the continued development of better algorithms, methods, and force fields, while improving the alignment of academic efforts with industrial needs. Molecular simulation has been identified as a promising technology for predicting thermophysical properties in the Vision 2020 Roadmap for the Chemical Industry. The industrial participation within the organizing committee was even stronger than for the first challenge, and the financial contributions from this sector, which were applied largely for prizes for the most successful entrants, were substantial. Further, the number and quality of the entries submitted to the challenge indicated an increased interest in the process, and the contest has attained a truly international stature, with entrants, judges, and organizers from around the globe.

The second Industrial Fluid Properties Simulation Challenge started on 10 September 2003 when the three problems in the challenge were announced at the 2003 Fall ACS meeting. Entrants had until Friday September 10, 2004 to predict vapor pressure and heat of vaporization (problem 1), Henry's law constants (problem 2), and heats of mixing for specific materials and conditions (problem 3). Benchmark values and uncertainties for the specific problems presented were determined by scientists at NIST and Dow Chemicals, through a combination of new experiments and extensive evaluation of available information. These benchmark results were used to evaluate the second challenge entries. There were five entries in problem 1, five entries in problem 2, and two entries in problem 3.

The entries were evaluated in a two-step, double blind process. In the first step, experts in the area of molecular simulation, who were not associated with the organizers nor were entrants, evaluated the overall scientific quality of the entries. Then the entries were ranked by the organizing committee in terms of how accurately the simulation based predictions of fluid properties reproduced the experimental values. The experimental values were not available in the open literature so the entries were predictions.

The results of the competition were announced at a special session of the National Meeting of the AIChE in November 2004. For some of the problems, the entrants were able to produce reasonable predictions for the unknowns, at a level nearly adequate for some industrial purposes. However, for the most challenging problems, especially heats of mixing of the assigned aqueous system, considerable work will be needed before the technique will produce reliable results. More information about the Challenge is found on the website:

<http://www.cstl.nist.gov/FluidSimulationChallenge/>

**Title:** Properties and Processes for Cryogenic Refrigeration

**Authors:** R. Radebaugh, P. Bradley, M. Lewis, (J. Gary and A. O'Gallagher, *Applied and Computational Mathematics Division*)

Cryogenic temperatures are required for many technology areas, including infrared sensors for surveillance and atmospheric studies; superconducting electronics, magnets, and power systems; to create clean vacuums in semiconductor fabrication processes; for liquefaction of industrial gas, and many other existing and potential applications. This project addresses issues associated with cryogenic refrigerators, i.e. cryocoolers, and materials performance that are limiting growth in all these technology areas. Proper measurements need to be established to characterize losses within cryocoolers and models need to be developed to optimize the design of such systems. Material properties at cryogenic temperatures also are needed by industry for the design of cryogenic equipment, but the data are difficult to find and interpret.

In the data and methodology area the layout of our web site has been redesigned to provide clear access to references for the database on cryogenic material properties and to add a graph of each property as a function of temperature between about 4 K and 300 K. The web site is in the process of being updated and we will continue adding the new information in the coming months. An invited book chapter on "Refrigeration for Superconductors" will soon be published in a special IEEE Proceedings on *Electronic and Large Scale Applications of Superconductivity*. This comprehensive article covers the fundamentals of cryogenic refrigeration for both small and large superconducting systems.

In the measurements area, various methods for the calibration of hot-wire anemometers used to measure oscillating flow in the presence of oscillating pressure were compared. Deviations of up to 20% were experienced relative to calibrations under steady flow conditions. We have developed two improved measurements techniques that give good agreement for oscillating flow and used the most accurate technique to measure the complex flow-impedance of an inertance tube. When these results were compared with our transmission line model for the tube the experimental results show about a 15-20% higher resistive component than the model.

As part of a CRADA (with a medical device company) we completed measurements on the performance of a simple pulse tube refrigerator for dermatological pens to about  $-90\text{ }^{\circ}\text{C}$ . Such temperatures are higher than what has normally been the operating temperature of pulse tube refrigerators, but our modeling predicted temperature performance quite well. Using a compressor with a piston-position sensor we were able to characterize the overall system performance for this device. We found that losses within the compressor were higher than expected; again suggesting needs for improvement in modeling.

In the future, we will continue expanding and improving the cryogenic materials database, and developing test methods and improvements in our cryocooler simulation models to address fundamental limitations to the efficiency of cryocooler systems.

