1988 Technical Activities

December 1988

Jesse Hord, Acting Director
Center for Chemical Technology
National Measurement Laboratory

U.S. Department of Commerce, C. William Verity, Secretary
Ernest Ambler, Acting Under Secretary for Technology
National Institute of Standards and Technology,
Raymond G. Kammer, Acting Director
Technical research activities performed by the Center for Chemical Technology during the Fiscal Year 1988 are summarized herein. These activities include work in the general categories of measurements (standards, processes, and equipment design), properties (thermophysical, thermochemical, and kinetic), and biotechnology (protein engineering and separations). They embody: development and improvement of measurement standards, measurement principles, and calibration services for pressure, temperature, volumetric and mass flow rates, liquid volume and density, humidity, and airspeed; generation (via accurate measurements and advanced predictive models) of reliable reference data for thermophysical, thermochemical, and kinetic properties of pure fluids, fluid mixtures, and solids of industrial and environmental importance; provision of fundamental understanding of protein structure-function and advanced technology for commercial scale separation of proteins; and development of improved correlations, models, and measurement techniques for complex flows, heat and mass transport, mixing, and chemically reacting flows of interest in modern unit operations.

Keywords: biotechnology; calibrations; chemical engineering; chemistry; data; flow; fluid properties; kinetics; measurement standards; pressure; process measurement; sensors; separations; solid properties; temperature; thermochemistry; thermophysics; unit operations.
INTRODUCTION

This document summarizes technical research activities of the Center for Chemical Technology (CCT) during Fiscal Year 1988 (October 1, 1987 through September 30, 1988). This Center is one of four such Centers in the National Measurement Laboratory of the National Institute of Standards and Technology.

The activities of the Center are focused on chemistry and chemical engineering in support of the chemical and related industries (including chemical, petrochemical, biochemical, petroleum, gas, energy, food and drug, paper, etc.). The goal of the Center is to provide the scientific foundation for reliable measurements and data bases that assure equity in domestic and international trade and enable innovation as well as improved design and control of chemical and related processes. The Center's research contributes significantly to the ability of U.S. industry to compete in world markets.

This summary report is presented in six sections, one for each participating Division in the Center: Chemical Thermodynamics, Chemical Kinetics, Chemical Engineering Science, Thermophysics, Chemical Process Metrology, and Temperature and Pressure. It summarizes project activities, cites primary publications, and closes with lists of conferences and workshops hosted, sponsored, or organized by the Center. CARB (Center for Advanced Research in Biotechnology) is a cooperative effort with the University of Maryland and Montgomery County, Maryland, and CARB's Fiscal Year 1988 research activities are included with those of its parent Division, the Chemical Thermodynamics Division.

The Center for Chemical Technology is comprised of Divisions formerly contained in the Center for Chemical Engineering, Center for Chemical Physics, and Center for Basic Standards within the National Bureau of Standards (NBS). During the summer of 1988 the NBS name was also changed to the National Institute of Standards and Technology (NIST).

If additional information is desired on any technical project reported herein, readers should address their inquiries to the appropriately identified project staff via the Center for Chemical Technology, National Institute of Standards and Technology, B256 Physics Building, Gaithersburg, MD 20899.
# TABLE OF CONTENTS

| ABSTRACT | iii |
| INTRODUCTION | iv |

## TECHNICAL ACTIVITIES OF THE
### CHEMICAL THERMODYNAMICS DIVISION

1. Introduction .......................................................... 1  
2. Goal ................................................................. 2  
3. Group Functions ..................................................... 2  
4. Selected Project Summaries ........................................ 3  
5. Publications ........................................................ 17  
6. Conferences .......................................................... 22  

## TECHNICAL ACTIVITIES OF THE
### CHEMICAL KINETICS DIVISION

1. Introduction .......................................................... 23  
2. Goal ................................................................. 23  
3. Group Functions ..................................................... 24  
4. Selected Project Summaries ........................................ 24  
5. Publications ........................................................ 42  

## TECHNICAL ACTIVITIES OF THE
### CHEMICAL ENGINEERING SCIENCE DIVISION

1. Introduction .......................................................... 55  
2. Goal ................................................................. 56  
3. Group Functions ..................................................... 57  
4. Selected Project Summaries ........................................ 58  
5. Publications ........................................................ 67  
6. Conferences .......................................................... 71  

## TECHNICAL ACTIVITIES OF THE
### THERMOPHYSICS DIVISION

1. Introduction .......................................................... 73  
2. Goal ................................................................. 74  
3. Group and Program Functions ..................................... 74  
4. Selected Project Summaries ........................................ 75  
5. Publications ........................................................ 92  
6. Conferences and Workshops ....................................... 100
TECHNICAL ACTIVITIES OF THE
CHEMICAL PROCESS METROLOGY DIVISION

1. Introduction ................................................................. 101
2. Goal .............................................................................. 103
3. Group Functions ............................................................ 103
4. Selected Project Summaries .......................................... 105
5. Publications ................................................................. 122
6. Conferences and Workshops ......................................... 127

TECHNICAL ACTIVITIES OF THE
TEMPERATURE AND PRESSURE DIVISION

1. Introduction ................................................................. 129
2. Goal .............................................................................. 130
3. Group and Program Functions ...................................... 131
4. Selected Project Summaries .......................................... 133
5. Publications ................................................................. 152
6. Conferences and Workshops ......................................... 154
TECHNICAL ACTIVITIES
OF THE
CHEMICAL THERMODYNAMICS DIVISION

S. Abramowitz, Chief

1. INTRODUCTION

The Chemical Thermodynamics Division provides measurement techniques, concepts, and data on the energetics and equilibria of chemical processes. Chemical thermodynamics is used to predict equilibria in chemical reactions, thermodynamic properties of high temperature refractory materials and gases, activities of aqueous solutions used in technologies varying from power generation and electrorefining to biotechnology. This Division develops the models necessary for correlating structure with thermodynamic properties, develops the science of calorimetry in order to obtain precise data from the microwatt to megawatt levels, carries out precise thermodynamic measurements, including those on Standard Reference Materials, develops the measurement capabilities for molecular structure determinations, and critically evaluates thermodynamic data in all phases for the use of industry, government, and academia.

Current emphasis is directed toward the needs of the emerging biotechnology industry. This Division is developing measurement and computational techniques and data bases for the crystalline structure of biomolecular species including enzymes, enzyme-substrate complexes, and DNA species. Efforts are under way to understand, on a molecular level, the relationships between biological function, structure, and energetics. The thermochemistry of generic processes of interest to biochemistry and biotechnology is being studied in order to develop standards and provide key data, to develop quantitative models for the energetics of these processes and estimation schemes of demonstrated reliability for the concomitant thermodynamic properties.

Research needs of four federal agencies and one industrial trade association are being addressed by the Division. Funding is received from the Department of Energy for development of data bases for nuclear waste and for determining chlorine mass balance during the combustion of municipal solid wastes. Combustion calorimetric data and estimation schemes and thermochemical tables are being developed for agencies of the Department of Defense. Computer algorithms and evaluated data bases for aqueous thermodynamics are being developed for the AIChE's Design Institute for Physical Property Data (DIPPR). In addition, the Division collaborates on problems of mutual interest with the Chemical Kinetics, Molecular Spectroscopy, and Thermophysics Divisions, the Center for Analytical Chemistry and the Institute for Materials Science and Engineering. The Division is also active in the ASTM, ANSI, ASME, CODATA, IUPAC and IAEA.
2. **GOAL**

The goal of the Division is to provide state-of-the-art measurement techniques, concepts, data, and data-predictive methods for chemical thermodynamic properties of chemical systems of industrial and environmental importance.

Major objectives of the Chemical Thermodynamics Division include:

- Application of the science of calorimetry to the needs of existing and new technologies through the design of novel calorimeters and the development of improved procedures to obtain enhanced measurement precision and accuracy.

- Development and certification of thermodynamic and physical properties of Standard Reference Materials for the use of existing and emerging technologies.

- Measurement of the thermochemical properties of key chemical species and processes including bioprocesses and phase transitions of aqueous biomolecular species.

- Provision of critically evaluated compilations of the thermodynamic properties of inorganic, organic, and bio-organic compounds in the gaseous, liquid, solid, and aqueous phases.

- Development of estimation schemes for the prediction of thermodynamic properties of organic, inorganic, and bio-organic species in the gaseous, liquid, solid, and aqueous phases.

- Development of measurement and computational methodology for the determination of the structure of biomacromolecular species using the techniques of x-ray diffraction.

- Development of experimental methodologies to determine the relationships between biological function, structure, and energetics of prototypical biological species including proteins and nucleic acids.

3. **GROUP FUNCTIONS**

The research of the Division is performed within three groups.

- **Chemical Thermodynamics Measurements - E.S. Domalski, Group Leader**

This Group develops methodology for the measurement of thermodynamic and
physical properties of organic chemical species, refractory materials, and large samples of heterogeneous materials. The Group develops new experimental techniques and provides key measurements and reliable estimation schemes. Major non-CCT sponsors of this research include the NIST Offices of Standard Reference Materials and Standard Reference Data, the Department of Energy, the Office of Naval Research, and the U.S. Army.

- Biothermodynamics and Biomolecular Structure - S. Abramowitz, Group Leader

This Group develops experimental methodologies and computer algorithms, including computer graphics, for the determination of the structure of biomolecular species (including proteins, enzymes, enzyme-substrate complexes, and DNA species); studies the relationships between biomolecular structure, function, and energetics; and determines the thermodynamic properties of prototypical biochemical species and processes of interest to biochemistry and biotechnology. A unique data base on the preparation, properties, and x-ray structure of biological macromolecules has been established.

- Chemical Thermodynamic Data Centers - M.W. Chase, Group Leader

This Group provides critically evaluated chemical thermodynamic data, estimation schemes, computer models and algorithms for inorganic and organic species in the solid, liquid, gaseous and aqueous phases. It evaluates data of interest to chemical, defense, bioprocessing and energy related technologies. Included in its non-CCT sponsors are the NIST Office of Standard Reference Data, Department of Energy, JANNAF Combustion Subcommittee (DOD) and NASA.

4. SELECTED PROJECT SUMMARIES

Chlorine Mass Balance Studies During the Combustion of RDF

E.S. Domalski, K.L. Churney, T.J. Buckley, A.E. Ledford, Jr.

The sources and fate of chlorine during the combustion of municipal solid waste (MSW) and refuse-derived fuels (RDF) continue to be an important environmental consideration which impacts significantly upon MSW and RDF as alternative fuels. Combustion measurements have been carried out in the multi-kilogram capacity combustor in excess air (25-50% oxygen). The purpose of the research during FY88 has been to determine the distribution of chlorine between the reaction products and to obtain chlorine mass balances for the combustion of RDF. Chlorine analysis of the combustion products showed that 80-85% of the chlorine is transferred to the volatile products as HCl and 10-15% of the chlorine resides in the ash. The addition of lime to the input RDF sample increases the amount of chlorine that is trapped in the ash residue. About 7-9% lime in the input RDF sample will increase the chlorine content in the ash from 10-15% to 45-50%. It has been demonstrated that lime is a very good binding agent for maintaining the integrity and
storability of dense RDF pellets. Combustion of synthetic samples composed of shredded and milled magazine print with 2% sodium chloride (NaCl) or polyvinyl chloride (PVC) showed no significant changes in the distribution of chlorine in the products between the volatile effluent phase and the ash, i.e., 80-85% chlorine in the effluent as HCl and 10-15% in the ash.

Two papers were presented at the 13th National Waste Processing Conference in Philadelphia in May 1988: "Chlorine Mass Balance during the Combustion of RDF" and "Evaluation of Data on Higher Heating Values and Elemental Analysis for RDF."

Combustion measurements have been performed on multi-kilogram samples of coal, mixtures of coal and RDF, and mixtures of coal with RDF and lime. The distribution of chlorine in the products of the mixtures will be compared to the results of similar large scale tests carried out in a boiler at the Argonne National Laboratory. The influence of the addition of catalysts, such as MnO₂, to the lime upon the chlorine distribution in the combustion products will be studied.

Calorimetric experiments were conducted to convert the multi-kilogram capacity combustor into a multi-kilogram capacity aneroid flow calorimeter. ASME will use this information to prepare standard performance test codes for determining the heating value of MSW or RDF. Conversion of the combustor to an aneroid flow calorimeter has provided energy balance closure with uncertainties of about 3%.

High Temperature Heat Capacity Calorimetry

D.A. Ditmars

Relative enthalpy data were obtained on pure tin and zinc in the liquid and solid phases in an isothermal phase-change calorimeter. Values for temperature of fusion, T_fus, and enthalpy of fusion, ΔH_fus, for tin were derived from the data for certification of SRM 2220 (Sn). In the data analysis, a hitherto unpublished approach to deriving the temperature of fusion from non-equilibrium partial-melting data was used. Similar measurements on zinc were started in FY 1988 and are projected for completion in FY 1989. Work is scheduled to measure the high temperature of fusion and enthalpy of fusion of two other candidate SRM's, aluminum and indium, during FY 1989.

Relative enthalpy data were obtained for barium and strontium between room temperature and their fusion temperatures.

A chapter on the design of drop calorimeters was completed and submitted for publication to the Committee of the European Thermophysics Conferences Organization.
Precision Oxygen Bomb Calorimetry

D. Kirklin, E.S. Domalski

Precision bomb calorimetry is the most reliable source of accurate enthalpies of formation. Enthalpies of formation have been determined for strained organic compounds, an organic phosphorus compound, and purine nucleosides. Precise and accurate enthalpies of formation are needed to determine the amount of strain energy in strained organic molecules. The lack of data on organic phosphorus compounds has hindered the development of an estimation scheme for important organic phosphorus compounds. A better understanding of the energetics of important biological species can be attained from the enthalpies of formation of important biological compounds.

Bomb calorimetric measurements have been performed on three important chemical systems. Preliminary measurements have been completed on a sample of 1,4-dimethylidicarboxylate cubane. A preliminary value of the strain energy in the cubane system has been calculated. Measurements have been completed on triphenylphosphate. This is the third compound of a series that has allowed derivation of group energy contribution values to estimate the enthalpy of formation of organic phosphorus compounds containing phenyl groups. Enthalpies of formation for the ribonucleosides of purine, adenine, and guanine have been derived from bomb calorimetric data.

Experimental results have been presented at one international conference, one national conference, and a contractors' conference for chemical defense research. Three papers have been prepared and one paper is in the final editorial stage.

A study of organic phosphorus compounds will be continued with alkyl phosphorus compounds. Advances in bomb calorimetry of organic phosphorus compounds will allow study of energetic biological compounds containing phosphorus. Strain energy studies will be continued on pure organic compounds to provide a better understanding of the energetics of strained organic species.

Bomb Calorimetry for Biotechnology and SRM Development

J.C. Colbert, E.S. Domalski, E. Diaz

The work on the characterization of hexaglycine was completed and included collaborations with NIST scientists B. Coxon and D. VanderHart on the NMR characterization. A manuscript was prepared and submitted for publication.

Modifications were begun on the microbomb calorimeter acquired from Margret Mansson (University of Lund) to incorporate an oscillating quartz thermometer as our temperature measuring device. This apparatus will be used in the study of strained organic species and prototypical biochemical species including peptides.
Preliminary calorimetric measurements were made on DL-leucyl-DL-leucine and L-valyl-L-valine. Work will be ongoing to acquire CO$_2$ recoveries for DL-alanyl-DL-alanine and glycylglycine.

A preliminary check on the internal energy of combustion of a candidate material for renewal of SRM Benzoic Acid 39j was made and a report submitted to OSRM. Measurements were completed and reports submitted to OSRM on SRM 1548 Mixed Diet, SRM 2692 1% Sulfur in Coal, and SRM 1632b Trace Elements in Coal.

**Defining and Designing DNA Sequences that Function as Origins of DNA Replication**

K. McKenney, J. Hoskins (University of Maryland), S. Wickner (National Cancer Institute)

This project is directed toward defining the DNA sequences required for phage P1 DNA replication. The origin of DNA replication for P1 has been restricted to a 310-base-pair fragment of DNA that contains a large number of interesting sequences and structures. These include two 9-base-pair dnaA protein binding sites, five 19-base-pair phage repA protein binding sites, and five GATC sequences that are sites for methylation by the dam methylase enzyme. We have defined the minimal origin of replication by making a family of deletions into the 310-base-pair fragment from each end of the fragment using Bal31 nuclease.

A 2000-base-pair fragment of P1 DNA was cloned and sequenced in M13 vectors. DNA was prepared, and the small 310-base-pair minimal P1 ori DNA was isolated and recloned in both orientations into M13 vectors. Bal31 nuclease digests were made and analyzed and appropriate deletion time points were chosen. The digests were transformed into cells to purify individual molecules (clones), amplified, and characterized by DNA sequence analysis. The DNA sequence defines the exact DNA base of each deletion. A number of deletions into each of the control sites were isolated, and double-stranded DNA molecules were purified and tested for their ability to function as an origin of replication in an in vitro replication assay. We have discovered that there is an absolute requirement for dnaA binding sites and a minimum of two and one half repA DNA binding sites. In addition, the dnaA binding sites have been modified in four ways. First, the spacing between the dnaA sites and the repA sites was increased. Second, the dnaA sites were "turned around" with respect to the repA binding sites. Third, the two dnaA sites were separated relative to each other by rotating the sites one half turn around the DNA helix. Fourth, the dnaA sites were duplicated and placed in a number of orientations and juxtapositions relative to each pair of dnaA sites and relative to the repA sites. Modifications one through three have had little effect on initiation of DNA replication in vitro. Modification four is currently being tested. In addition, the effect of the deletions on the ability of the origin to function in vivo is currently being tested.

This work should precisely define the limits of the P1 origin, provide a framework to compare the DNA structural and functional requirements for initiation of DNA replication, and indicate avenues for further research.

Protein Structure and Function in Regulation of Gene Expression

K. McKenney, M. Kantorow (George Washington University)

This project is aimed at understanding the relationship between structure and function of the cyclic AMP receptor protein, crp, in the regulation of gene expression. It binds to specific DNA sequences in the E. coli chromosome to effect the transcriptional activation of a number of genes involved in sugar utilization. It does not bind specifically to DNA unless it first binds cyclic AMP (cAMP). Thus, crp represents a protein with a "molecular switch" that can be turned on by the addition of cAMP to the pure protein in vitro or to the whole cell in vivo. The structural details of the "molecular switch" mechanism are being explored through the study of crp proteins whose amino acid sequences are altered either by natural mutations or by site directed mutagenesis. A remarkably efficient gene fusion method has been developed to facilitate the construction of a large number of modified crps. The method, which will be of general utility for efficient protein engineering, relies on the precise fusion of the modified crp gene to the lacZ ("blue") gene. The lacZ component of the fusion protein will cleave beta-chloro-indole-galactose to produce a blue plaque. This indicator allows one to easily distinguish the site-directed mutant crps from parental crps based on a change in plaque color on a lawn of bacteria growing on a Petri dish.

In addition to the demonstration of the general utility of the lacZ fusion method to identify and purify site-directed codon substitutions in gene coding sequences, we have begun to explore a new method that has the potential to bypass the requirement of synthetic oligonucleotides for protein engineering. This method uses DNA polymerase to misincorporate bases randomly throughout the crp gene and to subsequently plate the recombinants on indicator plates to identify those mutants that have incorporated stop codons in the crp gene. These are purified and characterized by DNA sequencing. Any one of these mutants can be used as a substrate to revert a specific stop codon to a readthrough codon (and hence an amino acid substitution in the crp protein) by using the misincorporation reaction and isolating the desired substitution as a blue plaque on the indicator plates.

Future plans include the purification of large quantities of the crp protein so that crystallization can be attempted in the absence of cAMP. The structure of crp with bound cAMP is already known, and a determination of the structure without cAMP by x-ray crystallography would yield important information on the structural changes that constitute the "molecular switch." We also intend to study the thermodynamics of folding/unfolding of the natural and modified crps in order to correlate observed variations in DNA binding specificity with the structural changes and thermodynamic stability of the proteins.
Catalytic Domain Analysis of Adenylate Cyclase

P. Reddy

The determination of the catalytic domain of an enzyme is the first step in understanding the enzyme's mechanism of action and specificity at the molecular level. In this project, the methods of molecular biology are used to elucidate the precise protein coding sequence required for catalytic activity of the adenylate cyclase (cya) enzyme. The protein has 95 000 molecular mass and has both a catalytic and a regulatory domain. It catalyzes the synthesis of cyclic AMP from ATP. The gene has been cloned and sequenced. We have recently developed an efficient system to hyperexpress this lethal gene product in cells and purified the protein to near homogeneity.

We have designed and made a three-membered family of synthetic oligonucleotides that facilitate the precise definition of the minimal catalytic domain of cya in this case and any gene in general. The synthetic oligonucleotides have three important components: (1) stop codons (TAA) are in all three reading frames; (2) the recognition sequence CATATG for the restriction endonuclease Ndel precedes and follows the stop codons; and (3) the sequence is self complementary (when denatured and renatured, the single-stranded DNA will form a duplex with blunt ends and hence be clonable). The members of the family differ in the number of bases between the Ndel site and the end of the oligo, either 0, 1, or 2 bases. The gene coding for adenylate cyclase is opened at various sites, the appropriate synthetic oligonucleotide is inserted, and the modified genes are characterized for their ability to produce a functional adenylate cyclase. The inserted stop codon causes premature translation termination and results in a "carboxy end" deletion in the protein. Sites in the adenylate cyclase gene were chosen that result in production of six "carboxy-deleted" proteins of 10, 20, 40, 50, 60, and 80 thousand molecular mass. Protein molecules of 40 k through full length have enzymatic activity. We can also study "amino-deleted" domains of cya by using the Ndel site introduced by the synthetic DNA and deleting the cya gene coding sequences between the natural cya ATG initiation codon (which is preceded by a Ndel site) and the point of insertion of the synthetic DNA.

We are now in the process of constructing the amino-deleted set of molecules which will be studied for activity. Then, we will combine the minimal carboxy end with the minimal amino end and generate this protein in large quantities for biochemical and physical studies.

Thermodynamics of Biochemical Processes

R.N. Goldberg, Y.B. Tewari, K. Fazio, J.C. Ahluwalia (Indian Institute of Technology)

Thermodynamic investigations of the hydrolysis of the disaccharides maltose, isomaltose, gentiobiose, and cellobiose have been completed. These studies involved the use of a high-pressure liquid chromatograph having a pulsed-amperometric detector for the determination of extents of reaction and
equilibrium constants. Microcalorimetry was used for the determination of
enthalpy changes as a function of temperature. The derived thermodynamic
parameters allow one to predict the thermodynamic behavior of these chemical
processes as a function of temperature and have also yielded information on
the relationship of the thermodynamic parameters to the structural features
involved in these disaccharides.

A review of ten major industrial processes utilizing enzyme-catalyzed
reactions has been completed. In it, the thermodynamic data for these
processes are summarized. This information, much of it determined in this
laboratory, can be used to calculate the extents of reaction and the energy
requirements for these processes as functions of operational variables such as
pH, ionic strength, metal-ion concentrations, and temperature.

A data base on the thermodynamics of enzyme-catalyzed reactions has been
initiated by searching the literature, and hard copies of those papers
containing the relevant equilibrium and calorimetric data have been obtained.
Approximately 1500 references have been located to date.

R.N. Goldberg and Y.B. Tewari organized a symposium on "Fundamental
Biochemical Processes" as a part of the 43rd Annual Calorimetry Conference.

Calibration Data for Differential Scanning Calorimetry

F.P. Schwarz

Thermodynamic data for the calibration of differential scanning
calorimeters have been extended up to 75°C by measurements of the unfolding
transition of lysozyme in HCl-glycine buffer. The data cover the temperature
range from 52°C at pH 2 to 75°C at pH 4. This overlaps and extends the data
previously generated for ribonuclease-a in HCl-glycine buffer, which covers
the range from 37°C at pH 2 to 64°C at pH 4. The calorimetric and van't Hoff
enthalpies of lysozyme increase linearly with transition temperature:

\[ \Delta H(\text{van't Hoff in kJ/mol}) = (432.7\pm1.7) + (5.81\pm0.24)(T_m - 337.2) \]

\[ \Delta H(\text{calorimetric in kJ/mol}) = (434.7\pm4.1) + (6.39\pm0.60)(T_m - 337.2) \]

where \( T_m \) is the transition temperature in kelvins. The results are
independent of the commercial source of lysozyme (provided that the solutions
are dialyzed), lysozyme concentration, buffer concentration, and scan rate.