**References:**

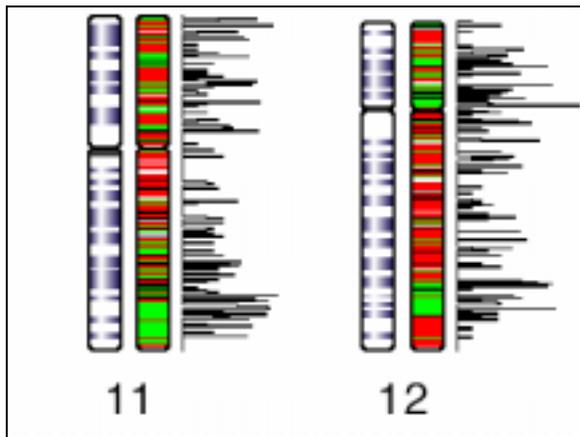
Ray Radebaugh, "The Development and Application of Cryocoolers Since 1985," Proc. Conf. On Cryogenics and Refrigeration (ICCR2003), Hangzhou, China, October, 2003.

P. E. Bradley, R. Radebaugh, R. Baily, and M. Haas "Comparison of Measurements and Models for a Pulse Tube Refrigerator to Cool Cryo-Surgical Probes," Cryocoolers 13, Plenum Press (2004) in press.

**Title:** Mass Spectroscopy in Health and Environmental Science

**Authors:** *Steve Stein, Pedi Neta and Lisa Kilpatrick*

The health of a cell and an organism is reflected by the proteins that it contains. The recent delineation of the human genome coupled with radically new, sensitive methods for biomolecule detection by mass spectrometry, has made it possible to measure a large fraction of these proteins, opening up a range of new, targeted methods for disease detection and prevention. To do this requires the ability to identify massive numbers of proteins, often under low concentration conditions and with poor separation so that any analysis experiment must deal with mixtures of hundreds or thousands of different proteins.



The use of mass spectra for protein identification is illustrated with recent work from the Peptide Atlas project. In this figure, the usual reproduction of the gene (in black and white) is coupled with a stick diagram representing the number of peptides identified by their mass spectra. The colored bands are an attempt to show whether there are more (green) or less (red) peptides than expected. The project has cataloged 225,000 spectra for more than 26,000 proteins. <http://www.peptideatlas.org/>

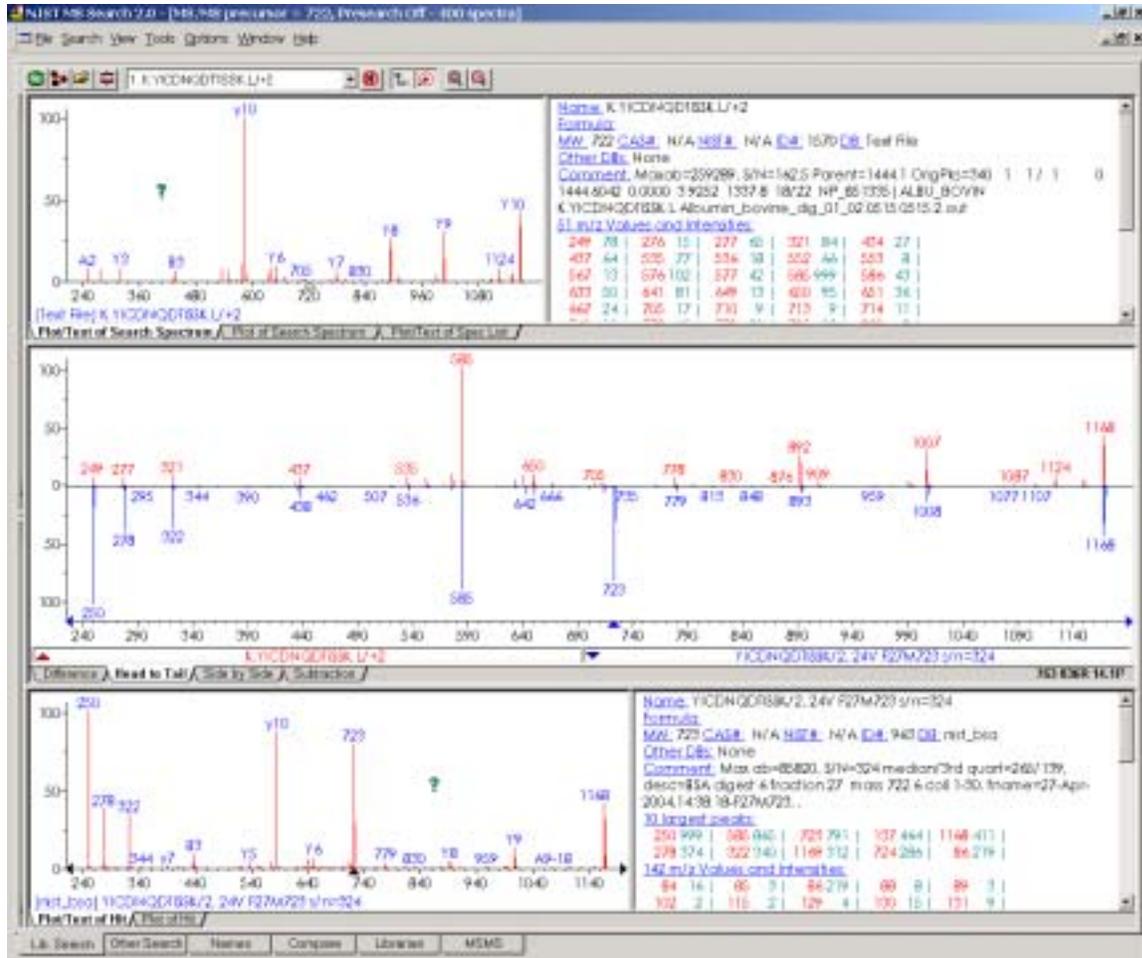
The number of spectra and proteins analyzed has grown dramatically in the last few years, but the little attention has been paid to the basic