Work is in progress to extend the thermodynamic calibration data up to
80-85°C using the unfolding transition of trypsin inhibitor in HCl-glycine
buffer.
Differential Scanning Calorimetry in Biothermodynamics

F.P. Schwarz, D. Atha (NIST Center for Analytical Chemistry), K. Ingham (American Red Cross)

Differential scanning calorimetry (DSC) measurements have been performed on solutions of fibronectin, a plasma protein responsible for clotting in the blood, in the absence and presence of heparin, an anticlotting agent. This system represents an interesting multidomain protein folding problem with effects due to inhibitor binding. Fibronectin is a glycoprotein composed of two nearly identical polypeptide chains joined together near the C-terminus by a pair of sulfide bonds. Each chain consists of five domains. We have confirmed the presence of two transition peaks, at 62°C and 70°C, in the denaturation of fibronectin, which were recently reported by Niedziadek et al. in Biochemistry 27, 7116 (1988). The high temperature transition peak is only about 25% of the total peak area and had not been identified prior to this recent work. Analysis of our DSC data in terms of cooperativity and specific enthalpy indicates that the first peak corresponds to the partial unfolding of all ten fibronectin domains, while the second peak is due to the additional unfolding of five of the domains.

The polysaccharide heparin can bind to several sites in the fibronectin. The binding of this inhibitor can change the thermodynamics of unfolding depending on the molecular details of the interactions. The DSC analysis of fibronectin with heparin bound shows that the cooperativity in the first transition is reduced from ten to five, while the cooperativity in the second transition remains the same. Thus it appears that the heparin is binding tightly to several domains of the fibronectin and causing them to unfold as one domain. In addition, the first transition temperature increases by 1°C, corresponding to an average binding constant of at least 1.5 X 10^3 mol^-1 at 62°C.

Preliminary experiments have been performed with a shorter segment of heparin which binds to fewer sites on fibronectin, with a correspondingly smaller change in the reduction of cooperativity in the first transition. We are presently doing DSC scans of fragments of fibronectin in the absence and presence of heparin to obtain more insight into the binding mechanism.

Biological Macromolecule Crystallization Data Base

G. Gilliland, D. Bickham (NIST Office of Standard Reference Data)

A crystallization data base, the Biological Macromolecule Crystallization Data base, has been completed and is now ready for distribution. This data base, which is accessed through a PC-based computer program, is intended to provide the examples and physical data required for the formulation of effective crystallization strategies for macromolecules.

The data base has been compiled from the scientific literature and contains crystal data and crystallization conditions for more than 1000 crystal forms of over 600 biological macromolecules. Data for proteins,
protein:protein complexes, nucleic acids, nucleic-acid:nucleic-acid complexes, protein:nucleic-acid complexes, and viruses have been included. The general information catalogued for each macromolecule includes the macromolecule name(s), the molecular mass, the subunit composition, the presence of prosthetic group(s), and the source of the macromolecule. The crystal data include the unit cell parameters, space group, crystal density, crystal habit and size, and diffraction limit and lifetime. The crystallization data consist of the crystallization method, chemical additions to the crystal growth medium, macromolecule concentration, temperature, pH, and growth time. A result of the compilation of the crystallization data was the development of a general strategy for the crystallization of soluble proteins. The strategy employs vapor diffusion experiments with the most frequently used crystallization agents and microdialysis against low ionic strength to maximize the possibility of obtaining crystals. This work has been published in the Journal of Crystal Growth.

The Three-Dimensional Structure of Recombinant Bovine Chymosin

G. Gilliland, E. Winborne (University of Maryland), J. Nachman (National Cancer Institute), A. Wlodawer (National Cancer Institute)

A high-resolution structure for a cloned version of the enzyme chymosin has been determined by x-ray crystallography. Chymosin is the principal enzyme involved in cheese production and was originally prepared from the stomach linings of calves. It is one of the oldest commercial enzymes. The chymosin used in the crystallographic studies was commercially cloned and expressed in escherichia coli. The structure has been determined with a resolution of approximately 0.23 nm and a crystallographic R factor of 0.19.

Chymosin belongs to a class of enzymes called acid proteases and has an active site structure which is very similar to other proteins in that class. Now that the structure has been determined, work is underway to design inhibitors and to model the catalyzed proteolysis in order to learn more about the mechanism and specificity of this important class of enzymes. Chymosin is similar to the enzyme renin, which is found in the blood and plays a role in regulating blood pressure. Thus, an accurate structure for chymosin may have use in drug design studies.

Ab Initio Reaction Field Method Development

W. Stevens, D. Garmer, M. Krauss (NIST Center for Atomic, Molecular, and Optical Physics), H. Basch (Bar Ilan University, Israel)

Final tests have been made of the first version of an ab initio reaction field computer program which will be used for quantum mechanical studies of complex systems. The reaction field approach divides a large molecular complex into an "active" region, which is to be characterized quantum mechanically, and a "spectator" region that may be modeled as an assembly of polarizable molecular fragments that are not directly involved in the
chemistry. How the boundary between the active and spectator regions is chosen depends on the properties or chemistry one wishes to study. We are currently choosing the boundary so that the interactions between fragments in the two regions is of the nonbonded type. The Hamiltonian of the active region consists of the normal Hamiltonian for the active electrons and nuclei, plus an effective Hamiltonian that describes the electrostatic and exchange repulsion interactions between the active and spectator regions, and a perturbation Hamiltonian that accounts for the polarization of the spectator fragments. It is the polarization term that provides the "reaction" of the spectator region to molecular structure changes that occur in the active region.

Tremendous saving of computer time is possible through the reaction field approach, since only the electrons in the active region need to be considered explicitly and the effective Hamiltonian between the active and spectator regions involves only one-electron integrals. Thus, molecular systems too complex for the standard \textit{ab initio} methods can now be studied. We have developed methods for obtaining the parameters for the effective Hamiltonians from \textit{ab initio} calculations on prototypical molecular fragments. These parameters appear to be transferrable at the functional group level, so very complex spectator regions can be modeled by a collection of predetermined "fragment potentials."

We have successfully tested this reaction field approach on a variety of hydrogen-bonded complexes consisting of water, formamide, and glycine. We find that the interaction energy surface for any pair of molecules can be reproduced to within 10-20\% when either of the molecules is replaced by the reaction field Hamiltonian. The largest absolute errors are due to the representation of the electrostatic interaction, which is truncated at octupoles for each expansion center. We have also treated complexes of formamide hydrogen-bonded to two water molecules and find the cooperativity in the hydrogen bonding is predicted very accurately when both water molecules are replaced by reaction field Hamiltonians.

The next steps in the reaction field development include testing the transferability of the parameters in larger molecules such as proteins, testing the validity of the distributed dipole polarizability approximation in interactions of charged species (particularly anions), the addition of dispersion terms to the perturbation Hamiltonian, and the development of integral gradients that are needed for geometry optimization. Long range goals include the development of molecular mechanical methods for modifying the geometric structure in the spectator region in response to changes in the active region. Applications of the reaction field program, in the coming year, will include models of the active site of carbonic anhydrase with different metal substitutions and a model of the active site in aspartyl proteases to determine the electrostatic potential and the relative energetics of proton transfers.
Cluster Model Analysis of Metal Binding Selectivity

W. Stevens, M. Krauss (NIST Center for Atomic, Molecular, and Optical Physics)

The binding of metal cations to proteins is important in both protein function and protein stability. We have used ab initio molecular orbital calculations to develop a model of cation binding energetics and selectivity. We have determined the binding energies of metal cations to octahedral clusters of water, formamide, and formate ligands, and have used these data to analyze Ca\(^{2+}\) binding sites in proteins. The intrinsic energetics of the first coordination shells provide a basis for evaluating the conformational behavior and the selectivity of cation binding. The total enthalpies of solvation and binding were modeled by estimating the Born polarization energy of the bulk relative to the first shell model cluster. Cluster reaction enthalpies were calculated for transferring Mg\(^{2+}\), Ca\(^{2+}\), and Na\(^{+}\) cations from a water cluster to the protein model cluster. Cluster size, determined by the distance between the cation and the closest ligand atoms, was found to strongly affect the binding selectivity between cations of the same and different charges. The selectivity is a function of both steric and electrostatic interactions. The model data have been applied to an analysis of the binding sites in the protein subtilisin BPN.

Thermodynamics of Iron Compounds


Recommended values for the thermodynamic properties of compounds of iron are being prepared for the CODATA Task Group on Thermodynamic Tables, which is preparing a book and data base that will include the thermochemistry and thermal functions for some 40 compounds and analyses of 7 high temperature systems. This effort will combine NIST work with evaluations made in Moscow, Stockholm, Grenoble and Harwell.

Iron. The thermal and volumetric properties of iron have been reassessed over the temperature range 250 K to 2400 K, and from 0.1 to 20 MPa. An accurate representation of the properties has been obtained over these ranges, which cover all metallurgical, but not all geochemical applications. Above 20 MPa and 2400 K, there are insufficient data to establish the melting line, and the few that exist may be inconsistent with the rest of the set.

Magnetite. The heat capacity of Fe\(_3\)O\(_4\), 0 to 325 K, and its entropy at 298.15 K have been reevaluated. The new recommended values for Fe\(_3\)O\(_4\) at 298.15 K are \(S = 148.3\pm2.4\) J/(mol·K), \(C_p = 152.8\pm3.0\) J/(mol·K) and \(H-H(0\ K) = 25.152\pm0.47\) kJ/mol. The values are based on low temperature \(C_p\) measurements in four laboratories on five distinct samples of synthetic Fe\(_3\)O\(_4\). Three of the samples are single crystals; two are polycrystalline. Data for the first three have been published only as graphs, and were obtained from the authors. The considerable differences among the results, e.g., \(S(298.15\ K)\) ranging from 146.1 to 152 J/(mol·K), are attributed to the samples and not to the
measurement process. Previously, S(298.15 K) had been taken as 146.1 ±0.15 J/(mol•K), based on precise measurements on only one of the samples considered here.

The reason for undertaking this study was another discrepancy. An optimization of the Fe/O system, considering both heat capacity and high temperature equilibrium data, predicts S(Fe₃O₄) at 298.15 K = 145.4±0.3 J/(mol•K). Since our study indicates that S is likely to be higher than the previously accepted value, not lower, attention has shifted to the remeasurement of Cₚ from room temperature to 1000 K. (Above 900 K there is a 4 J/(mol•K) difference between two sets of measurements). The experimental studies are being made at the U.S.G.S. and possibly will be made at the University of Michigan.

The Fe/O system (solid). The high temperature equilibrium data on reactions among Fe₂O₃ (hematite), Fe₃O₄ (magnetite) and Fe(1-y)O (wustite) and iron, and the Cₚ and H-H(298.15 K) data have been combined in a thermodynamic optimization of the entire system. A refinement of earlier models has been used. By elimination of data taken using methods now known to have systematic flaws and those sets showing major mismatches, the agreement between data and calculation has been improved by a factor of two. The results of this optimization have been recast into the "sublattice model" formulation that is gaining favor in thermodynamic modeling of high temperature phase diagrams. This recasting will be used in the modeling of the liquid Fe/O system at the Royal Institute of Technology, Stockholm, and later, for ternary systems.

**JANAF Thermochemical Tables**

M.W. Chase, S. Abramowitz

There are two projects in progress which will result in the generation of new and revised entries to the JANAF Thermochemical Tables collection. These activities are sponsored by AFOSR and the JANNAB Combustion Subcommittee. The first project deals with the study of species involving the alkaline earth metals.

The latter study is focused on the characterization of the species involved in combustion processes and is being done in conjunction with the Chemical Kinetics Division. This joint effort is designed to provide thermodynamic and kinetic information on the combustion processes resulting from the burning of propellants. The chemical species currently under study include many of the nitrogen oxides.

With an increasing emphasis on the development of a comprehensive data base on the elements, bibliographic and data files have been created and are being maintained. The aim is to provide a complete annotated bibliographic file which summarizes the thermodynamic information available on many elements. As the bibliographic file is updated, a corresponding data file, containing the experimental data, is updated. These data are available then for immediate comparison with the previously existing data and reanalysis.
The collection and analysis of temperature dependent data require not only a series of calculational computer codes, but also a technique for displaying the information. During the past year, a graphics routine was developed and directed specifically to the display of heat capacity, enthalpy, and vapor pressure data. Based on a commercially available software package, this routine easily permits the display of the experimental results and the evaluated results in a user specified temperature range and a user specified value range. The graph can be displayed on the terminal screen, in standard letter size hard copy, or in enlarged sizes up to 75 cm by 90 cm.

Chemical Abstracts

M.W. Chase, D. Bickham (NIST Office of Standard Reference Data)

During the past year, two of the Division's data bases were installed on the CAS/STN network. The JANAF Thermochemical Tables and the NIST Tables of Chemical Thermodynamic Properties are both available on-line through the Chemical Abstracts CAS/STN network system.

Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes


The Electrolyte Data Center (ELDC) will provide a data base of evaluated equations for thermodynamic properties of aqueous solutions of strong electrolytes. A prototype version was implemented on a mini-computer. The package was transferred to personal computers. Approximately 350 salts at 25°C are now covered by the package. The temperature dependence of the thermodynamic properties is to be added. This will be accomplished, for a large fraction of the salts, using Pitzer's values of the temperature derivatives. More accurate temperature dependencies are being added for the few salts (less than 20) for which such data are available.

Aqueous Thermodynamic Data Base

P. Wang (Guest Researcher), D.B. Neumann, D. Garvin

The development of the Aqueous Thermodynamics Data Base is a cooperative project with the Institute for Chemical Metallurgy (ICM) of Beijing, China. During this year, the package was improved to incorporate the data base of thermodynamic properties from the "NBS Tables of Chemical Thermodynamic Properties." The package was converted in limited form from a mini-computer to personal computers. Extended graphics capabilities were incorporated into the PC version to permit the display of E-pH (Pourbaix) diagrams. Arrangements were made through the NIST/OSRD for the continuation of this cooperative project with ICM.
The Corrosion Data Center at NIST is sponsored in part by the National Association for Corrosion Engineers (NACE). This group has also had a project to develop a personal computer package for E-pH (Pourbaix) diagrams. Under the aegis of the NIST/OSRD, an extensive test and comparison of the two packages were undertaken. A clear need was demonstrated for a single consistent and compatible data base of thermodynamic properties for both packages.

**Dielectric Constant of Water**

P. Wang (Guest Researcher), M.L. Jappas (Guest Researcher), D. Garvin, J.V.H. Sengers (Thermophysics Division)

A comprehensive program was undertaken to re-fit (provide a temperature-density dependent equation) the dielectric constant of pure water. This project arose as a result of new measurements of the dielectric constant of water. In addition, in 1974, the International Association for the Properties of Steam approved a release entitled "International Representation of the Static Dielectric Constant of Water Substance." It was recently found that the low temperature and pressure region of this representation was not sufficiently accurate to represent the derivatives of the dielectric constant with respect to temperature and pressure. Consequently it did not provide adequate values for the Debye-Hückel limiting law, i.e. the limiting behavior of thermodynamic properties of dilute aqueous solutions as a function of ionic strength. The re-fitting, which is near completion, has caused a reanalysis of the internationally accepted equation-of-state for pure water. Publication of the results of this work is expected in early FY89.

**NIST Tables of Chemical Thermodynamic Properties Data Base**

D.B. Neumann, P. Wang (Guest Researcher)

A search and retrieval package for the "NIST Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C1 and C2 Organic Substance in SI Units" has been prepared for personal computers. The package is under test and a paper describing the package has been submitted to the Journal of Chemical Information and Computer Sciences. On completion in the early part of FY89, the package will be made available by the NIST/OSRD.

**Estimation of Thermodynamic Properties of Organic Compounds**

E.S. Domalski, E.D. Hearing

An estimation method for the calculation of enthalpies of formation, heat capacities, and entropies, which consists of a group contribution value approach (developed by S.W. Benson and co-workers for gas phase organic compounds) has been extended to the liquid and solid phases for hydrocarbon compounds at 298.15 K. For consistency, the gas phase group values have been
re-examined as well. A comparison is provided between experimental and calculated values for over 1300 hydrocarbon compounds and will appear in J. Phys. Chem. Ref. Data, No. 4, 1988.

Group values for organic compounds containing the elements carbon, hydrogen, and oxygen (CHO) were developed. Group values for organic compounds containing the elements carbon, hydrogen, and nitrogen (CHN) and carbon, hydrogen, nitrogen, and oxygen (CHNO) will be developed.

An estimation algorithm has been developed to calculate the enthalpy of formation, heat capacity, entropy, entropy of formation, Gibbs energy of formation, and natural logarithm of the equilibrium constant for the formation reaction at 298.15 K for hydrocarbon compounds and CHO compounds. The algorithm and data bases on 1300 hydrocarbons and 1000 CHO compounds are on diskettes. The programs are being made user friendly. Technical notes describing the estimation algorithm, data bases, and estimation procedures will be provided as a package from NIST/OSRD in the near future.

An update of the J. Phys. Chem. Ref. Data Supplement published in 1984 has been prepared and entitled "Heat Capacities and Entropies of Organic Compounds in the Condensed Phase." The update, which includes about 1000 compounds, covers both reported data which were not included in the 1984 JPCRD publication (1881-1982) and data which appeared in the literature since 1982 (1982-1987).

5. PUBLICATIONS


Kirklin, D.R., Enthalpies of combustion of organic phosphorus compounds, Proc. of the 15th Annual National Conference of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers (NOBCChE), Phil., PA (Apr. 4-8, 1988).


In Progress:


Schwarz, F.P., A differential scanning calorimetry study of the interaction of inhibitors with ribonuclease-a at the denaturation temperature, Biochemistry (in press).


6. CONFERENCES

A symposium on Fundamental Biochemical Processes was organized by R.N. Goldberg and Y. Tewari as part of the 43rd Annual Calorimetry Conference, Bartlesville, Oklahoma, August 1988.
1. INTRODUCTION

Chemical kinetics is the discipline which treats the rates of chemical reactions, the factors which influence those rates, and the detailed mechanisms of the reactions. The process of transformation of one chemical compound into another is the very essence of chemistry, and the understanding of chemical reactivity is an important goal of science. Through combustion, energy is generated for electricity, automobiles and aircraft, and other needs of society. Through the medium of chemical reactions, industry takes raw materials and converts them into useful products, including therapeutic drugs. Only through an understanding of chemical rates and reactivity is it possible to comprehend complex environmental phenomena, such as variations in the ozone layer or the formation of acid rain.

The primary focus of the Division's programs is the generation of compilations and data bases of high quality evaluated chemical kinetic data adapted to the needs of various communities involved in work on applications of chemical kinetics; applications include chemical process development, environmental processes, combustion, and analytical chemistry. The work of the Division not only organizes a wide spectrum of kinetic data and thermodynamic properties of reactive intermediates for the industrial and academic communities, but also utilizes this data to extract general reactivity patterns and develop improved predictive theories and models. Major areas of uncertainty revealed in the course of evaluation activities often prompt studies in the experimental programs of the Division. The considerable breadth of ongoing experimental activities in the Division ensures that the expertise and insight needed for good data evaluation is available.

Another significant focus of Division programs is the development of measurement techniques to aid in the detection of reactive intermediate species for kinetic studies, as well as measurement techniques which utilize kinetics for other purposes, such as chemical analysis.

2. GOAL

The Chemical Kinetics Division is responsible for providing high quality evaluated chemical kinetic data for use in designing, controlling, and optimizing a wide variety of chemical processes. Associated experimental programs obtain benchmark data for compilations and data bases, and also provide reliable chemical kinetics data, measurement methods, theoretical
concepts, and models of chemical reactions and reaction mechanisms. The applications include combustion, new chemical feedstocks and technologies, atmospheric and planetary chemistry, effects of ionizing radiation on materials, biotechnology, flue-gas cleanup chemistry, acid rain, and toxic waste incineration. The Division works closely with industry and other government agencies directly and through technical standard-setting groups.

3. GROUP FUNCTIONS

The Chemical Kinetics Division is formally divided into four groups, but there is considerable overlap in the technical interests and even the personnel of the groups, as well as a great deal of variation in the nature of projects within a group. Three of the groups deal with experimental work and are loosely organized according to the type of experimental apparatus used. These are: (1) Ion Kinetics (which includes all the research carried out on three kinetic mass spectrometers); (2) Neutral Kinetics (projects involving kinetics of non-ionized reactants—mainly free radicals are studied using various spectroscopic detection techniques or end-product analysis); and (3) Radiation Chemistry and Kinetics (studies involving both ionized and non-ionized reactants generated by electron accelerators or gamma radiation). Most (but not all) of the expertise in the Division on condensed phase kinetics is found in the last group. The fourth group (Data Centers) includes three data centers, and encompasses all the projects associated with the compilation and evaluation of kinetic data. Scientists from the other three groups are heavily involved in this data-related work.

In this report, data evaluation activities will be presented according to subject along with the discussion of the corresponding experimental programs, even though the data centers are organized into a separate group. A separate discussion will be given of some of the data centers' activities connected with the development of distributable PC versions of the data bases of the Chemical Kinetics Division.

4. SELECTED PROJECT SUMMARIES

NEUTRAL KINETICS GROUP AND RELATED DATA CENTER ACTIVITIES

Combustion Chemistry: Chemical Kinetics Data Center Activities

W. Tsang, J. Herron, W. G. Mallard, R. Levin, F. Westley (Contractor), G. Zumwalt

A long range program in the Division, supported by the Department of Energy and the NIST Office of Standard Reference Data, has the goal of developing a quantitative understanding of the kinetic behavior of organic systems at high temperatures. In particular, work has been aimed at producing a complete data base of self-consistent, evaluated kinetic data for use in modeling hydrocarbon combustion. Recently, with external support from the Department of Defense, new activities have been initiated to expand the combustion data base to include compounds of interest for propellant combustion. The existence of a high quality combustion data base will
eventually make it possible to do away with extensive empirical testing in process design and optimization. The research program includes both the evaluation of thermal rate data important for combustion phenomena and a related program of experimental studies (described immediately below) which are driven by the needs of the data evaluation program.

Data activities on combustion kinetics are a primary activity of the Chemical Kinetics Data Center; W. Tsang is the senior data evaluator. During the past year, the data activities resulted in several important outputs. The archive of unevaluated chemical kinetic data for combustion chemistry (1971-1982) was published in the NSRDS-NBS series. This data base contains rate data on over 1900 elementary reactions. This core data base will be the basis of a more general chemical kinetics data base which will eventually include all kinetic data on gas phase chemical reactions. A supplement covering the literature published in 1983 has also appeared. Relevant publications are being identified and collected from the literature on a continuing basis. The total number of reactions covered in the data base now exceeds 2500.

The evaluation of the data to produce a self-consistent data base has resulted in four publications to date, which present a complete evaluation of data on combustion of the C$_1$-C$_4$ alkanes and methanol. The initial publication dealt with reactions involving methane, and Part 2 contained data on 64 elementary reactions involved in methanol combustion. During the past year, the third installment in this series, dealing with the reactions of propane, n-propyl and isopropyl radicals, was published (Journal of Physical and Chemical Reference Data), and the fourth evaluated compilation, dealing with the reactions of isobutane, isobutyl and t-buty1 radicals, is in press. The evaluated combustion data base now covers about 500 interactions of 35 reactive species.

Evaluation of existing experimental data on propene, allyl radical and 2-butene, carried out during the past year, extends the data base to include the reactions of unsaturated molecules and radicals. Where no experimental data are available, results from related systems have been used to extrapolate and interpolate. Development of these procedures has proved to be an important part of this work, since the multiplicity of possible reaction channels means that experimental data for these systems are generally incomplete. A paper will be published in Combustion and Flame on the methodology developed for extrapolating unimolecular rate data over extended temperature ranges.