reproducibility of peptide mass spectra and to the development of effective means of establishing their accuracy. There has not been any significant measure of the reproducibility of the spectra from the same individual, the reproducibility of the spectra from different individuals and the variations that are mapped to disease states. This information is required in order to establish reliable collections of peptide spectra for use in research and clinical studies,

The mass spectra for these proteins are being generated by liquid chromatography, mass spectrometry and specifically by LC/MS/MS. In these experiments the proteins are chemically broken apart by specific enzymes in well understood and predictable ways. The resulting mixtures are separated by liquid chromatography, the ions are produced by an electrospray apparatus and then the molecular ions are fragmented to give spectra that are characteristic of the specific peptide that has been eluted. The small components, peptides, can be identified and their identity and tied back to the genome. In this way, peptide spectra become fingerprints of the protein and can even establish its particular chemical state (such as post translational modifications). This mechanism has been refined by researchers around the world and the ease with which the experiments can be done is a major part of the explosion in information on the proteome.

The first large scale attempt to determine the variability of these peptide spectra is being done at NIST. In this project we are using thousands of openly available spectra along with some specific measurements made at NIST. By looking at the variability created by changing the apparatus and measurement conditions in well understood ways, we are beginning to understand the best way to establish a measure of confidence in a peptide spectrum and to define new

algorithms to compensate for this variability in identification of the proteins by electrospray LC/MS/MS. An example of the data can be seen on the figure below. Here we use a very slightly modified version of the NIST MS search software to display and search a given protein mass spectra produced from instruments at NIST both the NIST Gaithersburg labs and at the



NIST facilities at the Hollings Marine Laboratory in Charleston, SC with the data for the same protein from other laboratories.

Plans are being developed to build high quality libraries of commonly observed peptides from both directed measurements of selected proteins at NIST and from the vast and growing information available in repositories being developed in the health science community. This will enable a significant increase in reliability of protein identification as well as enable the development of refined methods for using sequence information for matching experimentally determined peptide spectra.

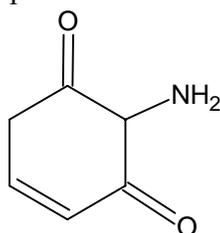
The scale of this work is very large, but the tools developed for use with EI mass spectrometry here at NIST along with tools for the specific problems raised with mass spectra of proteins in other institutions make the effort possible.

**Title:** The IUPAC NIST Chemical Identifier (INChI)

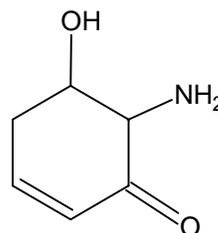
**Authors:** *Dmitrii Tchekhovskoi, Steve Stein, Steve Heller (Guest Researcher)*

The question of clearly identifying a chemical has been present almost since the beginnings of modern chemistry. As the number of chemicals grew, the need for systematic naming produced a number of results. The most widely adopted of these is that of the International Union of Pure and Applied Chemistry (IUPAC). But for many chemicals the resulting names are complex and so common names are still widely used. For most chemists, the graphical structure is the best method for identifying a chemical. The structure provides graphic information that can allow a rapid understanding of the properties of the chemical that a long text name can never provide.

The complications of names even for very simple molecules are illustrated below:



2-amino-4-cyclohexene-1,3-dione



6-amino-5-hydroxy-2-cyclohexen-1-one

The numbering of both the amino group and the double bond changes in these names because of a set of rules for establishing precedence in functional groups. The structures allow the chemist to see the direct connection between the two molecules.

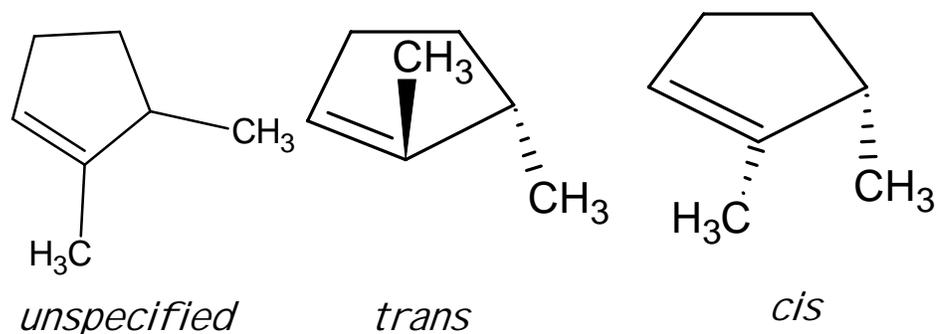
The complication with structures is that they are not easy to order in the sense that names can be ordered by simple alphabetical rules and they do not have an obvious storage method in the computer. Thus there has been a need to develop methods of describing a structure with a simple string that can be used both to order sets and to find a specific compound. Computer storage methods and search algorithms have been able for some time to process structural data but these have not been standardized (there is no agreed upon alphabet for structure representation in computers) and so the various systems for processing the data have not been able to easily communicate.

The need for a uniform and open standard that could be adopted by the entire chemical community generated the NIST/IUPAC project is to develop a chemical identifier – The IUPAC-NIST Chemical Identifier (INChI). The aim of the project was not to create another naming system, or at least not a naming system that would be usable in normal communication. The goal was to create a naming system that would allow computers to uniquely identify a chemical, regardless of how it is drawn based entirely on the connectivity of the molecule – that is what atoms are connected to what other atoms.

To accomplish this a lot of what is normally viewed as “chemical information” was discarded and the molecules were trimmed to the minimum information needed to differentiate one from the other. In addition, a layered approach was developed to deal with some of the more complex issues of chemical structure. For example the two molecules on the right below differ only in that one has the two methyl groups on the same side relative to the plane of the ring (on the right – called *cis*) and the other has the two methyl groups on opposite sides of the ring (in the center – called *trans*). On the left is a diagram that can be used to represent either of the molecules. The left diagram shows only the connectivity and does not specify if the molecule is *cis* or *trans*. The problem encountered prior to INChI is that the data retrieval was often dependent upon the

way the molecule had been drawn. There is often a need to distinguish between the cis and trans, and often a need to search for all possible forms, including cases where the configuration of the molecule was not known or it was known that a mixture was present.

The approach taken in developing INChI is a layered approach. This allowed as much



information as was known to be specified, the search could be performed only on the information known and the search could be stopped with less than full information. Thus in the case above, a search for the cis isomer could be allowed to stop when it matched the connectivity or continued to find only the molecules that matched the geometric isomer.

The methodology of INChI also conforms with the XML standards and the output of the method can be done in XML or in simple text.

The IUPAC NIST Chemical Identifier has been released for beta testing. The current version has been adopted by PubChem at NIH, is an integral part of the Chemical Markup Language (CML) standard and has been integrated by ACD Labs in their widely used commercial drawing program, ChemSketch. In addition INChI will be integrated into the next version of the Chemistry WebBook so that anyone with access to the Internet can make use of this technology.