New directions for the evaluated combustion data base have been dictated by important recent developments in the fundamental understanding of propellant combustion. At the recommendation of the JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry, and with the support of the Air Force Astronautics Laboratory and the Ballistics Research Laboratory, a program to supply the chemical kinetic data base for the gas phase decomposition of RDX is being initiated. A very important aspect of this data base will be the inclusion of reactions involving nitrogen-containing species such as NO, NO$_2$, HNO, and HCN. This work will complement the data base for hydrocarbon combustion.
Combustion Chemistry: Experimental Studies

W. Tsang, J. Walker (Contractor)

The experimental studies on combustion kinetics, which are carried out in two heated single-pulse shock tubes, have concentrated on unimolecular decompositions and reactions of hydrogen atoms with unsaturated species. There is a paucity of experimental results for these reactions, which are of interest for the data evaluation efforts. During the past year, studies have been published on the hydrogen atom-induced decomposition of phenol, aniline, isobutene, and a variety of chlorobenzenes, and additional work on reactions of o-chlorophenol, acetone, and dimethylether with H-atoms has been completed. The data generated in these studies have provided us with information which permits predictions of the rates and mechanisms of hydrogen attack on many unsaturated systems.

The studies of hydrogen atom reactions with polychlorinated benzenes (supported by the Office of Renewable Resources, DOE) are of importance because of the production of related toxic compounds (dioxins) in the incineration of hazardous wastes. Our approach to the problem treats the introduction of chlorinated species as a perturbation on the overall process of hydrocarbon combustion. The nature and relative amounts of the effluents that are frequently observed can be demonstrated to arise almost entirely from pockets of improperly mixed gases; a pyrolytic mechanism must govern the observed distribution.

A study of the unimolecular decomposition of 3-phenyl-2-butene to give benzyl and propenyl radicals was published. The results lead to a heat of formation for the vinyl C-H bond in propene of 460±8kJ/mol, a value which is very close to that taken for the data evaluations; the results do not support the low values suggested by some recent work. A very interesting consequence of this work is the implication that vinyl radical combination processes are very fast. Finally, in the area of nitro-organic chemistry, recent experimental results demonstrate that the main mode of decomposition of o-nitrotoluene is to form anthranil. This has very interesting implications with respect to the nature of the initiating process in TNT decomposition. Other studies involve the unimolecular decomposition of tetralin, phenotole, butylphenyl ether, n-amylbenzene, diethylether, and 3,3,4,4-tetramethylhexane.

Kinetics of Environmental Processes: Chemical Kinetics Data Center Activities

R.F. Hampson, J. Herron, F. Westley (Contractor)

The Chemical Kinetics Division has a long history of participation in the NASA Upper Atmosphere Research Program, with the Chemical Kinetics Data Center playing a key role. For example, two Division scientists are members of the NASA Panel for Data Evaluation; the Panel provides the definitive recommendations of chemical kinetic and photochemical data to researchers engaged in modeling stratospheric chemistry with an emphasis on ozone perturbations. For this Panel, the Chemical Kinetics Data Center has the primary responsibility for evaluation of the chemical kinetic data for all
reactions involving halogenated species. For each reaction, a recommended rate constant value, with a measure of its reliability and supporting documentation, must be provided. This work is also driven by participation in the IUPAC Commission on Chemical Kinetics, Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Our data center personnel have had primary responsibility for evaluation of the chemical kinetic and photochemical data for reactions of halogenated species, and currently also have primary responsibility for reactions involving nitrogen-containing species and oxygenated species.

These significant contributions to the body of gas-phase reaction kinetic data have an importance beyond the immediate goals stated above. The data also provide a basis for understanding fundamental energy exchange effects in unimolecular decompositions, correlating reactivity with molecular structure, and predicting reactivity in the aqueous/solution phase from gas phase data or vice versa. Further, most of the work is closely related to understanding combustion processes; indeed, some of the experimental results are equally important for both data bases.

**Kinetics of Environmental Processes: Experimental Studies**

M.J. Kurylo, T.J. Wallington (Oxford University, England), P. Dagaut (University of Orleans, France), R. Liu (Chinese Academy of Sciences, China)

In this research program, we carry out chemical kinetic studies which have direct applicability in important areas of atmospheric (as well as combustion) chemistry. The choice of experimental problems is strongly influenced by the needs of the data evaluation effort discussed above. For example, we obtain kinetic results which have applicability to understanding the formation of acid rain in the troposphere, the depletion of ozone in the stratosphere, or the formation of noxious pollutants through the burning of fossil fuels or through the atmospheric oxidation of organic effluents. In such areas, we have recently witnessed an impressive application of fundamental chemical kinetic and photochemical data towards the solution of problems in earth-system science.

In the experimental program, spectroscopic measurement techniques are applied to the detection and characterization of the chemical kinetics of small gas-phase free radicals in a controlled reactive environment. The experiments lead to highly accurate rate constants which are essential input parameters in the numerical modeling of complex chemical systems.

Due to the important role that peroxy radicals play as intermediates in atmospheric and combustion chemistry, recent work has been concerned with determining the ultraviolet spectra and measuring reaction rate constants for peroxy and alkylperoxy radicals. Other work has addressed the reactions of oxygenated organic compounds (alcohols, ketones, ethers, esters, and acids) with OH radicals; these reactions are the most significant oxidative step for these compounds in the earth’s atmosphere, as well as in combustion systems. Despite the increasing atmospheric abundance of such organic oxygenates, due to their emission during industrial or commercial use or their formation as intermediates in organic combustion, until now there have been relatively few
laboratory studies of the reactions with OH. The experiments were performed using the flash photolysis resonance fluorescence technique under conditions which permitted calculations of atmospheric lifetimes for the organics.

Through these studies, a vast body of experimental chemical kinetic gas phase data has been assembled for many molecules not previously addressed. For the first time, a detailed comparative analysis between the gas phase results and those from aqueous/liquid phase studies with the same molecules has been made. This correlation permits fairly accurate estimation of gas-phase rate constants when data exist only in the liquid phase or vice versa. This, in turn, helps to remove many of the measurement uncertainties associated with both gas phase and solution phase studies. Furthermore, such a correlation can potentially extend to the solution phase, the use of semi-empirical predictive techniques developed for gas-phase reactions based on structure-activity relationships such as discussed above.

During the coming year, experiments on the pressure dependent combination of ClO radicals will be initiated. Formation of the (ClO)\(_2\) dimer is considered to be an important process involved in the chemistry associated with the formation of the Antarctic ozone hole. Additional experiments will be conducted during the next several months aimed at determining the atmospheric lifetimes for several of the alternate compounds which are proposed by the chemical industry as replacements for chlorofluorocarbons (CFC's). This work is being coordinated with representatives of the Chemical Manufacturer's Association.

**Planetary Atmospheres**

J. Herron, W. Braun, A. Laufer (DOE), A. Fahr (Contractor)

A related project supported by the NASA involves investigations of the chemistry of radicals which are expected to play an important role in certain carbon-rich atmospheres. During the past year, attention centered on studies of the vinyl radical. The vacuum ultraviolet (VUV) absorption spectrum of the vinyl radical has been identified, making possible time-resolved kinetic studies of this radical. A high-temperature reactor is being constructed for further studies of the kinetics of vinyl radical reactions.

**Mechanisms of Laser Chemical Vapor Deposition: Experimental Studies**

W. Braun, H. Okabe (Contractor), R. Klein (Contractor), I. Price (Guest Researcher)

A newly initiated program to study the mechanisms of laser chemical vapor deposition has recently been funded by the Department of the Army. The work will involve studies of the photodissociation of organometallic compounds of the Group III-V elements. Under this program, work will be carried out to (1) measure the vacuum ultraviolet absorption cross sections for a number of organometallic compounds, (2) design and construct an apparatus to monitor resonance fluorescence-absorption to allow measurement of the time histories of the elements produced in these systems both in their ground and excited electronic states, (3) design and construct an apparatus
for vacuum ultraviolet laser photolysis and kinetic absorption detection to permit measurement of the time histories of various free radical species produced in the photodissociation process, and (4) measure the quantum yields of the major end-products produced in these systems. Such measurements will allow us to better understand the photochemical dissociation process and how the dissociation process is affected by laser wavelength and laser intensity, and how the reactive intermediates are subsequently influenced by the composition of the gas mixture and the reactor temperature. Final objectives will include a specification of the most suitable photolytic methods for producing both uniform and clean metal-atom films possessing optimum semiconductor properties.

Multichannel Ionization Spectroscopy of Transient Free Radicals

J.W. Hudgens, R.D. Johnson, III

Resonance enhanced multiphoton ionization (REMPI) spectroscopy provides new, previously unobtainable, data about the electronic structures of a wide variety of free radicals. The procedures used to observe these spectra also lead to very sensitive and selective schemes for the optical detection of the radicals. The technique can detect reactive intermediates not detected using laser induced fluorescence (LIF), Raman, or CARS spectroscopies. The technique involves tuning an intense pulsed dye laser so that the energy sum of two photons of laser light matches the energy of a Rydberg state of the radical of interest, thereby generating an ion which is detected by mass spectrometry.

This year marked a strong shift in the orientation of the REMPI research toward the study of systems of interest for semiconductor materials processing. REMPI detection schemes were developed for numerous silicon and germanium containing free radicals including SiH₃, SiCl, SiH, GeF, GeCl, and GeH₃, and also for CHF₂, CCl₃, CHFCl, CF₂Cl, and CFCl₂. Other work completed included the investigation of the spectra of cis- and trans-2-butene-1-yl, a pair of methyl substituted allyl radicals.

Substituent Effects and Bond Strengths

S.E. Stein, R. Chen,* M. Suryan,* F.-M. Wang,* A. Fahr (Contractor)

A systematic series of studies on the effects of substituents on carbon-carbon and carbon-oxygen bond strengths has been completed. Studies of substituted anisoles (methoxybenzenes) revealed very strong effects which generally followed known trends for cationic reactions. Ortho hydroxy and amino groups had exceptional bond weakening effects, probably due to a strong hydrogen bond in the product radical. Studies of ethylbenzenes showed much smaller and qualitatively very different effects. These measurements allowed the placement of a substantial amount of existing Electron Spin Resonance (ESR) work of these radicals on an absolute scale. A series of reactions generating substituted methyl radicals placed the stabilities of these ubiquitous radicals on an accurate relative scale for the first time. Trends were similar to, though effects were much larger than, those seen for benzy radicals. This work represents the first extensive series of studies of the
thermodynamic effects of substituents on bond breaking reactions. This work, supported by the Gas Research Institute, uses the very low pressure pyrolysis (VLPP) technique.

*Guest Researchers Sponsored by the Gas Research Institute

**Chemical Theory of Graphite**

S.E. Stein

Reliable methods have been developed for the estimation of H-atom and proton affinities of polycyclic aromatic hydrocarbons of arbitrarily large size. This procedure uses a parameterized form of the Hückel theory which was previously developed as part of this project for the treatment of large polycyclics. H-atom affinities depend primarily on the chemical structures near the site of addition, and for stable molecules differ little from three rings to infinitely extended systems. Proton affinities, on the other hand, depend both on nearby bonding and on the overall molecular size. In the limit of an infinite plane, proton affinities can be increased by as much as 250 kJ/mol by this size effect.

**Chemical Kinetics Data Center: Other Activities**

J. Herron

Sulfur hexafluoride is widely used as a dielectric in the electrical power industry and as a source gas in plasma etching processes. Work in the Chemical Kinetics Data Center on the evaluation of thermochemical and kinetic data for the species involved in the dielectric breakdown of sulfur hexafluoride has been extended to a consideration of the thermal stability of SF₆ and S₂F₁₀. In addition, a joint effort with the Electrosystems Division of NIST has as a goal computer modeling studies of the dielectric breakdown of this compound.

Earlier work on the thermochemistry of S-F compounds has been extended to some of the organic analogues, the sulfoxides and the sulfones. The thermochemistry of these compounds has been reviewed and new group values derived to permit the estimation of thermochemical properties for compounds for which no data exist. The development of the Plasma Chemistry Data Base will continue as a collaborative effort with the Electrosystems Division supported in part by the NIST Office of Standard Reference Data (OSRD). Related experimental work is carried out in the Chemical Kinetics Division by L.W. Sieck.

The compilation of gas-phase chemical kinetic data for all types of thermal gas-phase reactions is an ongoing activity of the Data Center. In order to retrospectively expand the coverage of the chemical kinetics data base to the earlier literature and to include reactants containing atoms such
as chlorine or silicon, which were not included in earlier coverage, data from older articles will be compiled for eventual addition to the database. This work is supported jointly by the NIST OSRD and the DOE.

The Second International Conference on Chemical Kinetics is currently being organized; it is to be held at NIST in July, 1989. Planning and implementation are being carried out using facilities of the Data Center.

ION KINETICS GROUP AND RELATED DATA CENTER ACTIVITIES

The Ion Kinetics Group has undertaken several projects utilizing kinetic mass spectrometry to study the chemical kinetics of ionized species. One important focus of the program is the development of experimental technologies and data bases for use in analytical chemistry laboratories. Projects include the development (under the sponsorship of the Department of Energy) of new analytical schemes for use with chemical ionization mass spectrometry and the standardization of operating conditions for the MS/MS analytical technique. The Division's new Mass Spectrometry Data Center maintains the well known data base of analytical mass spectra which is distributed by the NIST Office of Standard Reference Data.

The NIST/EPA/MSDC Mass Spectral Data Base: Establishment of a New Data Center

S.E. Stein, S.G. Lias, S. Kafafi (Univeristy of Cairo, Egypt), C. Mallard, R. Levin

A large computerized database of analytical mass spectra, originally developed 20 years ago by scientists at the EPA and NIH, has been distributed by the NIST since 1978, under an interagency agreement which assigned to EPA the responsibility for maintenance of the data base. The data base is used in the data systems of analytical mass spectrometers, and therefore, thousands of copies are in use in instruments around the world. The data base, in fact, is one of the most visible and widely known products distributed by NIST.

In 1987, S.E. Stein of the Chemical Kinetics Division developed a PC version of this data base with search software which was released for distribution to the public in September, 1987. During the first year after its release, this PC data base sold more copies than all other data bases distributed by NIST. Because the new PC capability made the data base more conveniently accessible to NIST scientists than it had been before, and because it was desirable for NIST to have better control over the quality of spectra in the data base, the Office of Standard Reference Data decided to bring the primary responsibility for the maintenance, evaluation, and updating of the data base into NIST from EPA. Accordingly, plans were made for a new Data Center, which was established on October 1, 1988.

During 1988, all of the functions necessary to produce a new edition of the Data Base were transferred from EPA to NIST. This involved a transfer of the archive of 77 000 mass spectra from the EPA computer, the translation of the archive to a PC version, the preparation of software to pinpoint errors in spectra, and the adaptation of the EPA "Quality Index" algorithm.
for the evaluation of the spectra. In addition, about 7000 new spectra were added to the archive. Some 2750 of these were obtained in an international exchange with the Soviet Union. This represented the largest increase in the size of the data base for many years and was the result of one year's work of the incipient Data Center.

During the coming year, the effort to improve and enlarge the data base will continue. Activities will include: (a) the location of errors in archival spectra and (depending on the nature of the error) the elimination of the spectrum from the archive or the correction of the error, (b) the examination of replicate spectra which differ from one another in any significant feature, and the choice of the better or best spectrum for inclusion in the data base, (c) the location of CAS Registry Numbers and addition of new spectra, as described above, and (d) the addition of new information on chemical structures. The work will continue on identifying compounds in the archive for which the existing nomenclature is obscure. There are several thousand poorly identified spectra in the archive which may eventually be retrieved for inclusion in the data base, and several thousand additional spectra which contain errors which can be corrected, thereby making the spectra eligible for inclusion.

**Standardization of Tandem Mass Spectrometers**

R.I. Martínez, B. Ganguli (Georgetown University)

The goal of this project is to determine experimentally whether it is feasible to build standard reference data bases for the widely used analytical technique, tandem mass spectrometry or MS/MS. Tandem mass spectrometry, a powerful technique for the analysis of multicomponent mixtures, is used extensively in a variety of applications. There are more than 300 analytical MS/MS instruments worldwide, and there has been much discussion about the need for a generic, instrument-independent data base for use with such instruments. However, a 1984 international interlaboratory comparison demonstrated that spectra taken on different instruments under nominally the same operating conditions could be radically different; a spectrum measured for known species in one such instrument cannot be used to identify those species in a different instrument.

The analysis involves generating the electron mass spectrum of the sample in the first chamber (the first mass analyzer, called \(X_1\)), mass-selecting a particular ion from that spectrum to be sent into a second chamber (an RF-only quadrupole mass filter, \(Q_2\)) where it interacts with a target gas, which brings about "collisionally-activated" dissociation (CAD) of the ion. The CAD spectrum which is observed (in \(Q_3\), the third mass analyzer) thus represents a mass spectrum of a particular ion, usually a fragment ion in the original spectrum. The poor irreproducibility of spectra from one instrument to another can be traced to problems in the complex ion-optics of such instruments, i.e. poor ion containment within \(Q_2\) or fringing fields between \(Q_2\) and \(Q_3\).
Under this project, which has been supported by the Environmental Protection Agency and by the Air Force, it has been established that instrument-independent branching ratios can be measured under single-collision conditions. The data being generated constitute the first elements of an absolute (generic) CAD spectral library. The current focus of the experimental work is: (a) to characterize the structures and dissociation dynamics of polyatomic ions, namely \( \text{C}_2\text{H}_3\text{O}^+ \) ions from a variety of source compounds, by measuring absolute reaction cross sections and branching ratios for CAD; (b) to assess the energy disposal in ion/molecule reactions (1-200 eV collisional energy range); and (c) to study collisional energy exchange in polyatomic molecules and molecular ions.

A second international interlaboratory comparison to assess which instruments are capable of generating instrument-independent spectra is now being directed by Martinez. Participants include instrument manufacturers as well as industrial and academic laboratories. Preliminary analysis of the data indicates that at least 50% of the instruments currently in the field can provide instrument-independent spectra.

Gas-Phase Thermochemical Properties of Ions: Ion Kinetics and Energetics

Data Center

S.G. Lias, R.D. Levin, S. Kafafi (University of Cairo, Egypt)

This Data Center handles other types of mass spectrometric data, namely ionization energies, appearance energies, proton affinities, electron affinities, and related heats of formation of ions. The Data Center also has as a goal the building of a data base of rate constants for ion/molecule reactions.

A major publication of the Data Center, "Gas-phase Ion and Neutral Thermochemistry" by S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, and W.G. Mallard, was published in the Journal of Physical and Chemical Reference Data during the past year. The publication gives evaluated heats of formation of approximately 8000 ions (5700 cations and 2400 anions). This landmark publication is an update of a 1978 NBS publication that sold over 1000 copies.

The 1984 Data Center publication "Evaluated Gas Phase Basicities and Proton Affinities of Molecules; Heats of Formation of Protonated Molecules" was the second most widely cited paper of that year; if 1987 citations are included in the analysis, the paper was the most cited publication. New data on approximately 500 molecules are being evaluated for an update to this publication, to be submitted for publication in 1989.

During FY88, the decision was made to expand Data Center activities to include the thermodynamics of ionic clusters, a field which is experiencing much interest now. Michael Mautner, a recognized expert in this area, has expressed an interest in building an archive of data and evaluating the collected data. The literature search will be started during FY89.
Gas-Phase Thermochemical Properties of Ions: Experimental Studies

L.W. Sieck, S.C. Lias, P. Ausloos, T. Buckley, M. Mautner

The generation of thermochemical information from gas-phase ion/molecule equilibrium constant determinations, and other ion/molecule reaction studies, is a long-standing activity of the kinetic mass spectrometry laboratories. The impetus for the work, which involves both the pulsed high pressure instrument and the ion cyclotron resonance spectrometer, is the ongoing data center activity concerned with ion energetics. The experimental program provides benchmark data needed for the evaluation activities.

During the past year, the ion cyclotron resonance instrument has been upgraded by the addition of a Fourier transform capability, which will provide much more accurate equilibrium constant and rate constant data in future studies.

Work involving the establishment of an absolute gas-phase acidity scale is continuing on the high pressure mass spectrometer. The goal of this extensive project is to define an interlocking ladder of acidity values relative to reference standards; we will investigate equilibria of the type $A^- + BH = AH + B^-$ as a function of temperature. The scale in current use is based on such measurements carried out at a single temperature, i.e., a ladder of free energy changes. In the absence of temperature-dependence data, these are converted to the corresponding ladder of enthalpy changes (acidities are related to the enthalpy changes) by assuming values for the entropy changes. The study in progress provides experimental data for the enthalpy and entropy changes. Analogous work concerned with proton transfer equilibria involving positive ions is also in progress.

Other work involves determinations of the thermochemistry of association ions such as RO$^-$ HSR, RS$^-$ HSR, RS$^-$ HOR, and CH$_3$CO$_2$$^-$ HOH, etc. The objective of this work is to develop correlation lines, for predictive purposes, which relate the dissociation energies to differences in the gas phase acidities of the two molecular partners. Such results have implications for predicting liquid-phase behavior from gas-phase data.

Plasma Etching: Experimental Studies (Reactions in SF$_6$)

L.W. Sieck

A high pressure mass spectrometry study of the reactivity of SF$_6^-$ toward a variety of fluorinated gases and SO$_2$ was completed. Although no reaction of any type was detected with SOF$_2$ and SO$_2$F$_2$, efficient F$^-$ transfer was found in all of the other systems. All of the reactions exhibited a negative temperature coefficient, i.e., the rate constants decrease substantially with increasing temperature. The various reactions studied were used to provide additional information concerning the gas phase F$^-$ affinity scale. The placement of SF$_5$ in the scale indicates that SF$_6^-$ is reactive towards several of the major stable by-products generated during electrical breakdown in SF$_6$. The information derived from these studies was used to generate a computer model which predicts the behavior of oxy-fluoride production during corona
discharge in high pressure SF₆; this in turn will provide new insight into the processes occurring in vapor-insulated high voltage systems and during plasma etching, both of which incorporate SF₆ as the gaseous dielectric. This work is carried out in collaboration with the Electrosystems Division of NIST.

RADIATION CHEMISTRY AND KINETICS GROUP

The Group aims at achieving a fundamental understanding of the effects of radiation on chemical and biochemical systems and utilizing radiation techniques for chemical kinetic measurements. Kinetic studies are carried out by pulse radiolysis (using a field emission source and a Van de Graaff based system with optical detection) and are supplemented with laser flash photolysis experiments. The aim of these studies is to understand the chemistry of reactive intermediates in solution and in biochemical systems. In general, these studies include examination of the mechanisms, rate constants, and equilibrium constants of reactions in a variety of chemical systems such as organic radicals and radical ions, inorganic radicals, and metalloporphyrins, both in aqueous and in nonaqueous solutions. Reactions of radicals with biological materials are also studied by product analysis using HPLC, GC-MS, NMR spectroscopy, and high-resolution mass spectrometry techniques. The scientific emphasis of the work also leads to data evaluation efforts and to published compilations of evaluated data. Accomplishments of the past year are described below.

Solar Energy Conversion and Storage: Metalloporphyrins and Colloidal Catalysts

P. Neta, G.S. Nahor (Hebrew University, Israel), S. Mosseri (Ben Gurion University, Israel) and A. Harriman (Royal Institute, England)

Metalloporphyrins may serve as efficient photosensitizers for solar energy conversion and storage. This is due not only to their broad absorption spectra in the visible light range but also to the rich redox chemistry of the various metalloporphyrins. The general aim of the project is to understand the electron transfer reactions of the various metalloporphyrins in order to be able to apply them in the photochemical decomposition of water to hydrogen and oxygen. The pulse radiolysis experiments are designed to concentrate on individual steps to obtain full understanding of each particular reaction and to develop the conditions for its optimal efficiency in order to incorporate it at a later stage in an overall solar energy conversion system.

In recent years, a research effort of this group has been concerned with the catalyzed oxidation of water to oxygen by oxidized forms of metalloporphyrins. An initial result was the finding that certain metalloporphyrin radical cations react with ruthenium dioxide catalysts in aqueous solutions to yield oxygen. It should be possible to optimize the efficiency of this process through changes in the nature of the catalyst and the porphyrin and changes in the reaction conditions. In the past year colloids of iridium oxides were prepared from chloroiridate ions by radiolysis and by chemical reactions in the presence of polymeric stabilizers. These colloids reacted with metalloporphyrin radical cations more rapidly than the
RuO$_2$ colloids and catalyzed water oxidation to O$_2$. More importantly, oxygen production photosensitized by ZnTSPP was evident at pH>7 with IrO$_x$, as compared with pH>9 with RuO$_2$, indicating a lower overpotential for the IrO$_x$ colloids as compared with that of RuO$_2$.

Other work involves investigating the reduction of water to H$_2$ on the surface of metal colloids. Pulse radiolysis is used to measure the bimolecular rate constants for transfer of an electron from a reducing radical to a colloidal platinum particle in neutral aqueous solutions. Radicals derived from various viologens, pyridines, and benzophenones reacted mostly with diffusion-controlled rates. Only the radicals from a negatively charged benzophenone derivative and p-nitrobenzoate ion reacted more slowly. The rates of reaction depend on the reduction potential of the compound, the charge of the radical, and presumably the self exchange rate. The differences between the various compounds were also expressed in the rate of hydrogen production by these compounds. Future work will explore the possibility of reducing molecules other than water on the surface of metal colloids, for example, reduction of N$_2$ to NH$_3$.

Radiation Chemistry of Organic Systems

P. Neta, S. Mosseri,* Z.B. Alfassi*

Since the redox reactions of some of the porphyrins discussed above have been studied in irradiated acetonitrile or methylene chloride, and since these solvents are often used for electrochemical studies on porphyrins, it appeared worthwhile to devote some attention to the basic radiation chemistry of these important solvents.

Studies on acetonitrile showed that cyanide ions are released upon radiolysis of the neat solvent or of its aqueous solutions, but only in the presence of oxygen. The mechanism involves formation of the acetonitrile radical, 'CH$_2$CN, which reacts with O$_2$ to give the peroxy radical (NCCH$_2$O$_2$'). Subsequent reaction of the peroxy radical results in the release of HCN.

Dichloromethane (DCM) is used as a solvent for radiolytic oxidation of various compounds. Therefore, the nature and the radiolytic yields of the various radicals produced in irradiated DCM were studied. Radiolysis of DCM leads to formation of primary oxidizing radicals and carbon-centered radicals. The latter react with oxygen to yield peroxy radicals. The yields and chemical behavior of these intermediates were studied by pulse radiolysis of DCM solutions containing various solutes: phenols, anilines, dimethoxybenzene, hexamethylenebenzene, cyclohexene, dimethylsulfoxide (DMSO), and zinc tetratolyporphyrin. At low concentrations, some of these solutes were found to be oxidized by two peroxy radicals, CH$_2$ClO$_2$' and CHCl$_2$O$_2$', with different rate constants. At higher concentrations, the solutes react also with the primary radicals (Cl atoms and the radical cations CH$_2$Cl$_2$') with diffusion-controlled rate constants. Cl atoms were found to be very reactive in electron transfer as well as addition and hydrogen abstraction reactions.

*(Ben Gurion University, Israel)
Study of Reactions of Peroxyl Radicals

P. Neta, R.E. Huie, S. Mosseri,* Z.B. Alfassi,* L.V. Shastri**

Peroxyl radicals are important intermediates in radiation chemistry and biology and play a major role whenever an organic radical is formed in the presence of oxygen. Peroxyl radicals are capable of oxidizing porphyrins, and the mechanism appears to involve an inner sphere electron transfer with an intermediate binding of the radical to the metal center. Recently the rates of oxidation of iron porphyrins, as well as of several organic substrates, by the three halogenated peroxyl radicals, CF$_3$O$_2$, CCl$_3$O$_2$, and CBr$_3$O$_2$ were compared. The order of reactivity of these radicals did not follow the usually-observed natural order; the ratios of electron transfer rate constants are generally 5:1:2.

To examine the effects of solvents and of substituents on an authentic outer sphere electron transfer reaction of peroxyl radicals, the reaction with chlorpromazine was chosen as a model. The rate constants for electron transfer were found to depend very strongly on solvent polarity (in various mixtures of water, 2-propanol, and haloalkane) and a good correlation was obtained between log k and the dielectric constant of the solvent mixture. This work was extended to studies with ascorbate, urate, and trolox. Again, the rate of oxidation by peroxyl radicals was found to be dependent on solvent polarity, and a detailed examination of this effect for a variety of radicals is under way. The solvent effect appears to be strong for the strongly oxidizing peroxyl radicals, such as the halogenated alkylperoxyl, but much weaker for the weakly oxidizing nonhalogenated alkylperoxyl, a puzzling result which is being investigated further.

A detailed study of the rate of oxidation of ascorbate by a large number of substituted methylperoxyl radicals was carried out. The absolute rate constants were found to increase as the electron withdrawing capacity of the substituent on the peroxyl group increases. A linear correlation is observed between log k and the Taft substituent constant $\sigma^*$ for a wide variety of substituents. However, the points for peroxyl radicals that contain halogens on the $\alpha$-carbon do not lie on the same line as those for the other substituents. This finding of more than one line for such a linear free energy correlation was corroborated with other compounds and suggests that the details of the electron transfer mechanism to peroxyl radicals vary somewhat with the electron affinity of the radical.

* Ben Gurion University, Israel
**Babah Atomic Research Center, India

Study of Reactions of Inorganic Radicals

R.E. Huie, P. Neta, C.L. Clifton, S. Mosseri,* Z.B. Alfassi*

Small, inorganic free radicals play key roles in many important chemical systems, for example, chemical transformations in atmospheric droplets, flue gas scrubbers, water treatment using either chemical or irradiation
techniques, and in biological systems. The most important inorganic free radical, OH, has been thoroughly studied; far less effort, however, has been expended on the many other free radicals likely to be important in these systems.

The autooxidation of SO₂ in aqueous solutions not only is a primary mechanism for the acidification of precipitation, but it is also critical in the behavior of flue gas scrubbers and in the biological effects of ingested sulfites. We have had an ongoing interest in the mechanism of this reaction, and in the past this project has generated a considerable body of data on the chemical reactions of the radicals SO₂⁻, SO₃⁻, SO₄⁻, and SO₅⁻. During the past year, absorption spectra, self-reaction rate constants, and rate constants for the reactions of SO₂⁻ and SO₃⁻ with O₂ were determined. Both pulse radiolysis and flash photolysis were used in this study; the use of each complements the other. Among the more interesting conclusions is that the self-reaction of the SO₂⁻ radical does not lead directly to dithionite, S₂O₄⁻²⁻, but rather first forms an intermediate which then slowly rearranges to that product. Another study relating to the autooxidation of SO₂ involved the reactivity of HO₂ and O₂⁻ toward HSO₃⁻ and SO₃²⁻. Essentially, O₂⁻ was found to be unreactive and HO₂ was found to react slowly with HSO₃⁻. Of considerable importance in the chemistry of atmospheric oxidation of SO₂, was the observation that both HO₂ and O₂⁻ react rapidly with SO₅⁻. This reaction could serve as a chain-termination reaction, so that atmospheric HO₂ might inhibit rather than initiate the oxidation of SO₂ in droplets.

Other studies of electron transfer reactions of inorganic radicals have been initiated because of the importance of these radicals in many chemical systems, the potential use of these radicals as probes for other systems, and the possibility that a better knowledge of their chemistry might lead to an improved theoretical understanding of electron transfer reactions. In recent years, the redox behavior of a number of inorganic radicals, towards organic and inorganic compounds, was examined, and the data were utilized for determinations of the redox potentials of several organic radicals. Recent additional studies have considered the reactivity of ClO radicals and the reactivity of Cl⁻ atoms uncomplexed with Cl⁻.

Most of the studies on the chemistry of small inorganic radicals have involved their electron transfer reactions. More complete studies on the hydrogen-abstraction reactions of some of these radicals are now being carried out. Rate constants for the reactions of SO₄⁻ with several alkanes, ethers, and alcohols have been measured, and the temperature dependence of the rate constants was determined for reactions with three of the alcohols. As expected, the activation energies correlate well with the bond strengths. The rate constant for the reactions of SO₄⁻ with the primary alcohols was linearly correlated with the number of carbon atoms, up to 1-hexanol. For the higher alcohols, however, the rate constant increases more rapidly than expected. This is the opposite of what has been observed in this Division for the reactions of OH radicals with primary alcohols in the gas phase. The reactivity of NO₃ toward a series of primary alcohols has also been determined, with similar results.

*Ben Gurion University, Israel
Biotechnology: Development of Biochemical Analytical Methodologies

M. Dizdaroglu, E. Gajewski, A.F. Fuciarelli (University of Alberta, Canada)

The work of this project involves the development of new analytical techniques for quantifying the effects of radiation or free radicals on DNA and nucleoprotein. The major thrust of the research has been the development of a methodology which is capable of separating and identifying, in a single analysis, the radiolytic products formed in irradiated solutions of biochemical samples. The methodologies developed in this research provide a tested analytical method for studying the chemical basis of the biological effects of free radical-producing processes such as radiation, and a potential method for the quantification of the process of the cellular repair of DNA base modifications. The techniques are sensitive enough that radiation-induced DNA damage can be studied at radiation doses which are considered to be biologically relevant (<10 Gy). Chemical characterization is achieved by the use of gas chromatography-mass spectrometry (GC-MS) coupled with selected-ion monitoring (SIM). The use of the GS-MS/SIM techniques developed in this work will in the future lead to a clearer understanding of the chemical basis of radiation effects on the nucleus of intact cellular systems and the enzymatic processes of the cellular repair of such modifications.

Within the past year, use of this GC-MS/SIM methodology has led to the first chemical characterization of a radiation-induced DNA lesion (8,5'-cyclo-2'-deoxyguanosine) in irradiated cultured human cells, and base damage in cellular DNA caused by stimulation of human neutrophils. (Neutrophils are a type of inflammatory cell, which play a key role in the defense of the body against infection). Also during this year, the separation and identification of a thymine-tyrosine crosslink (previously identified by this research) has been extended in vitro to thymine crosslinks with other amino acids in model systems, as well as in nucleoprotein. The occurrence of crosslinks between DNA and proteins of nuclear origin in irradiated prokaryotic and eukaryotic cells has been well documented since the mid 1960's, yet the chemical nature of this structure has remained elusive. The chemical structure of the thymine-tyrosine crosslink was conclusively identified as the dimer resulting from the formation of a covalent bond between the methyl group of thymine and the 3-carbon of the aromatic ring of tyrosine. The thymine-tyrosine crosslink has been isolated and conclusively identified in irradiated solutions of calf thymus nucleoprotein. Its formation is proportional to the dose of gamma radiation from 300 to 500 Gy. Crosslinks in nucleoproteins between thymine and other amino acids have also been separated, identified, and quantified. These studies are unique in that they represent the first chemical characterization of radiation-induced DNA-protein crosslinks in nucleoproteins.

The mechanism for the formation of DNA-protein crosslinks between thymine and aliphatic amino acids is thought to involve H-atom abstraction by hydroxyl radicals from aliphatic amino acids followed by addition of the amino acid radical to the C(6)-position of thymine, and subsequent oxidation of the adduct radical. The formation of the crosslink between thymine and tyrosine in nucleohistone is thought to result from H-atom abstraction by hydroxyl radicals from the methyl group of thymine followed by the addition of the resultant thymine radical to the C(3)-position of the tyrosine ring, and the subsequent oxidation of the adduct radical.
Radiation Chemistry and Kinetics Group Data Activities


A compilation of rate constants for reactions of peroxy radicals is being prepared by P. Neta, R.E. Huie, and A.B. Ross.

DATA CENTERS GROUP

S.E. Stein, J. Herron, R. Hampson, W.G. Mallard, F. Westley (Contractor), R.D. Levin, G. Zumwalt, S. Kafafi (University of Cairo, Egypt), W. Tsang, S.G. Lias

Three distinct, but closely interacting data centers are active in the Chemical Kinetics Division. The Chemical Kinetics Data Center is the primary repository of data on rate constants involving uncharged reactants; the Ion Kinetics and Energetics Data Center is concerned with rate data for ion/molecule reactions and data on ionization and appearance energies; and the newly-established NIST Mass Spectrometry Data Center maintains and updates the well-known NIST/EPA/MSDC Mass Spectral Data Base.

As has been made clear in the foregoing discussion, the scientific data evaluation activities are closely tied to the experimental programs and usually involve the same scientists. In this report, the scientific content of the data center activities is discussed under the appropriate group activities to make obvious the close relationships. In this section we describe the other data center activities. In addition to data evaluation activities, the centers provide the computer expertise and other support services for the production of data bases and data compilations by Chemical Kinetics Division scientists.

Very important progress has been made during the past year in the computerization of the Chemical Kinetics Division Data Centers. All the data base activity is now handled exclusively using personal computers. Versatile software has been developed for all aspects of the data center activities including data entry, organization, retrieval, and dissemination. All data entry now is done using software designed specifically for the chemical kinetics data programs, which automatically tests for errors and redundancy and significantly increases the overall efficiency of data entry and organization. Data evaluation efforts also rely on software developed especially for use with Chemical Kinetics Division data bases.

Each of the three Chemical Kinetics Division data centers now has a distributable data base for use on personal computers. The mass spectral data base was first distributed in a PC version in September 1987, and the Chemical Kinetics Data Base and Ion Energetics Data base were recently submitted to the
NIST Office of Standard Reference Data for internal review. A major update of the Mass Spectral Data Base was also recently completed.

These PC-data base products have exceptionally short data retrieval times, made possible because of the extensive use of "index files." The data bases have been carefully designed to be easy to use and attractive to the eye. The Chemical Kinetics and Mass Spectral Data Bases allow the user to generate graphic representations of the data. The formats designed for the data bases greatly simplify the finding of data and the updating of the data bases.

New search options are being developed for searching modes not feasible using a conventional hard copy format. For example, the recent update to the mass spectral data base incorporated innovative new features including the ability to import and export spectra to and from the data base, the capability to call the data base programs from other programs, the ability to compare two sets of graphic data using a split screen, and several sophisticated new search systems.

An exciting development during the past year, which has important implications for the work of other NIST chemical data centers, was the incorporation of information on molecular structure for about 40,000 of the compounds in the mass spectral data base. A computer tape containing "connection tables" for most of these compounds was located, a program was obtained for converting this information to X,Y-coordinates, and it was modified to use on the PC data files so that the molecular structures can be displayed graphically. Considering the high level of chemical complexity of the majority of the compounds in that data base and the inherent difficulty in deducing complex structures from chemical names, the addition of structures to the data base vastly simplifies the use of the data base.

Because structural information was not available for many compounds of interest (for example, for those for which new mass spectra were obtained), approximately 3500 new structures have now been added to the original collection of structural information. During the coming year, additional structures will be added, and structural information will be incorporated into the other Chemical Kinetics Division data bases. This structural information will be used in the future for searching the data bases on the basis of specified chemical structures and for creating smaller, specialized data bases for specific classes of compounds.

Because of the central role that structural information will play in future versions of these (and other chemical data bases generated at NIST), a complete set of "connection tables" will be maintained in the Chemical Kinetics Division Data Centers. Industrial users of the data base enthusiastically support the development of this new resource.

A program for modeling complex chemical reactions, using microcomputers, has been written and made available to the technical community. This program, entitled "acuchem," can be used to predict the temporal profiles of reactant and product species in terms of a set of elementary chemical reactions. The program is being distributed with a companion graphics program. Over 120 copies have been sent to university, government, and industry laboratories.
5. PUBLICATIONS


Braun, W., Dagaut, P. and Cadoff, B.C., Kinetic studies using a highly sensitive microphone detector, (submitted to NIST J. Res.).


Clifton, C.L., Altstein, N. and Huie, R.E., Rate constant for the reaction of NO_2 with sulfur(IV) over the pH range 5.3-13, Environ. Sci. Technol., Vol. 22, p. 586 (1988).


Cui, J.P., He, Y.Z. and Tsang, W., Rate constants for hydrogen atom attack on some chlorinated benzenes, J. Phys. Chem. (in press).


Dizdaroglu, M. and Gajewski, E., Selected-ion mass spectrometry: assays of oxidative damage to DNA, Methods in Enzymology (in press).


Huie, R.E., Clifton, C.L. and Altstein, N., A pulse radiolysis and flash photolysis study of the radicals SO$_2^{\cdot}$, SO$_3^{\cdot}$, SO$_4^{\cdot}$, and SO$_5^{\cdot}$, Radiat. Phys. Chem. (in press).
Huie, R.E., Clifton, C.L., Altstein, N. and Ouellette, P.A., Rate constants for the reactions of O$_2^-$ and HO$_2$ with HSO$_3^-$, SO$_3^{2-}$ and SO$_5^-$, J. Geophys. Res. (submitted).


Johnson, R.D., III and Hudgens, J.W., Two photon resonance enhanced ionization spectra of the 3p\(\pi\) D \(^2\Pi_{\gamma}\) \((v' = 0,1,2) \leftrightarrow X \ ^2\Pi_{\gamma} \ (v'' = 0)\) bands of the CF radical between 355 and 385 nm, J. Phys. Chem., Vol. 91, p. 6189 (1987).


Kurylo, M.J., Wallington, T.J. and Dagaut, P., Gas phase studies of substituted methyl peroxy radicals: the UV absorption spectrum and self-reaction kinetics of CH3OCH2O2; the reaction of CF2C1O2 with Cl Atoms, J. Photochem. Photobiol., A: Chem. (in press)


Martinez, R.I., Dynamical prerequisites for generic CAD spectra, ESL-TR-88-XX, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, FL, 1988 (submitted).


Nahor, G.S., The decay of a zinc porphyrin π-radical cation in the presence of a negative polyelectrolyte and iridium(IV) oxides, a pulse radiolytic study, Langmuir (submitted).


Ozturk, F., Moini, M., Brill, F.W., Eyler, J.R., Buckley, T.J., Lias, S.G. and Ausloos, P.J., Reactions of C_{5}H_{5}^{+} and C_{5}H_{3}^{+} ions with acetylene and diacetylene, J. Phys. Chem. (submitted).


Tsang, W., Unimolecular processes over extended temperature and pressure ranges, Combustion and Flame (in press).

Tsang, W., Mallard W.G. and Herron, J.T., Progress in the development of a chemical kinetic data base for combustion chemistry, Proc. of the 11th CODATA Conference (in press).


Wallington, T.J., Braun, W., Beck, K.M. and Gordon, R.J., Comparison of the optoacoustic and Hg tracer methods for the study of energy-transfer processes in gas mixtures, J. Phys. Chem. (in press).


TECHNICAL ACTIVITIES
OF THE
CHEMICAL ENGINEERING SCIENCE DIVISION

L.L. Sparks, Acting Chief

1. INTRODUCTION

Reliable engineering data and well-documented characterization of process mechanisms form the basis for design and operation of plants and facilities in the chemical, biochemical, petrochemical, petroleum, gas and other processing industries. State-of-the-art information in these areas enables U.S. industry to compete effectively in the world marketplace. Increased emphasis on environmental effects has created a growing need for alternative processes which operate with closer tolerances, emphasize higher yields, and stress internal recycling made possible by separations. The development of accurate process models, for the design of the newer and less conventional plants and to improve conventional ones, requires reliable and well documented process characteristics as well as accurate models for the transport operations and dynamics represented within these industrial processes. Activities needed to address these chemical process industry needs are laboratory determination of elemental process mechanisms and characteristics, theoretically based predictive models for subprocesses involving and using complex fluids and solids, and analysis of the dynamics of engineering systems.

In addition to contributions directly related to process design and operation, and concomitant environmental compatibility, the work of the Division also involves many areas of research done in support of other segments of the private sector and other government agencies. This externally supported research constitutes a major part of the planned effort in achieving the goals of the Division. Problems being addressed are, in general, directed to specific needs of industry, trade associations, NASA, DOD, etc. The research results, however, are applicable to and available for a broad spectrum of scientific, industrial, and academic needs. The data and procedures for accurate and verifiable custody transfer of chemicals and fuels, heat transfer data and models for the National Aerospace Plane, basic studies of combustion in oxidizing atmospheres, data and models for the properties of advanced materials, and refrigeration techniques are examples of basic and applied research being done in support of National programs.

In all areas that relate to the research of the CCT-Gaithersburg Divisions, close collaborative interactions have been developed. There is strong collaboration with the Thermophysics Division to integrate fluid and solids properties with process mechanisms and models, and with the Chemical Process Metrology Division in flow research. These collaborations include several joint projects sponsored by other agencies, and there are ongoing efforts to expand our synergistic efforts in all areas of mutual interest.
One of the primary focuses of research in the Division is on industries related to the rapidly expanding field of biotechnology. For the most part, a thorough and quantitative understanding of the behavior of separation factors and transport mechanisms of these new biochemical systems does not presently exist, especially as these relate to products created by genetic engineering. The complexity of the phenomena involved and the vast array of products and processes encountered preclude the possibility of a purely experimental or correlative approach. The approach must be one which includes experiment, theory, and evaluation so as to yield accurate process and related transport phenomena, and which facilitates the development of generic predictive models that are applicable to a broad range of bio-substances. The theoretical effort will break new ground in understanding separations at the molecular level, phase equilibria involving multiple phases, biological system behavior, heat and mass transfer, and other unit operations. Experimental efforts include membrane separation of amino acids and two-phase aqueous extraction. Other extensions of the state of the art in separation technology are anticipated in the Division’s long-range plans.

The research of the Division addresses scientific issues of national interest in which NIST expertise and its impartial position are critical to an acceptable resolution, as with the highly accurate measurement and modeling of the flow of fluids such as natural gas, selected fluid mixtures, and cryogens. Standard Reference Materials, Standard Test Methods, and Standard Data are developed for selected thermal properties of solid materials of interest to the chemical and related industries. The majority of the effort is directed toward problems of the future. These include, but are not restricted to: (1) transport processes related to the efficient use of gases and liquids such as natural and synthesis gas, methanol, etc., for use as chemical feedstocks and fuels; (2) utilization of more selective separation processes; (3) bioproduct separation/purification technology needed for large scale manufacture of biochemicals; and (4) new techniques for management and disposal of potentially harmful chemical wastes. The strategy is to perform basic research, generic to the science underlying the chemical, biochemical, and petrochemical processing industries, which requires the special role of NIST as an impartial national laboratory excelling in measurements and their interpretation.

2. GOAL

The goal of the Division is to provide: (1) evaluated generic engineering design data and elemental process engineering models, (2) standard measurement procedures and test methods; and (3) predictive techniques, correlations, computer codes, and underlying theories. These are the tools needed by the chemical and related industries to design, control, and develop new manufacturing processes and by other government agencies to continue our Nation’s leadership role in defense, space exploration, and environmental issues.

The primary means of accomplishing this goal is by providing theoretically based modeling and predictive techniques, state-of-the-art measurement techniques, and advanced understanding of elemental process mechanisms. The approach is to conduct research on fundamental concepts, explore new ideas
and phenomena, and develop predictive models in synergism with experimental programs. The endeavors nurture development of new processing techniques, provide accurate models of transport phenomena, and lead to understanding of advanced engineering concepts. An essential corollary of these efforts is the critical evaluation and correlation of experimental measurement techniques which lead to the development of voluntary standard measurement practices and test methods.

3. GROUP FUNCTIONS

The research of the Division is organized into three technical groups: Transport Processes, System Dynamics, and Properties of Solids.

- Transport Processes - S.K. Sikdar, Group Leader

The Transport Processes Group performs experimental, theoretical, and mathematical modeling research in membrane processes, separation of gases and biochemicals, heat transfer, reactor design, and transport processes in microgravity. The products of these activities comprise design data, models, and measurement techniques and methods, which will help chemical and biochemical process industries to operate and control processes more efficiently. Membrane separation research is focused on the purification of acid gases by facilitated transport and on separating species from aqueous and organic solutions. Heat transfer research addresses the need to understand heat transfer properties of supercritical fluid mixtures near the critical point. A major program on biochemical separation is directed toward providing protein separation data and models for two-phase aqueous extraction.

- System Dynamics - J.A. Brennan, Group Leader

The System Dynamics Group performs research to provide data, measurement methodology, and thermodynamic criteria for the optimum application of fundamental principles in physical process operations—including flow metrology at normal and extreme conditions, fluid management in normal and low gravity, and mass and energy changes in multicomponent, multiphase systems—to support programs of other government agencies and industrial trade organizations and to promote efficiency and measurement accuracy in the chemical and related industries.

- Properties of Solids - L.L. Sparks, Group Leader

The experimental and analytical research of the Properties of Solids Group is focused on the thermal properties (thermal conductivity, thermal expansion, and heat capacity) of industrially important solids such as foams, fibers, fiberboards, aggregates, metals, ceramics, composites, and polymers. Programs are in place to study oxidation in the presence of oxygen at high temperatures and pressures, efficiencies and new concepts of cryogenic refrigeration, and concepts and evaluation of reactors to deal with hazardous waste.
4. SELECTED PROJECT SUMMARIES

TRANSPORT PROCESSES GROUP

Membrane Separations with Reversible Chemical Interactions
Data, Mechanisms, and Modeling


The use of membrane systems, as components in the separation of species in gas and liquid streams, is an emerging technology. It offers fundamental advantages in energy efficiency, selectivity, and process integration. Chemical interactions between the separating species and the membrane phase can be used to enhance the selectivity and productivity, as in facilitated transport, or can be a cause of performance decline, as in ultrafiltration. The fundamental characteristics of chemical interactions between solutes and membrane phases are being studied for a number of applications, which include: (1) selective separation of gases by immobilized liquid ion-exchange membranes; (2) gas separations using inorganic membranes; (3) macromolecule separations using ultrafiltration membranes; and, (4) small organic molecule separations using polyelectrolyte and ion-exchange polymers.

The experimental program includes varying the chemical and structural nature of the membrane phase and measuring single and multicomponent permeation rates, sorption equilibria, and transport parameters. Phenomenological modeling is being done to predict transport rates; statistical models are being developed to predict effects of anisotropic pore structures; molecular dynamic models are being investigated to study the effect of phase transitions on separations in single pores, and unit operations models are being developed to investigate integrated membrane performance in system configurations.

GAS SEPARATION BY ION EXCHANGE MEMBRANES: We have successfully developed membranes to selectively separate acid gases from H₂, with greater selectivity than any prior reported systems. Using a gel perfluorosulfonic acid (PFSA) membrane, obtained by swelling in glycerine, which contained the carrier ethylene diamine, we obtained CO₂ selectivity over H₂ in the range 20-40. Using the same membrane, we obtained an H₂S separation factor (over H₂) of 95. Using hindered amines as carriers, we have also achieved selectivity of H₂S over other acid gases, such as CO₂.

AMINO ACIDS ISOLATION/SEPARATION BY ION EXCHANGE MEMBRANES: We have successfully cast a thin (10μm) film from solutions of the PFSA polymer. We have also made a composite membrane by casting a thin PFSA polymer layer on a microporous hydrophilic support. These thin membranes have been tested for high amino acid permeation rates. Potential uses of these membranes in amino acid isolation are being explored.
CHITIN-CHITOSAN MEMBRANES: We have cast this membrane from the chitin-chitosan mixture. Flux data have been collected on selective separation of aliphatic and aromatic amino acids. A gel form of this membrane has been developed by selective crosslinking. The gel membrane has been found to allow permeation of macromolecules.

*University of Calcutta, India

Heat and Mass Transfer to Supercritical Fluid Mixtures
M.C. Jones, G.R. Hardin, S.M. Selim (Colorado School of Mines)

The application of supercritical extraction on an industrial scale requires a knowledge of the transport behavior of mixtures of supercritical solvents and products in equipment for continuous processing such as extraction vessels, heat exchangers, and fractionation columns. In this work, such behavior is studied on a small scale; the approach is to apply fundamental principles of transport mechanisms to precise measurements made on mixtures with well-documented thermophysical properties.

Current emphasis is on measuring heat transfer coefficients accompanying phase disengagement for mixtures of hydrocarbons in carbon dioxide. Such measurements are necessarily made in the vicinity of a critical solution point. To date, binary mixtures of n-decane/CO$_2$ and n-pentane/CO$_2$ have been studied at mixture compositions on both sides of the lower critical solution point. Visual observations show that unique hydrodynamics accompanies phase disengagement and under some conditions gives rise to unexpectedly high heat transfer coefficients. Similar behavior has been observed also in disengagement of analogous liquid-liquid mixtures possessing lower consolute points. A theoretical study of the possible role of thermocapillarity is being undertaken, and an attempt is being made to elucidate the appropriate correlating parameters.

Studies of Free Convection in Porous Media
by Residence Time Distributions
M.C. Jones, R.A. Perkins, J.D. Wolfe

The structure and dynamics of the global flow patterns of free-convective flows in confined porous media is an important area of study for many engineering applications. In this project, funded by the Department of Energy, Office of Basic Energy Sciences, a new experimental approach is being developed based on the principles of residence time distributions. Earlier work has shown these to be sensitive indicators of such flow patterns.

On the experimental side, a new laser-fluorescence fiber optic probe of superior sensitivity has been successfully developed. Arrays of such probes are being used with fluorescent dyes to detect time-resolved flow patterns in fluid-saturated containers filled with uniform glass spheres subject to free-convective flows under precisely controlled conditions. In order to interpret the experimental results, a computer code is under development in
which the progress of a tracer can be followed in three dimensions for convection patterns appropriate to a range of Rayleigh numbers and through-flow Peclet numbers. The role of nonlinear drag and of anisotropic dispersion for both heat and mass transport is being studied. Unsteady flows known to exist at high Rayleigh numbers are of particular interest.

Transient Heat Transfer to Liquid Hydrogen

B. Louie, W.G. Steward (Contractor)

Liquid hydrogen has been identified as an appropriate coolant for new electrical conductor applications, including high-T<sub>C</sub> superconductors. The objective of this program was to determine the time of the onset of nucleate boiling and the heat transfer behavior of liquid hydrogen at times less than 10<sup>-3</sup> s when high heat fluxes were applied. An apparatus using square wave and step power inputs to platinum foil resistors in liquid hydrogen has been built and results have been obtained.

Heat fluxes ranging from 1 to 75 W/cm<sup>2</sup> were applied. In general the temperature at the metal surface increased until the onset of nucleate boiling occurred at approximately 5 x 10<sup>-4</sup> s. At this time the data exhibited a peak in the temperature rise of 8 K, followed by stable, lower temperatures indicative of steady state nucleate boiling. Immediately prior to nucleate boiling, the trend in the data followed classical transient conduction theory. The data at very short times, however, indicated earlier transition periods which have not been reported for other cryogens. This behavior may be explained by a nonuniform temperature distribution within the platinum resistor.

Investigation of Alternative Non-Toxic Heat-Transfer Fluids for Thermal-Control Systems in Spacecraft

P.J. Giarratano, J.F. Welch

NIST has been asked by the NASA Johnson Space Center to evaluate existing pure substances, including commercially marketed heat transfer fluids, for potential use in two-phase thermal-control systems in manned spacecraft. Stringent constraints are imposed on candidate fluids. Among these are nontoxicity, nonflammability, chemical stability, and good thermal performance. Ultimately, the development of a new fluid meeting the above constraints may be required. In view of the likely high cost, long term, and complexity of such a development, an extensive and quantitative evaluation is required to establish the need and/or specifications for the possible development.

The first phase of the NIST work (now complete) was to develop a methodology for the quantitative evaluation of existing substances. A data base of 850 chemical substances have been ranked and sorted according to this methodology.
The second phase of the study will extend the evaluation to commercially available fluids.

**NASA Space Station Fluid Physics/Dynamics Facility Experiment Module**

P.J. Giarratano

NASA is actively pursuing the development of modular, multi-user, experimental facilities for microgravity experiments in the Space Station. NIST has been funded to act in an advisory and consultative role in the development of the specifications for the Fluid Physics module.

The initial effort (now complete) was to provide to the NASA Lewis Research Center preliminary requirements for potential experiments in the field of heat and mass transport in fluids.

The second objective of the work will be to aid NASA in the assessment of their design concept once it is formulated. This will involve interaction with the NASA Lewis Research Center design team and may consist of modification or further definition of the earlier generated requirements.

**Bioseparation by Two-Phase Extraction: Partitioning Methods and Measurements**


The objectives of this activity are to develop and evaluate novel, scalable methods for the separation of biomolecules and bioparticles, to measure and predict the separation of immiscible aqueous phases, and to develop and evaluate novel, scalable methods of phase contacting and demixing. The aqueous two-phase extraction technique is an important alternative to chromatographic methods. The major goal of this program is, therefore, to provide data and understanding necessary for the design of industrial bioseparation processes using this technique.

A number of novel methods have been developed using inexpensive phase-forming polymers as solutes that drive phase separation. Affinity ligands (also inexpensive) that enhance partition coefficients over 10-fold have been developed. These have been applied to the purification of alcohol dehydrogenase from a thermoanaerobe, an enzyme with significant industrial potential. Procedures for measuring multiple partition coefficients using 2-dimensional gel electrophoresis have been developed, and simpler procedures that are not confounded by the presence of phase-forming polymers are being sought. A chromatographic method for the rapid estimation of multiple partition coefficients has been tested.
Modeling Aqueous Two-Phase Systems and Protein Partitioning

H. Cabezas (University of Arizona), D.C. Szlag, J. Evans

Parallel to the experimental efforts directed toward developing methods and partitioning data bases on polymers and protein systems, we have attempted to develop mathematical models capable of predicting phase diagrams and protein partition in two-phase systems. We have succeeded in exploiting T.L. Hill's formalism to derive equations which correctly predict experimental phase-diagram data based on known properties of polyethylene glycol (PEG) and dextran. Phase separation in PEG-salt systems and partition coefficients of proteins are under continuing investigation. Laboratory measurements of solution parameters are being performed in connection with theoretical studies as a means of testing predictions.

Aqueous Two-Phase Contacting in Spray Columns

R. Rao (University of Bombay, India), S.K. Sikdar, D.C. Szlag

Mass transfer and demixing rates are important practical variables in two-phase extraction, and pragmatic goals include the maximization of both. We introduced the concept of dispersing one phase into the other in a spray column and collected mass transfer and hold-up data on a two-meter column. Contacting in a spray column obviates the need of a centrifuge to disengage the phases. We continue to study drop dynamics, and the effect of multiple stage operation on protein recovery.

It has been found that demixing rates can be enhanced substantially by allowing phase separation to occur in a constant electric field.

Electrokinetic Separation Methods

P.W. Todd, R. Hertz, R. Rao (University of Bombay, India)

Free electrophoresis is another important alternative to chromatographic methods, as it holds the potential to purify sample streams without precipitation or adsorption. As in the case of two-phase extraction, it is also applicable to bioparticles.

Cell separation: Studies on density-gradient and re-orienting density gradient electrophoresis of bioparticles and cells have been initiated.

Isoelectric focusing: The replacement of ampholytes with buffers in recycling isoelectric focusing, a process invented by M. Bier, can significantly enhance biomolecular activity and reduce costs at the pilot-plant scale. Experiments using borate and citrate buffers indicate that it should be possible to use these buffers for recycling isoelectric focusing in pilot-plant operations and that the effectiveness of the method could be enhanced by algorithmic control. Two-dimensional gel electrophoresis is a suitable analytical method for analyzing results.
Single Crystal Growth by Osmotic Dewatering

S.K. Sikdar, P.W. Todd, C. Walker, D. Lund

We have developed a generic method for growing single crystals using the technique of osmotic dewatering, and tested the method by growing large crystals of triglycine sulfate and lysozyme. In this method, a solution of the candidate substance in a reverse osmosis (RO) membrane container is contacted with an outer solution of a salt (such as NaCl or (NH₄)₂SO₄). Slow but controllable dewatering takes place because of the difference in osmotic pressures between the solutions. The nucleation point is approached slowly and nucleation and subsequent growth take place at low supersaturation, thus providing good single crystals. X-ray studies are being planned for these crystals to ascertain quality. The method also has potential for inorganic crystals.

SYSTEM DYNAMICS GROUP

Slush Hydrogen Production and Characterization

R.O. Voth, P.R. Ludtke, D.E. Daney, J.D. Siegwarth, V.D. Arp, P. Storch

Future high performance aircraft will require high performance fuels. One candidate for fueling the National Aerospace Plane is a mixture of solid and liquid (slush) hydrogen. At the present time, two production methods are being investigated. One method uses an auger arrangement to scrape the frozen hydrogen off a refrigerated surface, and the other method uses a reduced pressure freeze-thaw procedure. Both production methods produce slush that can be stored for extended periods and has acceptable flow characteristics. In addition, the auger method of production includes a study of the effect of auger size so that laboratory tests can be scaled to full production requirements.

Optimum production, storage, and transfer of slush will be critical to the successful use of this fuel. Therefore, experimental and analytical studies will be conducted to determine the most efficient production methodology. Coupled with these studies will be an investigation of the instrumentation required for measuring pressure, temperature, flow rate, density, and mass quality.

Metering of Natural Gas and Cryogenic Liquids

J.A. Brennan, S.E. McFaddin, C.F. Sindt, R.R. Wilson, J.D. Siegwarth

At the core of this work is a flow facility capable of providing accurate and precise mass-based data for flowing cryogenic liquids and ambient temperature gas. There are three projects currently under study. The first is designed to provide substantial improvement in the metering of natural gas by means of orifice and turbine type flowmeters. This multi-year
program, funded by the Gas Research Institute, includes an extensive series of measurements on 7.6 cm and 10.2 cm diameter orifice meters. Also under investigation are swirl phenomena, flow conditioning concepts, and pipe roughness effects. The work in Boulder on gas flow is closely coordinated with similar work on water flow in the Chemical Process Metrology Division. The second area of flow research utilizes the flow facility to evaluate new measurement techniques and to perform special tests on meters to provide measurement traceability to NIST. These tests are performed with liquid nitrogen. The third area of flow research is concerned with high velocity flows (over 50 m/s) and utilizes water from a local hydroelectric plant since such velocities are well beyond the range available in a laboratory. The purpose of this work is to assist NASA in developing reliable flowmeters for the Space Shuttle Propulsion System.

Process Thermodynamics
V.D. Arp, D.E. Daney, P.R. Ludtke, J.D. Siegwarth, R.O. Voth

This work is designed to provide engineering, principally cryogenic engineering, expertise to other government agencies to solve or provide the basis for solution of a variety of problems. Current research includes (1) reviewing and evaluating thermodynamic modeling of cryogenic systems in support of high energy physics experiments at the Los Alamos National Laboratory, and (2) performing experiments and analyzing the fluid mechanics and thermodynamics on the transfer and storage of large quantities of fluids such as liquid hydrogen, oxygen, and superfluid helium with application to fluid management in low gravity environments. The work in area (1) is supported by the Department of Energy, and in area (2) by the National Aeronautics and Space Administration.

PROPERTIES OF SOLIDS GROUP

Thermal Properties of Advanced Materials
J.B. Filla, D.L. Rule, D.R. Smith, L.L. Sparks

Ceramics, polymers, and composites which combine two or more advanced materials continue to be developed as replacements for metals and plastics in electronic components, high performance engines, and structures where strength, weight, and thermal tolerance are critical. Research on these materials has traditionally been in the areas of processing and mechanical properties. Thermal properties must be known for advanced applications now being contemplated, or, in some cases, actually incorporated in working designs. The properties in question include thermal conductivity, thermal expansion, heat capacity, and thermal diffusivity.

Five Group projects, intended to address these needs, were active in FY88. They included (1) continued development of a steady-state thermal conductivity apparatus to allow ceramics and ceramic composites to be studied to 1270 K, (2) operation of a guarded-hot-plate thermal conductivity
apparatus to allow ceramic fiber insulation to be studied to 800 K, (3) modification of an existing optical dilatometer, (4) operation of an apparatus to study the steady-state conductivity of composites at low temperatures, and (5) operation of a cut-bar apparatus to study the conductivity of ceramics at moderate temperatures.

**Cryocooler Studies**

R. Radebaugh, I. Vazquez, P. Storch, K. McDermott, S. Geschwenter, J. Gary,* J. Zimmerman†

As part of an ongoing NASA/Ames contract, a second pulse tube refrigerator was built using a small compressor of 25 cm³ displacement. Optimization studies for that system were completed, which led to a low temperature of 67 K with 2 W refrigeration at 80 K. The optimum pulse tube size was found to agree well with the theoretical model that was developed as part of this work. Work on a two-stage pulse tube refrigerator began in FY88. So far a temperature of 41 K has been reached, although optimization studies of the system have just begun. The advantage of the pulse tube refrigerator is that it is relatively efficient and it has no moving parts at low temperatures. It has great potential for use in cooling infrared sensors in satellite applications.

Under a Wright-Patterson Air Force Base contract, several regenerator materials have been studied in the 8-25 K temperature range. These regenerators would be used in the lowest temperature stage of Stirling or Vuilleumier cycle cryocoolers for cooling infrared sensors. The regenerators were tested under realistic operating conditions. In most cases, the materials were in the form of powder with a particle size of 227 μm. The materials studied cover a wide range of heat capacities. They include brass, Pb + 5% Sb, GdRh, and Nd. An interesting result found from these studies is that the low heat capacity materials perform reasonably well as regenerators because of the contribution of the void volume gas to the overall heat capacity.

The use of adsorbers as compressors for gas refrigeration systems permits the elimination of a moving part. As part of a Kirtland AFB program to develop these compressors for Joule-Thomson refrigerators, we are providing the fundamental data on adsorption isotherms. Measurements in FY88 include N₂ gas on 4 different carbon adsorbers. A new adsorption cell was also constructed for measurements with methane, ethane, and carbon monoxide up to a temperature of 300°C. Measurements of the thermal conductivity of carbon with helium gas adsorbed was measured in the 6-300 K temperature range. We discovered a new effect in which the adsorbed film transports a very large heat flow for temperatures below about 50 K and film thickness greater than about 0.5 monolayers. The anomalous heat transport is much less with N₂ gas.

*NIST Center for Applied Mathematics
†Contractor

65
Metal Oxidation and Ignition/Combustion in High Pressure Oxygen

J.W. Bransford, J.A. Hurley, K.M. McDermott

A program to study the oxidation rate and ignition/combustion characteristics of a number of metals and alloys in oxygen, at pressures up to 34 MPa, has been undertaken for NASA. This program is not only of interest to NASA and the aerospace industry, but also to producers, transporters, and users of liquid and gaseous oxygen.

In one experiment, we heat the top surface of a cylindrical sample by a specially tuned and focused CO$_2$ laser beam. Interior and exterior temperatures are measured before, during, and after ignition. High-speed movies of the ignition and ignition/combustion process are also made. From the above data, spontaneous ignition temperature, ignition temperature, and ignition/combustion morphology can be determined. NASA will use the results to design safer components for launch vehicles, such as the Space Shuttle, which use large quantities of liquid oxygen at high pressures. The results are also directly applicable to industrial handling of high-pressure oxygen.

A second experiment will generate more fundamental data: oxidation rate as a function of temperature and oxygen pressure. To obtain this data, a Thermogravimetric/Differential Thermal Analysis (TGA/DTA) apparatus has been designed and is presently under construction. The data from this apparatus, in conjunction with heat-transfer studies, can be used to evaluate the suitability of a material for use in specific oxygen system applications.

Development of SRM's

D.R. Smith

Research has been directed toward the establishment of several thermal property Standard Reference Materials (SRM's).

Research for the development of high-temperature insulation SRM's is funded by DoE. These insulation SRM's will fill an existing gap in the range of available thermal conductivity SRM's and are of interest to researchers and manufacturers in the chemical, insulation, and building industries. Microporous fused silica, solid ceramic, and ceramic fiber insulation are currently being developed as SRM candidates. Work is beginning on determining thermal conductivity of expanded-foam insulations.

Reaction Systems

B. Bateman, J.F. Welch, J.D. Siegwarth, R. Widrig, M. Scurry, T. Zacher, K. Johnson, G. McKinney

Under a continuing effort supported by the Air Force, a test bed has been developed to test novel reactors at unusual conditions. Of particular interest is the ability to test gas/solid/liquid reactions at low pressure.
The preliminary phase of this project centered on evaluation of density and viscosity of liquid solutions to be used in the reactor test phase. Measurements of density and viscosity were made on aqueous electrolyte solutions at temperatures from 253 to 292 K. Previously, no such data existed in the literature for solutions such as concentrated KOH in water below the normal freezing point of water. As a result of these measurements, new empirical expressions were developed which complement and extend those previously reported for such solutions above 273 K.

Another research effort, focusing on chemical reactions at unusual conditions, has been initiated to address some of the problems associated with destruction of hazardous chemical wastes. The advantages of oxidation in supercritical water include: (1) conditions are such that only one phase exists, therefore, no mass transfer resistances due to phase boundaries occur; (2) a liquid-phase oxidant is used thereby assuring intimate mixing and substantial reduction in the capital and operating costs compared to systems using compression of gas phase oxidants (O2, air); (3) no pretreatment of the feed stock is required; and (4) the process may be used to treat organics at very low concentrations in the aqueous phase.

The focus of the effort is to investigate the application of oxidation of organic chemical wastes in supercritical water. A continuous flow reactor has been constructed to operate at 33 MPa and 800 K. Preliminary results indicate that compounds such as aromatics and substituted glycols can be readily removed from aqueous waste streams. Typical conversions are 90 to 95 percent, with residence times on the order of a few seconds and feed concentrations of 5000 ppm organic in water.

5. PUBLICATIONS


Callanan, J.E., Acosta, S.M., Brown, R.J.C., Westrum, E.F., Jr. and Weir, R.D., The thermodynamics of ammonium indates, II. The heat capacity of the ammonium pentabromoindate monohydrate salt \((\text{NH}_4\cdot\text{InBr}_5)\cdot\text{H}_2\text{O}\) from 7.8 to 348 K, J. Chem. Thermodyn., Vol. 20 (in press).

Callanan, J.E., Weir, R.D. and Westrum, E.F., Jr., The thermodynamics of the divalent metal fluorides, II. Heat capacity of the fast ion conductor \(\text{BaSnF}_4\) from 7 to 345 K, Int. J. Thermophys. (submitted).


Dale, B.E., Predicting the thermodynamic parameters of protein unfolding, Science (submitted).


Evans, J.D. and Sikdar, S.K., Biodegradable plastics: The time is now?, Chemtech. (submitted).


6. CONFERENCES


The 43rd Annual Calorimetry Conference, Bartlesville, OK, Aug. 1988. J. Callanan was chairman elect of the conference.


AIChE Summer National Meeting, Denver, CO, Aug. 1988. B.R. Bateman was national program vice chairman.
TECHNICAL ACTIVITIES
OF THE
THERMOPHYSICS DIVISION

N.A. Olien, Chief

1. INTRODUCTION

The research of the Thermophysics Division focuses on the thermophysical properties and dynamic behavior of fluids and solids, with particular emphasis on properties and substances of current and future importance to the chemical and related industries.

The approach is to conduct research on fundamental theoretical models, new concepts and phenomena, and predictive algorithms in synergism with experimental programs. The experimental research is aimed at developing new measurement techniques and providing highly accurate data for the properties of carefully selected pure fluids and mixtures, as well as high temperature solids, which are representative of broad classes of fluids and materials encountered in many industries. An essential ingredient of these efforts is the critical evaluation and correlation of data leading to the publication of Standard Reference Data. Standard Reference Data take the form of conventional correlations and tables, but more recently the form has been predictive models as computer code. These codes are an important product of this research.

All industrial processes and certainly those in the chemical and fuel industries are steadily moving toward alternative and more complex base feedstocks, which in turn yield more complex, and often corrosive and hazardous, conversion products and often involve higher temperature processes. Modern plants must handle a larger variety of feedstocks and must produce a broader range of output products. A very significant factor in the application of the research described here is the widespread use of process simulation and computer-aided design in the development, optimization, and control of processes and plants in the chemical, fuel and related industries. Key ingredients of all process simulators are the data and models for the properties of fluids and other materials encountered in the processes. Major outputs of the research program described here are property data in the form of predictive theoretical models and correlations which can be readily incorporated into process simulator and process control algorithms.

Thermophysics Division research addresses scientific issues of national importance for which NIST expertise, and its impartial position, are critical to data acceptance and to the resolution of problems of equity in trade for such products as ethylene, natural gas, steam, and carbon dioxide. The majority of the work is directed toward problems of the future. These
include, but are not restricted to, the following: (1) fluids encountered in natural gas and oil processing, refrigeration and foam blowing, high value and commodity chemicals from new feedstock sources, and new processing techniques such as supercritical extraction; (2) fluid mixtures encountered in bioprocess engineering, which are essentially aqueous solutions containing macromolecules; and (3) high temperature solid and fluid property needs of government agencies for energy, defense, and aerospace (e.g., DoE, DoD, NASA), where NIST expertise can provide specific results. The strategy is to perform basic research, generic to the science underlying the chemical, fuel, power, and aerospace industries, which requires the special role of NIST as an impartial national laboratory excelling in experimental and theoretical results and their interpretation.

2. GOAL

The goal of the Division is to provide standard measurement procedures, benchmark experimental data, and reliable methods of predicting key thermophysical properties of industrially important chemicals, fuels, and related fluids, and of high temperature solids. These data are used in the innovation, design, and control of chemical processes, to ensure equity in domestic and international exchange of products, and by NIST and others as benchmark data to extend versatile computational techniques which reliably predict the properties of broad classes of substances over extended operating ranges.

The output of this program assists the chemical, fuel, power, refrigeration, polymer processing, aerospace, and related industries in maintaining and enhancing their competitiveness in the international marketplace by making their processes more efficient, more able to accept a broader array of input feedstocks, and by providing avenues for the development of new products.

3. GROUP AND PROGRAM FUNCTIONS

The research of the Division is performed within two groups and one Division Office program.

GROUPS

* Equation of State and Statistical Physics (Gaithersburg, MD)-M.R. Moldover, Group Leader

This Group conducts experimental, theoretical, and computer simulation studies of the thermodynamic and transport properties of fluids, fluid mixtures, and solids, including supercritical and aqueous systems, polar fluids and mixtures, refrigerants and refrigerant mixtures, interfaces and wetting layers, and liquids, glasses, and molecular aggregates. The Group develops new measurement techniques, thermodynamic models, and molecular theories to describe the thermophysical behavior of condensed matter, and provides critically evaluated technical information (data, theoretical
models, computer models) on these thermophysical properties. Major non-CCT sponsors of the work of this Group include the DoE, NASA, and the NIST Office of Standard Reference Data (OSRD).

• Properties of Fluids (Boulder, CO)-W.M. Haynes, Group Leader

This Group has a research program which integrates experimental measurements, theoretical studies, and critical evaluation of data, all designed to lead to a basic understanding of fluid behavior. Outputs are data and theoretically based predictive models for the properties of technically important complex mixtures and pure fluids. The fluids of interest include common inorganics, industrial chemicals, hydrocarbons, refrigerants, coal conversion products, heavy oils, and biochemical solutions. Principal non-CCT sponsors of the work of this Group include the DoE, the Gas Research Institute, the DoD, industrial consortia, and the OSRD.

DIVISION OFFICE PROGRAM

• Subsecond Thermophysics (Gaithersburg, MD)-A. Cezairliyan, Project Leader

This program develops dynamic (millisecond and microsecond) measurement techniques and performs measurements of selected thermophysical properties of high temperature materials over the range 1500 - 10 000 K. Materials investigated include high temperature conductors and nonconductors, refractory materials, metallic composites, and high temperature Standard Reference Materials. The unique capabilities of this laboratory provide the means to perform accurate measurements in temperature regimes and at high heating rates where conventional techniques fail.

4. SELECTED PROJECT SUMMARIES

EQUATION OF STATE AND STATISTICAL PHYSICS GROUP

Aqueous Systems at High Pressures and Temperatures

J.M.H. Levelt Sengers, J.S. Gallagher, R.D. Mountain, G. Morrison, M.L. Japas (Guest Researcher), H. Sato (Guest Researcher)

(1) Organizational activities occurred at all levels, from the local to the international.

At the 10th Symposium on Thermophysical Properties at Gaithersburg, June 1988, Levelt Sengers co-organized and chaired five sessions on aqueous solutions. She, Gallagher, and Japas presented papers on aqueous solutions at this meeting.

At NIST, collaborative projects have been started with Neumann, Garvin, Archer and Wang in the Chemical Thermodynamics Division. One of these is an up-to-date formulation of the dielectric constant of water and steam, for
recalculation of the Debye-Huckel initial slopes at all temperatures and pressures. Another is a joint proposal for evaluation and improvement of existing models of aqueous electrolyte solutions at high temperatures, and for modeling such solutions at lower densities typical of supercritical water. This proposal is expected to receive the backing of the ASME Research Committee on Water and Steam.

On the national level, Levelt Sengers has participated in the merger of the ASME Research Committees on Water and on Steam, is on the Executive Board of the Joint Committee, and is the National Delegate to the International Association for Properties of Steam (IAPS). She also presented a talk on steam as a supercritical solvent at an International EPRI meeting (Cycle Chemistry in Fossil Plants) in Seattle, August 88.

On the international level, Levelt Sengers, Gallagher, and Japas attended the one-day Seminar on Chemical Thermodynamics in Industrial Water at the IAPS meeting in Vancouver, August 1988, and all gave presentations at the IAPS working group sessions. Levelt Sengers chaired the Working Group-A sessions and participated in the Prague Program Committee meeting.

IAPS-sponsored collaborations have been those on the refractive index of water and steam (with Schiebener) now nearing completion, and, with Sato, a collection of all experimental data on thermodynamic properties of water and steam; both projects are intended to be J. Phys. Chem. Ref. Data publications.

(2) Scientific progress in the past year includes a new model for the temperature dependence of Henry's law at high temperatures (Japas and Levelt Sengers, accepted, AIChE J.), a molecular dynamics study of hydrogen bonding in water at high temperatures (Mountain, J. Chem. Phys., in press), a thermodynamic model for NaCl in steam at near critical and supercritical temperatures (Gallagher and Levelt Sengers), and an experimental determination of the coexistence curve and electrical conductivity of an ionic fluid near a consolute point (Japas)--fully nonclassical behavior was found.

Morrison prepared a manuscript that exhaustively models electrolyte solutions near the critical point of water. The paper was prepared for the Proceedings of the Symposium on High Temperature Aqueous Chemistry that was held in August 1987, in Provo, Utah, and will appear in J. Solution Chem. in early 1989.

**Thermodynamic Properties of Fluid Mixtures**

E.J. Clark, J.M.H. Levelt Sengers, G. Morrison, M. Patron (Guest Researcher)

Clark replaced the pressure transducer and made several other improvements in the piston-driven visual variable-volume VLE apparatus and took some vapor pressure data on isobutane. She designed a simple visual variable-volume cell and gas handling system for study of phase equilibria in pressurized polymer solutions.
Morrison, with assistance from Patron, set up and calibrated the mechanical oscillator (vibrating tube) dilatometer, which now operates between 0 and 90°C.

Morrison finalized the design of the high-pressure continuous-dilution dilatometer, gathered all the parts for it, and began its fabrication. A bath was also constructed for this instrument.

Levelt Sengers continued her NATO collaboration with Peters in Delft. A paper was drafted for the Prausnitz Festschrift and the November 1988 AIChE meeting, on the topic of tricriticality in propane - n-alkane systems.

Work on the system C₂H₆ - CO₂ has been postponed in view of the urgency of the work on refrigerants.

Critical Survey of Compiled Data Sources for Bioprocess Engineering

J. Hubbard, J.M.H. Levelt Sengers, E.J. Clark

This study addresses questions concerning data requirements, data availability and quality, measurement techniques, and correlation methods for compiled data sources relevant to biotechnology and bioprocess engineering. The procedure is to use library and other data base sources (computerized or not) to extract information on compiled data for carefully selected topics, where relevance to bioengineering is the primary criterion for selection.

Reports take the form of annotated, critical bibliographies on such topics as isoelectric points of proteins (as determined by gel electrophoresis), oxygen solubility in bioreactor media, and oxygen mass transfer through the gas-liquid interface in bioreactors. The product will consist of a collection of these reports along with specific recommendations for future data acquisition and evaluation, plus recommendations for the development of new measurement techniques and correlation methods in bioprocess engineering.

Electrophoretic Light Scattering From Macromolecular Solutions and Colloidal Dispersions

J.B. Hubbard, A.K. Gaigalas,* S. Woo*

The analysis of quasi-elastic scattered laser light from a salt-containing solution in the presence of an external electric field is called electrophoretic light scattering (ELS). In an "ideal" colloidal dispersion or macromolecular solution the Lorentzian half-width gives the diffusion coefficient while the Doppler shift gives the mobility, which can then be related to the surface charge of a particle. ELS is superior to conventional light scattering because of the ease of resolving mixtures whose components have different surface charges. Compared to gel electrophoresis, ELS is a sensitive in-situ diagnostic probe rather than a separation technique. In ELS, no concentration gradients are produced, the fluid medium is well-characterized, and very large particles such as cells or bubbles are not
trapped as in a gel. We have begun an experimental ELS study of latex sphere dispersions in electrolyte solutions to test our equipment design and to scrutinize current theories. By using a low frequency AC electric field we have succeeded in completely eliminating electro-osmotic convection, which is the most important resolution-limiting nuisance in all current commercially available ELS devices. In addition, we have observed novel low frequency harmonics in the ELS homodyne correlation function which are apparently related to electrohydrodynamic instabilities in the electrical double layers surrounding the colloidal particles. A publication based on these results is in preparation. In addition, we have recently published a theoretical analysis of the effects of conformational dynamics of solvated macromolecules on the observed spectrum. The idea is that one can use ELS to monitor simultaneously both the statics and dynamics of biologically significant conformational changes, such as protein denaturations. As a future project, we plan a novel study of ELS in a gel-like medium as a direct probe of particle-gel dynamical interactions.

*Chemical Process Metrology Division

**Computer Simulation Studies of Liquids and Agglomerates**

R.D. Mountain, J.G. Amar

The molecular level computer simulation of the properties of liquids has proven to be an essential technique for evaluating formal, statistical mechanical models of condensed matter. Our program both develops and utilizes simulation methods to model thermal properties of fluids in terms of the molecular level interactions. The NIST supercomputer is an essential tool for this work. During the past year, our efforts have been directed towards: (a) glassy states of liquids, (b) the structure of high temperature reduced density states of water, (c) fluid-fluid phase equilibria, and (d) the development of an optical diagnostic probe of soot agglomerates. The work on water and phase equilibria is related to experimental work in the Division. The work on agglomerates is a collaborative effort with the NIST Center for Fire Research.

Our investigation of glassy states of a simple mixture has resulted in a novel measure of the ergodic properties of supercooled and glassy states. This measure, called the energy metric, is being investigated further as it provides a new way of thinking about the structure of the theory of glass formation. The degree of hydrogen bonding present in water has been determined for a model of water for temperatures between 273 K and 1100 K and for densities between 100 kg/m$^3$ and 1000 kg/m$^3$. A scaling property for hydrogen bonding as a function of temperature exists for densities greater than 600 kg/m$^3$ and does not exist for densities less than 450 kg/m$^3$. A new approach to the simulation of fluid-fluid phase transition has been examined. It is more efficient than other methods for liquid-gas calculations but not so for liquid-liquid calculations. A scheme for using optical properties to characterize soot agglomerates has been proposed. This scheme, which employs the complex index of refraction, the UV scattering, and the optical absorption of the agglomerates, yields the size of the agglomerates, the
number of primary particles making up the agglomerates, the size of the primary particles, and the concentration of agglomerates in a sample. This scheme was developed using simulation-generated agglomerates and their calculated optical properties as a guide and as a test case.

Low-Frequency, Low-Shear-Rate Viscosity Measurements

R.F. Berg, M.R. Moldover
Collaborators: J.S. Huang (Exxon), J. Ritter (University of Virginia)

As part of a NASA-sponsored project for testing the theory of dynamic critical phenomena, we have developed a unique viscometer. The viscometer is a torsion oscillator which operates at a low frequency (0.5-5 Hz) and a low shear rate (0.05-0.5 /s⁻¹) and can be used at pressures to 10 MPa. The viscometer was used to measure the viscosity enhancements that occur near the consolute points of binary liquid mixtures. These mixtures are models for the liquid-vapor systems to be studied in microgravity. The results for four mixtures have been published in the Journal of Chemical Physics. This work will be the definitive experimental reference for the critical exponent of the viscosity for many years.

In collaboration with J.S. Huang, a study of the viscosity increase near the percolation transition of a microemulsion has been published.

Spherical Acoustic Resonators for Thermophysical Properties and Standards Measurements

M.R. Moldover, A.R.H. Goodwin, B.A. Younglove, N.V. Frederick
Collaborators: J.B. Mehl (University of Delaware), J.P.M. Trusler (Imperial College, London)

The 3-liter resonator that had been used to measure the universal gas constant R was used to make exceedingly accurate measurements of the speed of sound in argon near the temperature of the triple point of gallium (Tg). This is one of several highly reproducible fixed points that are being established for the 1990 International Temperature Scale. In 1990, the present International Practical Temperature Scale (IPTS68) that is used to calibrate all thermometers, will be replaced with a new scale that better approximates the thermodynamic temperature T for which thermodynamic calculations and relationships are exactly true. We found that Tg = (302.916 9 ± 0.0005) K and that near Tg the error in IPTS68 is: T - IPTS68 = (-6.5 ± 0.5) mK. This resonator will be used to redetermine the triple point of mercury (approximately 233 K) and to interpolate between the mercury and the gallium points.

We have demonstrated the feasibility of measuring the volumetric thermal expansion of a resonator with an accuracy of 2x10⁻⁶ by using in situ microwave resonances. This technique will be used to extend acoustic thermometry to very low and very high temperatures.
A 1/8-liter resonator was assembled in Gaithersburg for measuring the speed of sound and ideal gas heat capacity in two environmentally acceptable refrigerants. This resonator and its associated pressure vessel and thermostat were designed to make speed of sound measurements accurately, rapidly, and routinely. In the temperature range -60°C to +70°C, an isotherm can easily be measured in one working day.

Refrigerants and Refrigerant Mixtures

G. Morrison, J.S. Gallagher, L.A. Weber
Collaborators: D. Didion*, M.O. McLinden*

As part of the long-term goal of the refrigerant mixture project, M. McLinden and G. Morrison presented a paper at the 1988 AIChE Spring Meeting in New Orleans that summarized their work on mixtures. They have found that the behavior of refrigerant mixtures falls into a definite pattern, in which the salient molecular parameter is the dipole moment divided by the effective hard kernel volume. This quantity, effectively a surface charge density arising from the charge separation that produces the dipole, can be related to composition variations in the mixture as well as the mean value of the empirical mixing parameter. The charge density and these empirical mixing quantities appear to be related by the same factor for all mixtures. They also found that this quantity could be incorporated into the modified hard sphere equation of state; doing so nearly eliminated the undesirable density dependence of the hard kernel and attractive term parameters in the equation of state.

The year has also seen a redoubled effort in property measurement for the proposed alternative "ozone safe" refrigerants. The saturation properties of four pure materials and one mixture have been measured by G. Morrison and D. Ward. The speed of sound and determination of the perfect gas heat capacity for two pure materials have been measured by M. Moldover and A. Goodwin by using the spherical acoustical resonator. L. Weber measured the dilute gas properties for two refrigerants with the automated Burnett apparatus. Finally, J. Schmidt and H. Chae have measured the surface tension of two refrigerants. These measurements provide a broad data set on which to base the correlation work being done by M. McLinden, with charts being produced by J. Gallagher. This effort draws together a unique collection of skills and talents in addressing the serious matter of industrial change-over to the alternative refrigerants.

*NIST Center for Building Technology

The Langmuir Film Balance

G. Morrison
Collaborator: I.L. Pegg (Catholic University)

When the automated film balance was under development, two phenomena were examined as a way of testing the versatility and sensitivity of this instrument. These phenomena were related to a measurement of the "liquid-
vapor" spreading pressure of pentadecanoic acid at 35°C, a temperature that is disputably above the critical point for this material. The measurement indicated the presence of two-phase equilibrium and the nature of the transition between two "liquid" states in the same material. The study concurred with a recent assertion that the transition is first order, in definite conflict with a long-held view that the transition was of higher than first order. Detailed measurements were made of this transition, the liquid-expanded to liquid-compressed transition, to study its high temperature behavior; as the temperature is raised, the molar area change becomes progressively smaller. There are several scenarios that could lead to the disappearance of the transition. In pentadecanoic acid, the transition appears to intersect another phase line, the monolayer collapse transition; the high temperature behavior is thus apparently obscured. In addition to the work on single-component monolayers, preparations are being made to study binary mixtures with a "liquid-liquid" immiscibility. Preliminary measurements on a mixture of octadecan-1-ol and 9-cis-octadecan-1-ol have been made. This study will lead to study of mixtures of more complex species, phospholipids and cholesterol, for example, which are the major components of many plant and animal cell and organelle membranes.

Interfacial Phenomena


The model we developed last year for predicting liquid-vapor interfacial tensions in the critical region of mixtures, such as CO2 + butane, from phase equilibria measurements, has been applied to predicting the surface tension of liquid air and to correlating recent measurements of the surface tension of argon + krypton mixtures.

Interfacial structure of the liquid-liquid interface in several binary mixtures, including carbondisulfide + methanol, nitrobenzene + n-decane, methanol + cyclohexane, and isobutyric acid + water, have been studied using state-of-the-art ellipsometry in wide temperature ranges approaching the consolute points of the mixtures. The data were used to test theories of the interfacial structure. One class of theories, known as density profile theories, describes the interface as having a smooth variation of density (composition, refractive index, etc.) as one moves from deep in one phase through the interface and into the second phase. A second class of theories, known as capillary wave theories, describes the interface as a sharp interface roughened, however, by capillary waves or ripplons. Our ellipsometry indicates that both theories (density profile and capillary wave) predict an interfacial thickness that is smaller than the measured thickness. The temperature-dependent thicknesses of all of the mixtures studied can be scaled with the bulk correlation length to obtain a universal number. At present, the best model that describes the interface is a combined density profile and capillary wave model. An important implication of the model is that the interfacial tension must increase for short wavelength ripplons.
This implies that an interface confined to a small pore or a nucleating droplet has an interfacial tension much higher than that of the macroscopic interface. We are attempting to test this by direct measurements.

Theoretical efforts have focussed on mechanisms for stabilizing very thin liquid films against external fields such as gravity. The dispersion force mechanism has been studied, and measurements agree quantitatively with theory in the special case of a nonpolar pure fluid in contact with a single vertical wall. The theory now predicts the thickness of thin films of a polar phase that intrudes between an ionizable substrate, such as glass, and a nonpolar liquid phase. The theory predicts the thickness changes upon the addition of high concentrations of salt.

PROPERTIES OF FLUIDS GROUP

Corresponding States Theories of Fluid Mixtures

J.F. Ely, J.R. Fox, M.L. Huber
Collaborators: D. Erickson (Conoco), R.T. Jacobsen (University of Idaho),
T.S. Storvick (Guest Researcher)

In recent years there have been great advances in our microscopic understanding of fluid mixture behavior. Nonetheless, one of the most reliable methods for predicting mixture thermophysical properties is based on corresponding states concepts which were theoretically formulated many years ago. In this project, we are attempting to further improve corresponding states models for systems which contain large size and polarity differences. The approach incorporates computer simulations for model mixtures which provide the radial distribution function as well as other thermodynamic data. Theoretical approximations are then made for the radial distribution functions with the results being incorporated into the statistical mechanical expressions for various properties. Thus far, we have developed an equation of state model which is nearly exact for model Lennard-Jones mixtures with size ratios up to 2. Current work involves extending these results to real fluids.

In addition to these classical studies, a new approach to the improvement of corresponding states methods is being developed. The method uses "field space" transformations to describe fluid mixtures in terms of the behavior of a pure fluid in a fashion very similar to traditional "one fluid" corresponding states theories, but with two important differences. The structure of traditional corresponding states methods leads to nonphysical predictions for the properties of dilute mixtures when coupled to the most accurate of pure fluid correlations. This is corrected in the new structure. And the calculation of phase equilibria is numerically simplified in the new forms, possibly leading to significant savings in design and process simulation work. A version of the theory, with the pure fluid described by a cubic equation of state, is currently being tested with experimental binary mixture data.
Supercritical Fluid Properties

Collaborators: W.D. Seider (University of Pennsylvania)

Industrial interest in enhanced oil recovery using near-critical carbon dioxide, in supercritical fluid extraction of fuel materials, foodstuffs, and pharmaceuticals, and in near-critical custody transfer of commercial chemicals, has pointed out the need for accurate data and predictive models for supercritical fluid mixtures. Currently five projects are in progress which address various aspects of supercritical fluid properties.

The first project, which is sponsored by a consortium of four companies, one trade organization, and NIST, deals with the measurement and correlation of PVTx data for carbon dioxide-rich mixtures. Thus far, experimental data have been obtained for one quaternary, one ternary, and four binary mixtures. In addition, a predictive model for the thermophysical properties of these systems has been developed that is more accurate in the near-critical region than earlier models. The model, DDMIX, is being distributed by the NIST Office of Standard Reference Data and will be available on-line in the Chemical Abstracts Network Service.

In the second project, a base of high accuracy, nonanalytic equations of state has been developed for various pure fluids. Most recently, equations for methane, normal and isobutane, n-pentane, and carbon dioxide have been obtained. In the near future rescaled 32-term BWR equations will also be available for propane. These equations will be used in advanced corresponding states models.

In the fourth project, a supercritical fluid chromatograph has been developed as a tool for physicochemical measurements. Supercritical fluid chromatography assumes a natural role in thermophysics research as an intermediary between gas chromatography and high performance liquid chromatography. The supercritical fluid chromatograph is being used for studies of diffusion phenomena, heat capacity ratios, and partial molar volumes.

Finally, the fifth project is concerned with supercritical fluid extraction applications in biotechnology. The potential for extraction of foods and pharmaceuticals using nontoxic solvents such as supercritical carbon dioxide has intrigued researchers for several years. Numerous laboratory-scale separations have been demonstrated, but industrial scale-up has lagged behind due to the complexity of supercritical fluid extraction process design and control. This project is geared toward developing cost efficient extraction processes which can be easily operated. The work is currently focused on β-carotene, or provitamin A. This material is a high cost, moderate volume commodity which is used extensively as a natural food coloring and to provide vitamin A supplements in foods. The research involves both an experimental and theoretical component. Measurements are being made of the solubility, vapor pressure, and transport efficiency of β-carotene in supercritical carbon dioxide. These data are then correlated
with a suitable equation of state which is part of a unit operations computer simulation package. The ultimate goal of the project is to provide an optimized predictive simulation routine which can be used industrially to design and control supercritical fluid extractions on an industrial scale.

**Predictive Computer Packages**

J.F. Ely, M.L. Huber, R.D. McCarty, J.C. Rainwater
Collaborator: R.T. Jacobsen (University of Idaho)

One of the primary outputs of the group is a collection of predictive and/or correlative computer programs which are packaged for end use by practitioners in science and engineering. Primary packages of this nature which have been distributed in the past year are MIPROPS, DDMIX, CO2PAC and SUPERTRAPP. All of these programs are interactive in nature and designed to be user friendly and usable on microcomputers as well as mainframes.

MIPROPS is a program which calculates the thermodynamic and transport properties of twelve pure substances. DDMIX calculates the thermophysical properties of mixtures (up to seventeen components) with the emphasis placed on highly accurate mixture densities. CO2PAC calculates the properties of pure carbon dioxide using the Schmidt-Wagner equation of state formalism. Finally, SUPERTRAPP calculates the thermophysical properties of mixtures (up to twenty components from a list of 125) using the extended corresponding states model. All of these except CO2PAC are available from the NIST Office of Standard Reference Data for a nominal charge.

As new models and results are obtained, the list of programs and their ultimate utility will grow. The extended corresponding states model has recently been used in the development of computer packages for air and for mixtures of metallic hexafluorides and perfluorinated hydrocarbons. The power of the extended corresponding states method (using shape factors) for predictions has been demonstrated in the development of these latter two packages, for which experimental data are extremely limited and/or nonexistent. The work on air properties has also led to a substantial experimental project to improve the quality of low temperature data for air and related mixtures.

**Complex Fluid Systems**

T.J. Bruno
Collaborator: G.A. Mansoori (University of Illinois)

Fluid property research has been moving rapidly in the direction of the study of ever more complex systems. As a result, new experimental techniques and theoretical methods are being developed to handle such systems. Currently, one part of this effort involves the behavior of biological fluid mixtures. Aqueous two-phase partitioning has been analyzed from a molecular point of view, and statistical mechanical models have been investigated for
the interpretation and prediction of such phenomena. Using experimental data for the polyethylene glycol-dextran-water system, it has been shown that these models qualitatively predict the general features of the phase behavior of these systems although the current models fail to provide quantitatively accurate results.

Heat of mixing measurements are being made on a series of five-membered ring compounds (furan, tetrahydrofuran, thiophene, tetrahydrothiophene, pyrrole, and pyrrolidine) to examine the effects of hydrogen bonding in aromatic liquids and liquid mixtures. These data will aid in the development of the theoretical means of predicting the thermophysical properties of broad classes of these mixtures.

Another area of recent work is the thermophysical properties of reacting fluids. Under conditions of high temperature and high pressure, even simple fluids can undergo extensive chemical decomposition. A comprehensive analytical and reaction screening facility has been developed to help characterize the behavior of these systems. Experimental data and subsequent correlations have been provided for methanol, benzene, and toluene. Protocols for characterizing reacting fluids, for performing reproducible measurements on them, and for reporting data from such measurements have been proposed. Development of novel instrumentation, such as a gas chromatographic detector based on catalytic cracking, is also being pursued.

PVT Measurements and Correlation

Collaborators: R. Masui (National Research Laboratory of Metrology, Japan)

The group has four operational apparatus to measure the PVT properties of fluids: an automated isochoric PVT cell operating between 80 K and 450 K for pressures to 35 MPa; a high temperature, isochoric-Burnett expansion PVT cell for 300 K to 900 K with pressures to 50 MPa; a low temperature magnetic suspension densimeter operating between 80 K and 320 K at pressures to 35 MPa; and an automated balance densimeter for 300 K to 500 K at pressures to 20 MPa. Recent results have been obtained for CO₂, CO₂ + N₂, CO₂ + CH₄, CO₂ + N₂ + CH₄, CO₂ + C₂H₆, CO₂ + N₂ + CH₄ + C₂H₆, R-13, methanol, benzene, and toluene. Planned measurements include carbon dioxide plus hydrocarbons, N₂ + O₂ + Ar (air), hydrocarbon mixtures simulating natural gas, pentanes, and binary mixtures with components exhibiting large differences in size and/or polarity.

A primary output of the group is the correlation of PVT data. Comprehensive correlations have been completed for methanol, benzene, and toluene using a nonanalytic equation of state. The Schmidt-Wagner equation of state has been applied to light hydrocarbons and carbon dioxide with excellent results, especially in the extended critical region. The 32-term modified BWR equation, which has been used extensively for many fluids, has been applied to monomethylhydrazine. A new comprehensive equation of state is currently under development for helium.
Phase Equilibria Studies

V.G. Niesen, J.E. Mayrath, T.J. Bruno, M.J. Hiza, J.C. Rainwater, S.L. Outcalt

Accurate phase equilibria data and models are essential in the design and operation of separation units in the chemical process industry. Several apparatus are available in our group for the acquisition of such data. A moderate temperature (300 K to 450 K) phase equilibria apparatus has been modified to include measurement of liquid and vapor phase densities using vibrating tube densimeters. After calibration with nitrogen and water at temperatures from 300 K to 400 K for pressures to 14 MPa and densities between 0 and 1 g/cm³, the apparatus was tested with measurements on carbon dioxide, normal butane, and their mixtures. Both the phase behavior and density results agreed within experimental uncertainty with reliable literature values. Other recent measurements have included butanes with refrigerant R-13. Current work includes binary mixtures of nitrogen and normal butane, and carbon dioxide and propane, and ternary mixtures of nitrogen, carbon dioxide, and normal butane and air related mixtures.

A phase equilibria apparatus for measuring dew and bubble point pressures from 325 K to 800 K at pressures to 35 MPa has been recently used to obtain data for the methanol and water system over the range 350 K to 650 K. This automated apparatus is unique in that residence times have been minimized for fluids that react or decompose at high temperatures, and no sampling is required after a known composition is introduced and maintained in the cell. A prototype differential refractometer cell for use at high pressures (70 MPa) and high temperatures (800 K) is undergoing performance tests. This technique will provide a real time, nondestructive, in situ means for the determination of binary mixture compositions at extreme conditions encountered in new technologies in the energy industry.

An apparatus is available for measurements of the fugacity of binary mixtures containing hydrogen. This technique employs a semipermeable membrane (palladium/silver) through which hydrogen, but not the second component, can penetrate. By measuring the properties of pure hydrogen, the fugacity of hydrogen in the mixture can be determined. Results have been obtained for hydrogen with methane, ethane, propane, isobutane, CO₂, and CO. Measurements are now in progress for hydrogen and ethylene; a study of the hydrogen + ammonia and hydrogen + butane systems will follow. Our low temperature VLE apparatus is currently being reactivated for measurements on mixtures of air components.

Accurate correlation of VLE data in the critical region is extremely important in many industrial applications. It is precisely within this region that conventional methods fail to converge and/or are inaccurate. A model first developed by Leung and Griffiths has been modified to provide accurate correlations of phase equilibria data that cover an extended critical region from the critical pressure locus to about half the critical pressure. This model has been successfully applied to a large number of binary mixtures containing helium, nitrogen, oxygen, carbon dioxide, hydrogen
sulfide, benzene, refrigerants, alkanes, olefins, alcohols, and ethers. The model has recently been extended to ternary mixtures of ethane, n-butane, and n-pentane and of nitrogen, oxygen, and argon (air) and has been used to predict interfacial tension. A mathematically complex model has been derived to accommodate VLE in the presence of liquid - liquid equilibria (LLE). New theoretical understanding of the nature of the critical locus has been achieved. Future plans include extension to azeotropic systems and to the one-phase supercritical region, correlation of coexisting enthalpy data, and development of predictive techniques using this model.

**Thermodynamic Property Measurements and Correlation**


There is an awareness in industry that data for the derived thermodynamic properties (e.g., heat capacity, velocity of sound, enthalpy) of even simple fluids and mixtures are sparse. Further, the predictions of such properties from an equation of state are unreliable without data to check and optimize the forecasts. Isochoric heat capacity ($C_V$) data have been obtained for three mixtures of CH$_4$ and C$_2$H$_6$ from 100 K to 320 K at pressures to 35 MPa. When combined with previous data on pure CH$_4$ and C$_2$H$_6$, a heat capacity data base consisting of five compositions has been assembled for development and testing of theoretically based predictive models. These results are of immediate relevance since the CH$_4$ + C$_2$H$_6$ binary system is the most important binary system in the natural gas industry. Also, isochoric heat capacity data have been measured for N$_2$ + O$_2$ + Ar (air) from 64 to 300 K at pressures to 35 MPa. $C_V$ measurements on three compositions of CO$_2$ + C$_2$H$_6$ are in progress. The transient hot-wire apparatus has been used for obtaining heat capacity, $C_p$, results over wide ranges of the fluid surface.

The natural gas industry is very interested in using sonic nozzles as secondary flow measurement standards, but has been hampered by the lack of accurate sound speed data upon which to base performance. Using a cylindrical resonator, sound speed measurements have been made on twelve gaseous binary mixtures of natural gas components, with methane as the major constituent, and on four multicomponent mixtures simulating compositions of industrial importance. These measurements cover a temperature range from 250 K to 350 K at pressures to 10 MPa. These results represent the only accurate sound speed measurements for gaseous mixtures other than air. These data are being used to develop a highly accurate predictive model for sound speeds in natural gas and similar mixtures.

A new spherical resonator is being constructed for wide-range sound speed measurement from 80 K to 400 K at pressures to 10 MPa. This apparatus, which will greatly expand our existing capabilities, will require innovative development of transducers suitable for high temperatures and high pressures. The data obtained from this apparatus will aid in the advancement of flow metering and the development of predictive models.
Transport Property Measurements, Correlations, and Theory

Collaborators: C.A. Nieto de Castro (Lisbon University), W.A. Wakeham (Imperial College), A. Laesecke (University of Siegen), L.J. Van Pooien (Calvin College)

In recent years industry has become increasingly aware that transport properties play a significant role in process design and that accurate knowledge of these properties can lead to substantial economic benefit. Our work on transport properties of fluids encompasses the development of new measurement techniques, the utilization of advanced apparatus to obtain accurate data, the correlation of available transport property data, studies of kinetic and transport theory, and the development of wide-range predictive models for transport properties. Measurements of viscosity and thermal conductivity are vital to complete the data base needed by the design engineer and correlator and are a necessary adjunct to PVT and thermodynamic properties. Further, the study of the transport coefficients is interesting from a scientific standpoint as it demonstrates the behavior of a fluid not in equilibrium.

We have an ongoing program to measure the viscosities of dense fluids and fluid mixtures, from 80 K to 700 K, with pressures to 35 MPa, using two different piezoelectric quartz crystal viscometers. Our new high temperature viscometer has recently been performance tested with measurements up to 50 MPa. Measurements on ethane, carbon dioxide, and their mixtures have been completed. The low temperature viscometer has recently been used to obtain viscosity data for liquid toluene and R-13. These data have again demonstrated the power of examining the dependence of the fluidity (viscosity⁻¹) of liquids on molar volume, and using this representation as a simple method for correlating viscosity data for liquids.

For accurate thermal conductivity measurements the transient hot-wire technique is recognized as state-of-the-art. Our low temperature hot-wire apparatus covers temperatures from 80 K to 330 K at pressures up to 70 MPa. During the past year we have concentrated on obtaining results for the thermal diffusivity and the specific heat, C_p, along with the thermal conductivity, using the transient hot-wire apparatus. So far we have carried out measurements for argon and nitrogen in the low temperature apparatus with an average uncertainty of 5% in C_p and less than 1% in the thermal conductivity. In addition, a new high temperature transient hot-wire thermal conductivity apparatus has been developed. It operates at temperatures between 300 K and 775 K with pressures up to 70 MPa. After testing with argon and nitrogen, measurements of standard reference quality are planned on toluene and benzene.

We are completing new correlations for the thermal conductivity and viscosity of methane, ethane, propane, and argon. Dilute gas data are represented with theoretically based kinetic theory expressions. The critical enhancement contribution to the thermal conductivity has also been modeled with an expression with strong theoretical foundation. Finally, the
excess contributions for both transport coefficients have been described with polynomial functions that represent the data within experimental uncertainty. Analogous studies for ethane, propane, and the butanes are in progress. The transport properties of binary mixtures of methane and ethane have been studied experimentally in this laboratory; correlations of the thermal conductivity and viscosity surfaces have been completed.

There is an ongoing effort to develop an improved theory for the critical enhancement in the thermal conductivity of mixtures, which has been observed experimentally in this laboratory. Finally, we have in recent years developed the first successful microscopic theory of the initial density corrections to viscosity and thermal conductivity. Calculations of generalized collision integrals have been extended to lower reduced temperatures and show good agreement with recent data for benzene and methanol vapor. In addition, a new version of the TRAPP (Transport Property Prediction) model has been developed which substantially improves the prediction of mixture viscosity and thermal conductivity. Finally, nonequilibrium molecular dynamics simulations are being carried out to form the basis for a corrected Enskog theory of fluid transport.

**Neutron Scattering**

H.J.M. Hanley, G.C. Straty
Collaborators: J. Hayter*, C. Glinka**
N. Clark (University of Colorado) and D. Aastuen (University of Colorado)

This work is an experimental part of a large-scale program in our Division to study complex liquids. It is carried out in conjunction with parallel theoretical work on the structure of liquids and is concerned with the similarities and differences between "simple" and "complex" fluids. The specific objective is to examine long-range correlative or collective molecular motion in the liquid via the structure factor, \( S(Q) \), using neutron diffraction. Test systems have included glycerol and a suspension of latex spheres in water. Glycerol was selected because it can be made to exhibit characteristics ranging from those of the most simple to those of very complex fluids by varying the temperature. Latex suspensions were used to obtain benchmark data in preparation for forthcoming measurements on these systems under shear. Such data also offer a unique opportunity for testing theoretical models since the interparticle potential is well characterized, and its strength can be "tuned" by the introduction and variation of ion concentrations in the solution.

Specific tasks carried out during the past year were: (a) preliminary measurements of the change in \( S(Q) \) of very viscous glycerol due to shear using a newly constructed shearing apparatus and the NIST SANS (small angle neutron scattering) and BT6 spectrometers; (b) measurements of \( S(Q) \) of carefully prepared latex suspensions of various concentrations using the NIST SANS spectrometer and the newly installed cold neutron source (the latter samples were found to exhibit long range solid-like correlations at high concentrations); and (c) completion and preparation for testing of a versatile automated general purpose shearing apparatus for the study of fluids under shear using neutron scattering. With regard to item (c),
results from these apparatus will be most instructive and essential to understanding the microstructure of liquids and to meet our objective of differentiating between simple and complex liquids. Furthermore, the cells will upgrade the capability of the NIST reactor facility to handle fluids in nonequilibrium. There is strong industrial (and biological) interest in shearing equipment.

*Oak Ridge National Laboratory  **NIST Institute for Materials Science and Engineering

Non-Newtonian Fluid Behavior

H.J.M. Hanley, J.C. Rainwater, M.L. Huber
Collaborators: D.J. Evans, J.P. Morriss (Australian National University), S. Hess (Berlin Technical University)

This program addresses theoretical problems related to the overall goal of studying complex liquids. The work is carried out in conjunction with parallel experimental work on neutron scattering and the structure of liquids and is concerned with the similarities and differences between so-called "simple" (e.g., argon, nitrogen) and "complex" (e.g., polymers, highly branched hydrocarbons, hydrogen-bonded liquids) fluids. It was largely motivated by the observation from computer simulation that simple liquids can display rheological or non-Newtonian characteristics usually only associated with liquids of very complex structure. In this context, it is preferable to classify liquids in terms of a relaxation time of the fluid's microstructure. Simple liquids have relaxation times of the order of \(10^{-14}\) s, while for complex liquids, the time is one second or greater.

There is a connection of this work to the goal of predicting fluid properties and behavior. Prediction procedures for complex liquids are largely adapted from methods developed for simple liquids, incorporating improvements in a systematic manner based on an understanding of the shortcomings of the methods.

The differences between isomers such as isobutane and normal butane have been investigated using computer simulation. These isomers exhibit polymeric behavior, and the results to date indicate that isobutane is viscoelastic. Work on the rheological characteristics of simple fluids is continuing with a re-examination of earlier Weissenberg effect calculations and a re-assessment of the importance of shear dilatancy and finite compressibility. The radial distribution function and structure factor have been calculated as explicit vector functions in two dimensions and by using an expansion in moments or spherical harmonics in three dimensions. A technique has been developed to measure the structure factor of a two-dimensional liquid by transferring the coordinates of the particles in a model liquid to photographic film, which is then regarded as a scattering medium for laser light. Statistical noise can be largely removed by spline-smoothing without changing the three-dimensional structure factor in the physically important regions. The three-dimensional
structure factor has been compared with light scattering experiments on sheared colloidal suspensions, and the essential qualitative features of those experiments are reproduced correctly.

Other recent work includes: study of the effect of shear on the pair correlation function of a liquid through tensor rank four, and derivation and testing of a theory to predict the correlation function; continued work on the development of computer simulation programs to simulate liquids under shear and to show their relationship to experiment; and continued study of an exactly solvable weak potential model under a flow field more general than planar Couette flow.

SUBSECOND THERMOPHYSICS PROGRAM

Thermophysical Measurements by Dynamic Methods

A. Cezairliyan, A.P. Miiller, R.F. Chang, R.A. MacDonald, J.L. McClure, G.M. Foley, P.J. Giarratano,* T. Baba (Guest Researcher)

The goal of this program is to develop and utilize techniques capable of highly accurate measurements of thermal, optical, and electrical properties of technically important materials at high temperatures using very high heating rates. Experimental capabilities include millisecond techniques that allow measurements of heat capacity, thermal expansion, electrical resistivity, phase transition points, and latent heats; microsecond techniques for measuring thermophysical properties at heating rates of $10^7 - 10^8$ K/s; and millisecond techniques for such measurements in a microgravity environment. Plans for the immediate future include the development of dynamic techniques for measurements on nonconducting materials and theoretical studies relevant to dynamic measurement techniques.

Research is under way to develop a system for the measurement of thermophysical properties of electrically conducting liquids at high temperatures (above 2000 K) in a microgravity environment. Efforts were concentrated in the study of the geometrical stability of the liquid specimen when heated rapidly by the passage of an electrical current pulse through it in a microgravity environment. Diagnostic experiments were performed on aircraft operated by NASA. The experiments on board the aircraft were conducted by P. Giarratano. Excursions in the liquid phase could be seen from the results of the high-speed films and the pyrometric recordings. In order to improve the geometrical stability of the specimen, a triaxial configuration for the specimen and the current leads was studied, an experimental chamber was constructed, and experiments were conducted in aircraft. The results of the experiments with the triaxial configuration indicate the feasibility of measuring surface tension near the melting point of the specimen. The surface tension of copper has been measured with this new method. Work in this direction will continue.

The laser-pulse thermal diffusivity system, which became operational a year ago, was used to perform definitive measurements on graphite in the range 1500-2500 K. The results indicate a very high degree of
reproducibility (better than 1%) and suggest that the system can be used to obtain accurate data, on both electrically conducting and nonconducting materials, with implications to develop Standard Reference Materials for thermal diffusivity at high temperatures.

A recently developed microsecond-resolution pulse heating system was used to measure the heat of fusion of molybdenum in an effort to obtain accurate thermophysical properties data on refractory metals, in their solid and liquid phases, at high temperatures, in ground-based experiments.

*Chemical Engineering Science Division

5. PUBLICATIONS


Bruno, T.J., Supercritical fluid chromatograph for physicochemical studies, NIST J. Res. (in press).


Gallagher, J.S., McLinden, M.O. and Morrison, G., Thermodynamic diagrams for refrigerant mixtures, ASHRAE Trans. (submitted).


Levelt Sengers, J.M.H. and Sengers, J.V., van der Waals-fund, van der Waals laboratory and Dutch high-pressure science, Special Issue of Physica (submitted).


Magee, J.W. and Ely, J.F., Isochoric (p,v,T) measurements on CO2 and (0.98 CO2 + 0.02 CH4) from 225 to 400 K at pressures to 35 MPa, Int. J. Thermophys., Vol. 9, No. 4, pp. 547-557 (1988).


Nielsen, G.C., Morrison, G., McLinden, M.O. and Levelt Sengers, J.M.H., Use of computer algebra to locate critical loci of fluid mixtures, AIChE J. (submitted).


Romig, K.D., Jr. and Hanley, H.J.M., Phase equilibria from the one-fluid model, Cryogenics (in press).


6. CONFERENCES AND WORKSHOPS

CONFERENCES


American Institute of Chemical Engineers 1988 Summer National Meeting, August 21-24, 1988, Denver, CO. Neil A. Olien, Meeting Program Chairman. In terms of number of sessions, papers presented, and attendance, this was the largest Summer meeting in AIChE history.

WORKSHOPS

First Workshop on Subsecond Thermophysics, Gaithersburg, MD, June 20-21, 1988. Organized and chaired by A. Cezairliyan.

Workshop on Thermophysical Property Data Needs for Ozone-Safe Refrigerants, Gaithersburg, MD, September 22, 1988. Jointly sponsored by the NIST Center for Building Technology and the NIST Center for Chemical Engineering.
TECHNICAL ACTIVITIES
OF THE
CHEMICAL PROCESS METROLOGY DIVISION

H.G. Semerjian, Chief

1. **INTRODUCTION**

The research of the Chemical Process Metrology Division is focussed on the development of new measurement techniques for process sensing, diagnostics, and control. Particular emphasis is placed on measurement methods and data that are needed for process control in the chemical, biochemical, and related industries.

The approach has been to conduct research on new experimental methods and engineering science underlying reliable measurements and data bases; this work is complemented with theoretical and computational modeling of processes under investigation and transport processes affecting sensor performance. The research is aimed at (a) investigation of new engineering and scientific principles which can be utilized for measurement of physical or chemical quantities in industrial processes, (b) development of accurate measurement methods and measurement standards for industry, and (c) providing primary calibration services for a wide segment of the U.S. industry and the scientific research community. These measurements include temperature, velocity, flow rate, humidity, composition and concentration, pH, particle size and number density, volume fraction, and other quantities of interest in multiphase reacting and nonreacting process streams. Emphasis is on the development of on-line, and where possible in-situ, measurement techniques needed for control of industrial processes.

Current projects address several of the research areas mentioned above. An extensive data base has been developed on orifice discharge coefficients to improve the accuracy of flow metering in gaseous and liquid streams. This work represents a major contribution towards equity in the domestic and international trade of oil and gas, as well as other commodities. Other projects on vortex shedding flowmeters and installation effects (supported by industrial consortia) have also resulted in experimental data critically needed for improvement of the current flowrate measurement technology. Electromagnetic field methods have been successfully applied for measurement of solids fraction in slurry flows, and a prototype sensor is currently undergoing field tests. Electrochemical techniques have also been used for measurement of diffusion coefficients in liquids and are now being extended to porous media. Optical techniques have been developed, particularly for measurements in single phase and multiphase reacting flows. They have been successfully applied to provide data on temperature, gas composition, particle size distribution, and gas/solid reaction rates in flames, fluidized bed reactors (FBR), plug flow reactors (PFR) and other high temperature reacting flows. Solid-state sensors, utilizing iridium oxide and tin oxide, are being developed for pH and chemical composition measurements in process streams. Thin film thermocouples have been demonstrated to provide temperature measurements in harsh environments (e.g., in ceramic engines).
with good temporal resolution. Finally, computational models have been developed to simulate chemically reacting flows, formation and oxidation of particles, and transport processes in high temperature reacting flows.

Future trends in the Chemical Process Industry are directed toward transition to higher-value added products, increased biochemical production of pharmaceuticals, foodstuffs, specialty chemicals, and fuels, and increased production of chemicals and materials for microelectronics, photonics, and high temperature applications. The Division's programs are being developed to address many of the critical technical problem areas and measurement needs within these emerging technologies. Several new and exciting projects are underway to provide new measurement methods for biochemical reactors - optical diagnostic techniques have been demonstrated as useful tools for substrate, product, and cell concentration measurements in fermentation systems; an electrophoretic light scattering technique is being developed as a new tool to monitor protein transport processes; electric field effects will be investigated to study their role in transport through biological membranes and possible use in bioreactors. Techniques developed for particulate measurements in flames are being extended to study formation of silica particles; these techniques will provide data needed to improve chemical processes used in the fabrication of optical fibers. Laser diagnostic techniques, used for temperature and gas phase composition measurements in flames, will be extended to study chemical vapor deposition, laser enhanced CVD, plasma etching, and other processes used in microelectronics fabrication. Laser based diagnostic techniques are also expected to make a significant contribution towards optimization of powder atomization processes, one of the most promising processes in metals processing and for production of high temperature ceramics. Finally, existing high temperature reactor facilities (FBR, PFR) have been modified to study pyrolysis and combustion of chlorinated hydrocarbons. This project will provide critically needed data to address a major national concern - disposal of hazardous wastes. Developments in these emerging areas of research will be closely monitored, and the Division's research priorities will be modified to meet anticipated measurement and data needs.

The Division has been striving to develop and maintain all possible forms of technology transfer. Industrial consortia have been one of the most successful forms of this transfer and the Flowmeter Installation Effects Consortium has attracted a substantial membership. There are also collaborative efforts with several instrumentation companies, who are interested in utilizing NIST-developed technology toward development of commercial instruments. Details of these interactions are reported in the main body of this report.

The Division has continued providing calibration services in mass and volumetric flow, air speed, humidity, volume, and liquid density to a variety of clients across the country. The recent upgrading of these facilities will make it possible to serve the U.S. industry more effectively.
2. **GOAL**

Within the framework of the Center, the Chemical Process Metrology Division's main concern is the science of measurement in homogeneous and heterogeneous flow systems with and without chemical reaction.

The goal of the Division is to provide the chemical and related industries and other government agencies with the measurement techniques, fundamental data, and the underlying scientific principles pertinent to homogeneous and heterogeneous flows with and without chemical/biochemical reactions at ambient and elevated temperatures. A key element in the pursuit of this goal is the study of surface, transport, and kinetic phenomena in the environment of sensing and diagnostic tools.

Further, process measurement is the key component of any process control loop, the proper function of which is essential to maintaining the highest quality of manufactured goods and, in turn, the competitive edge of the U.S. industry on domestic as well as foreign markets.

In parallel with its research work, the Division maintains state-of-the-art calibration services for flowrate, volume, density, humidity and air speed, thus providing industry and other government agencies with traceability of their instrumentation to national standards and thus assuring equity in domestic and international trade.

3. **GROUP FUNCTIONS**

The research activities of the Division are carried out within four Groups:

- **Fluid Flow Group** - G.E. Mattingly, Group Leader

  The mission of the Fluid Flow Group is to study the fundamentals of fluid flow with the aim of advancing the state-of-the-art in flow metrology and of applying these principles toward improving and expanding the NIST flow measurement capabilities, as needed, for single phase gases and liquids (water and hydrocarbons) and multiphase systems (sand-water mixtures).

  Research is primarily focused on flow phenomena in conduits as well as in free surface flows in geometries pertinent to the technologies used in the chemical and related industries.

  The Fluid Flow Group maintains responsibility for the NIST fluid flow rate and airspeed calibration services and for the maintenance and upgrading of the relevant national standards. The Group is responsible for the transfer of fluid flow measurement technology to industry, other government agencies, and public institutions.
• Multiphase Reacting Flows Group - A.K. Gaigalas, Group Leader

The mission of the Multiphase Reacting Flows Group is research on multiphase flows at ambient and near-ambient temperatures with and without chemical reactions. The ultimate purpose of this activity is to (1) provide fundamental data, (2) develop improved measurement techniques for on-line process diagnostics, and (3) develop mathematical models for improved understanding and control of physical, chemical, and biochemical processes.

Particular emphasis is placed on the development of advanced diagnostic techniques utilizing electromagnetic and acoustic fields and electrochemical phenomena. Focus of the future activities of this Group will be on biochemical processes.

The Multiphase Reacting Flows Group bears the responsibility for NIST calibration services in liquid density and volume.

• High Temperature Reacting Flows Group - A. Macek, Group Leader

The High Temperature Reacting Flows Group conducts fundamental research on chemically reacting flows, especially those with gas-solid reactions involving solid particles either formed or entrained. The research includes advanced optical, nonintrusive measurement techniques for high temperature reactors such as combustors and fluidized bed reactors.

Particular emphasis is on the use of laser scattering and extinction techniques for particle characterization, laser tomography for temperature and composition measurements, laser induced fluorescence (LIF) for composition measurements, and emission spectroscopy for temperature measurement. The scattering/extinction techniques are being adapted to the study of gas-solid chemical reactions relevant to chemical vapor deposition and to ceramics and powder metallurgy.

A significant segment of the research activities in this group is the extension of the LIF techniques to optical diagnostics of species (nutrients, substrates, metabolic intermediates, and products) in biochemical reactors.

• Process Sensing Group - K.G. Kreider, Group Leader

The Process Sensing Group performs research directed toward the development of process sensors with particular emphasis on solid state sensors for chemical species, humidity, and temperature. Reactive sputtering is used to deposit films; a comprehensive surface analytical facility is used to characterize the surfaces of films and bulk materials where chemical reactions take place.

For gas sensing, the focus of the research is on tin oxide films, while iridium oxide forms the backbone of the work on ionic sensors. Furthermore, thin film thermocouples deposited on metal, ceramic, and polymer substrates are the subject of study.
The Process Sensing Group is responsible for providing the NBS calibration services of humidity and for the maintenance of the humidity national standard.

4. SELECTED PROJECT SUMMARIES

CALIBRATION SERVICES

Calibration and Test Services Performed by the Chemical Process Metrology Division

G.E. Mattingly, A.K. Gaigalas, K.G. Kreider

In the past year, the CCT calibration services have satisfied industry and government requests for a number of metrological tasks in the areas of fluid flowrate, liquid density and volume, air speed, and humidity measurements. Additionally, the techniques and facilities for performing these services have been assessed and are being upgraded so that the levels of measurement uncertainty are better quantified and reported for publication in the appropriate literature. In the specific calibration services offered to U.S. industry, activities are summarized as follows:

<table>
<thead>
<tr>
<th>Service</th>
<th>Number of Items Calibrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>38 (30 for industry)</td>
</tr>
<tr>
<td>Volumetric Containers</td>
<td>88 (81 for industry)</td>
</tr>
<tr>
<td>Aerodynamic Devices</td>
<td>74 (54 for industry)</td>
</tr>
<tr>
<td>Reference Standard Hydrometers</td>
<td>73 (73 for industry)</td>
</tr>
<tr>
<td>Humidity</td>
<td>81 (78 for industry)</td>
</tr>
</tbody>
</table>

These calibrations generally establish a traceability link between the standards of the respective calibration requester and the national standards maintained by NIST. In this way, a basis for the assurance of all the measurements produced in the requester's laboratories is provided.

Besides these services, a number of in-situ calibrations were performed by NIST personnel in the customers' laboratories, providing improved traceability links between actual installed instrumentation and the national standards for these measurements.

FLUID FLOW GROUP

Fluid Flowrate Traceability

G.E. Mattingly

The Calibration Coordination Group (CCG) of the Department of Defense (DoD) has initiated a metrological program to establish realistic traceability for the fluid flowrate measurements made in the Primary Standards Laboratories of the Army, Navy, and Air Force. This program is
focused on liquid hydrocarbon measurements because of the crucial role these play in critical engine performance tests. Accordingly, CCG has set fluid flowrate measurement accuracy improvement goals for their Primary Standards Laboratories of ± 0.05% for liquids and ± 0.1% for gases. The NIST/CCG program to establish realistic flow measurement traceability is viewed as the initial step in attaining these goals.

To initiate this program, NIST, with DoD flow metrologists, designed a round robin flow measurement program tailored to DoD needs. Repeated initial testing was conducted at NIST and a first round of testing was performed. To date, the initial phase of this round robin testing program has successfully produced tests in some twenty facilities; these include DoD, industrial, and other national laboratories which were tested at DoD's request. This program is being expanded to include larger meters and flowrates; it is planned to expand the program to test laboratories using air as the flowing medium. When such programs are fully established and are conducted on a continuing basis, realistic traceability will be quantified among participant laboratories. This will benefit the flowmtering community, both national and international.

Flowmeter Installation Effects

G.E. Mattingly, T.T. Yeh

The increasing cost of feedstocks has necessitated flow measurements with increased accuracy. Similar requirements also exist throughout the continuous process industries where precise measurement and control are essential to optimize productivity. Improvements are especially needed in specifying metering installations in "nonideal" situations. High measurement accuracy is sought for meters retrofitted into existing piping systems--not originally designed for "ideal" meter installations. Currently, available meter installation specifications give little or no guidance to attain desired levels of performance. This program, which is being supported by an Industry/Government Consortium, is designed to provide such guidance.

Experimental studies of pipe flows are being conducted at NIST/Gaithersburg, using laser Doppler velocimetry (LDV) to study the secondary swirling flows produced downstream of selected piping configurations. To date, these results quantify pipeflow profiles for both time-averaged and turbulent velocity components as well as swirl-angle and power-spectral density distributions. Recently, the program has completed the study of several elbow-out-of-plane configurations and a standard single elbow configuration. To demonstrate that satisfactory performance can be predicted for meters in "nonideal" installations, a turbine type meter and several sizes of orifice type meters were successfully tested. Current experiments focus on assessing flow conditioner effectiveness using LDV. In this way, detailed results will be produced to determine what effect these devices have on pipe flows.
The results of this program will improve fluid flowrate measurements and, in turn, quality assurance, industrial productivity, and competitiveness --both domestically and internationally. These activities are being coordinated with other metering projects at CCT/Boulder and elsewhere. The results of this research are being put directly into new U.S. flowmetering standards.

**Supersonic Inert-Gas Metal Atomization**

G.E. Mattingly, P.I. Espina, S. Ridder*, F. Biancaniello*

Metal atomization, the production of rapidly solidified fine powders through the interaction of high pressure gas jets and liquid metal streams, is an emerging technology that offers considerable promise for improved industrial productivity in the metallurgical industries. Such powders enable manufacture of components with high strength-to-weight ratios, improved fracture toughness, unique magnetic properties, and high corrosion and fatigue resistance. To assist U.S. Industry in this area, the NIST Office of Non-Destructive Evaluation (NDE) has formed an industry-government consortium to develop and demonstrate process models, measurement methods, and expert systems needed to monitor, control, and optimize the productivity of this process in a Supersonic Inert-Gas Metal Atomizer (SIGMA).

To attain this objective, a NIST team has been formed which brings together four different capabilities, metallurgy, fluid flow, optical diagnostics, and automation. In this program, the Fluid Flow Group has conducted a range of experiments on the fluid phenomena and interactions that occur through the operation of a generic atomization die, a device which produces liquid metal breakup and powderization through flow field interactions. The flow research strategy is to begin with the gas-only flow field and determine the characteristics of this flow as operating conditions (i.e., temperature and pressure) are made closer to those used in the actual process. These tests have involved a range of measurement methods which have focused on the velocity and pressure distributions in the gas-liquid interaction zones. These measurements have supplemented and enhanced our previous shadowgraph and schlieren results to give both qualitative and quantitative descriptions of the gas only and the gas-liquid flow fields. High speed holography of the gas-liquid flows has been performed. For the first time the rapid liquid and droplet motion has been recorded and shows the details of the liquid break-up patterns.

*NIST Institute for Materials Science and Engineering

**MULTIPHASE REACTING FLOWS GROUP**

**Mass Transport in Porous Media**

B. Robertson, A.C. Van Orden, A.K. Gaigalas

An experimental study of flow through porous media has been undertaken in order to predict dispersion of hazardous wastes from ruptured underground
tanks. The flow of water in porous materials has been visualized using magnetic resonance imaging (MRI). Water flow in an initially dry bed can be detected directly since the protons in water give a large signal. For observing flow in a wet bed, a dilute solution of manganese ions in water can be used to displace the pure water. The manganese ions quench the MRI signal so the solution can be distinguished from pure water. In order for this technique to be useful for quantitative measurements, it is necessary to have a calibration of the amount of signal quenching caused by different amounts of manganese in solution. This calibration was performed in preparation for a study of flow in a saturated tuff, a volcanic deposit. A sample of tuff was obtained from D. Evans of the University of Arizona. Calibration procedures for determining the water content in the rock were developed.

Additional measurements of ion transport in porous media will be made by measuring the AC electrochemical impedance, as a function of frequency, of a porous medium saturated with an aqueous salt solution. The impedance at low frequencies depends on the mass transport of ions, which is governed by adsorption of the ions onto the surface of the pores and by diffusion of the ions both in the liquid and on the surface. The low-frequency measurements give much more information about mass transport than the usual measurement of the high-frequency electrical conductivity of the saturated porous medium. These measurements will be related to the results of the MRI measurements on porous media.

**Measurement of Solids Fraction in Two-Phase Flows**

W.G. Cleveland and A.K. Gaigalas

A technique has been developed to measure the fraction of solids suspended in a flowing water-based slurry. It is assumed that the slurry is flowing in a conducting pipe which acts as a waveguide for radio waves. By measuring the speed of radio waves propagating in the flowing slurry and comparing it with the value for pure water, it is possible to infer the amount of solid material carried by the water stream. Tests of the technique in the laboratory have demonstrated a high degree of accuracy. Attempts to adapt the instrument to the mill environment are in progress. Nonintrusive antennas have been designed and installed in the prototype sensor, and their performance is excellent. The one remaining problem is air entrainment in the process stream.

The sensor's operational characteristics are being investigated in a paper pulp loop simulating industrial process conditions. As expected, the major contribution to measurement bias is the presence of air in the paper slurry. Careful preparation of the pulp slurry has alleviated this problem somewhat. Otherwise, small discrepancies between the expected and measured dielectric constant are most likely due to the nature of the parameter fitting algorithm. A small instability in the convergence of the algorithm is under investigation.
Detection of Bubbles with Ultrasound

C. Gingrich, W. Cleveland, A.K. Gaigalas

Work with the radio frequency (RF) solids fraction sensor has demonstrated that many slurries contain air bubbles which bias the measured value of the solids fraction. By combining the RF meter with a bubble detection scheme, it will be possible to extend the measurement to three phase systems.

A bubble detection scheme was selected which provides a unique output in the presence of bubbles. The scheme is based on the resonant radial oscillations which bubbles undergo in the presence of a driving pressure oscillation such as that caused by a sound wave. The solid particles may scatter the sound wave, but they will not exhibit a resonant response. Thus by detecting the resonant oscillations, it will be possible to detect the presence of bubbles. The detection of the radial oscillations will be done by scattering an ultrasound beam (0.5 MHz) from the bubbles. The oscillations will be driven by a low frequency (20 kHz) sound wave. An apparatus has been developed to verify the proposed bubble detection technique, and modeling of the detector response has been initiated.

Electrophoretic Light Scattering (ELS)

S. Woo, A.K. Gaigalas, J.B. Hubbard*

The object of this study is to develop a technique to monitor protein transport processes. It is well established that gel electrophoresis can be used to identify a variety of proteins. The technique is based on the differences in protein response to an electric field. ELS also uses the variability of surface charge on the protein to detect differences in electrophoretic velocity. The major difference is that ELS occurs in situ and is orders of magnitude faster than the gel method.

During last year, the major effort involved measurement and interpretation of the response of latex spheres to AC electric field perturbations. Measurements were taken over a frequency range from 10 Hz to 1000 Hz. A homodyne detection scheme was utilized; in this case the measured response consisted of an exponential decay modulated by the motion induced by the electric field. The overall decay constant provided a measure of the diffusion constant while the magnitude of the modulation gave a value of the electrophoretic mobility. It was found that the electrophoretic mobility of latex particles varies with frequency. The variation is most likely due to inertial effects. The measured diffusion coefficient did not depend on the frequency of the applied electric field. At lower frequencies (f < 50 Hz), the response of the latex particles was nonlinear as indicated by the presence of large second harmonic components in the modulation of the correlation function. The nonlinear behavior most likely arises from the hydrodynamic interaction between the particles and the fluid. The presence of nonlinearity complicates the connection of the zero frequency (DC)
electrophoretic mobility to that observed at higher frequencies. The study of the frequency response is continuing; in addition, a heterodyne detection scheme is being implemented.

*Thermophysics Division

**Electrochemical Measurement of Diffusion Coefficients**

B. Robertson, A.K. Gaigalas, B. Tribollet,* C. Deslouis*

A new electrohydrodynamic (EHD) method has been developed for measurement of the Schmidt number in solutions, and the results have been compared with those obtained using the DC method of Levich utilizing a rotating disk electrode. With the EHD method, the speed of rotation of the disk is modulated sinusoidally, and the resulting sinusoidal variation of the limiting current is measured. The advantage of the EHD method is that it does not require measuring the area of the electrode, the number of electrons transferred in the redox reaction, or the concentration of the limiting reactant, as does the DC method. The two methods agree within 1 percent when the EHD measurement is done at a low disk velocity.

The method can be used to obtain a measurement of the diffusivity of a protein that undergoes a redox reaction, as do many proteins. This measurement will be compared with the ELS measurement of diffusivity. Also a knowledge of the diffusion coefficient in the pure liquid is necessary for studying mass transfer in a porous medium.

*University of Pierre and Marie Curie, Paris, France.

**Electric Field Effects on Transport Through Membranes**

R.D. Astumian

The active transport of many ions and molecules is governed by specific enzymes imbedded in the cell membrane. The control of these transport enzymes is of great importance for optimizing and controlling bioreactors.

The electroconformational model formulated by R. Astumian and T. Tsong suggests a mechanism by which enzymes can utilize energy from external electric fields to transport molecules across membranes. Lactose permease, a well studied protein, will serve as an excellent model system to experimentally test the predictions of this model. These experiments will also demonstrate the potential for utilizing electric fields to control active membrane transport in practical systems.

**Biodegradation of Metals**

A.C. Van Orden, S. Woo

Nuclear waste containers are designed to last for approximately 1000 years. The design material for these containers, in two of the planned
repository locations, is A-216 carbon steel. This project seeks to estimate the enhancement of the corrosion rate of these containers by microorganisms. Microorganisms may enhance or induce corrosion by altering the normal electrochemical processes associated with the corrosion of the metal interface.

A variety of microorganisms contribute to the biodegradation of metal interfaces. The work will be focused on two bacteria which are known to be widely distributed and which have been implicated in the corrosion of metals. The two types of bacteria which have been chosen are species of a sulfate reducing bacteria and a species of an iron oxidizing bacteria. The experimental facilities have been completed, the microorganisms have been acquired, and the culturing activity has been initiated.

The experimental work is aimed at elucidation of the mechanisms for biodegradation. The action of microorganisms will be monitored electrochemically and optically by fluorescence imaging. The electrochemical measurement gives the total metal dissolution rate while the fluorescence measurements provide an indication of the quantity of metal which has been taken up by the microorganism.

HIGH TEMPERATURE REACTING FLOWS GROUP

Destruction of Hazardous Waste in Fluidized Beds

A. Macek, N.D. Amin, S.R. Charagundla

Control of products of incomplete combustion, generated during incineration of hazardous wastes, requires an understanding of rates and mechanisms of thermal decomposition and oxidation of its principal constituents (mainly chlorinated hydrocarbons). The experiments to provide such an understanding should be performed under well-controlled operating conditions which simulate full-scale incineration systems. A literature survey, made earlier under EPA sponsorship, showed that fluidized beds offer a promising option for efficient incineration of a wide variety of wastes, including chlorinated hydrocarbons.

The first experimental step was a preliminary study of oxidation of two simple model compounds, propane and methyl chloride. These experiments were performed in a fluidized bed reactor which had been designed and used previously for coal combustion studies. Recently, a new reactor was constructed, allowing longer in-bed residence times, better temperature and chemical composition control of fluidizing gases, and better mixing of model compounds with the fluidizing gas. The reactor has been equipped with a set of on-line gas monitors for determination of destruction efficiencies of organic compounds. Oxidation of propane and methyl chloride was studied at temperatures ranging from 250 to 650°C in beds consisting of particles having different chemical compositions. Increasing catalytic effects were demonstrated as one proceeds from silica to alumina to chromia.
Particle Formation in High Temperature Reacting Flows

M.R. Zachariah, H.G. Semerjian

Investigations are under way to explore the feasibility of using flames as the reacting environment for the formation of refractory particles. The goal of the project is to investigate the underlying physico-chemical processes leading to particle formation and growth, and suggest ways in which one might control the underlying chemistry and physics through changes in process parameters, to affect the final product purity, particle size, and polydispersity. Additionally, several nonintrusive laser diagnostic techniques will be used to evaluate and clarify their limitations and advantages for different applications.

Current efforts have focused on the formation of silicon dioxide particles in a hydrogen/oxygen counter-flow diffusion flame with addition of silane to the fuel. This geometry has been shown to provide a flat, highly uniform environment suitable for optical probing. Temperatures have been measured by both fine-wire thermocouples and OH absorption techniques. In-situ particle size data were obtained using dynamic light scattering and/or scattering assymmetry measurements. These two techniques give comparable results. Particle number densities were determined using static light scattering techniques in conjunction with Mie scattering theory calculations.

Previous results showed that the silane loading, the equivalence ratio, and the temperature affect particle size, shape, and number densities. In addition, the results suggest that particle formation and the eventual growth mechanism are highly coupled to the precursor gas kinetics. Most recently, other silicon containing compounds have been used as the starting material in order to investigate precursor effects. In addition, two numerical models have been developed to simulate the various aspects of particle formation and growth processes. The simulations account for consumption of the reactant, nucleation, and growth, for a given time-temperature history. Future plans include extension of particle formation studies to other refractory oxides and other reactor geometries, e.g., flat-flame burners.

Particulate and Droplet Diagnostics in Spray Flames

C. Presser, A.K. Gupta,* H.G. Semerjian

Dynamics of spray flames are being studied to investigate droplet vaporization, pyrolysis, combustion, and particulate formation processes, and to delineate the effect of chemical and physical properties of fuels on these processes. The results of this study will provide an experimental data base
for the development and validation of spray combustion models being developed by JPL, Sandia, and Los Alamos National Laboratories. The experiments are being carried out in a spray combustion facility, with a movable-vane swirl burner, which simulates operating conditions in practical combustion systems. A combination of nonintrusive probing techniques is being used to obtain comprehensive data on the spray combustion characteristics, including soot particle and droplet size, number density and volume fraction, gas composition, and velocity and temperature fields.

Current research is focused on two areas, namely the effect of fuel properties and atomizer geometry on spray and flame characteristics. To address the first question, experiments are planned with heptane and No. 6 residual oil as fuels, in addition to the earlier experiments with kerosene. Heptane is a single-component fuel which will provide extensive data for modeling efforts. The experiments with No. 6 fuel oil will provide data which are of greatest interest to industry, because of the difficulties encountered in atomization, flame stability, and pollutant emission characteristics. Current flow visualization experiments carried out with heptane have already shown significant differences in flame stability and emission characteristics.

Laser ensemble scattering and Doppler velocimetry measurements are being carried out with an air-assist atomizer typical of those used in industry, especially for heavy fuels. Unlike the pressure atomizer studied previously, this injector can provide different atomization characteristics by varying the atomizer air flow rate for the same fuel flowrate; it thus allows one to study the effects of atomization on overall spray and flame structure. This research nozzle is also being used by investigators at the University of California-Irvine and Carnegie-Mellon University; this will allow for direct comparison with our results and establishment of a broad experimental data base. In addition to the ensemble light scattering measurements, data will be obtained with other measurement techniques: (a) phase/Doppler interferometry; (b) light intensity deconvolution technique (single particle counters); and (c) laser diffraction technique (ensemble line-of-sight). In an effort to reduce data acquisition times and to provide single particle counting capability, a new detection system has been assembled in which two detectors are used to measure both scattering coefficients (Q_{HH} and Q_{UV}) simultaneously, thus determining the instantaneous values of the polarization ratio and particle size.

*University of Maryland

**Optical Diagnostics for Metal Powder Atomization Systems**

C. Presser, S. Ridder,* F. Biancaniello*

Particle size measurement techniques have been evaluated to determine their applicability to jet break-up and droplet formation processes in a metal powder atomization chamber. The techniques of interest to measure particle size, number density, and velocity include: (a) phase/Doppler interferometry and (b) scattering intensity deconvolution techniques. These systems will be used for diagnostics in the atomization chamber to provide
data for development of process models, for input into expert systems, and for process optimization. High-speed cinematography of the upstream portion of the metal spray has indicated the time-dependent nature of the metal atomization process. In addition, a laser diffraction technique has been chosen to provide particle size distribution measurements along a line of sight near the exit of the chamber. This particle size distribution, averaged along a cross section of the process stream, can then be used for process feedback and control. Currently, experiments are underway to demonstrate the feasibility of particle size measurements through the exit section of the atomizer chamber which has been modified to incorporate two windows 180° apart. Interpretation of data obtained through an optically thick stream is the focus of the present work.

*NIST Institute for Materials Science and Engineering

**Numerical Modeling of High-Temperature Reacting Flows**

R.W. Davis, E.F. Moore

High-temperature reacting flows are, in general, typified by strong coupling between fluid mechanical and chemical kinetic processes. In most practical systems, such reacting flows are characterized by large fluctuations in species concentration and temperature which occur over small spatial intervals. In order to gain an improved understanding of such complex reacting flows, a joint numerical-experimental program is being carried out.

Because of its simple flow configuration, this program focuses on the axisymmetric jet diffusion flame. A numerical model of this flame has been developed as part of a joint computational-experimental research effort to study the structure of unsteady diffusion flames. This work is being carried out in cooperation with the Wright Patterson AFB. The model includes buoyancy effects and is currently being used to study the dynamic interactions between the flame surface and the surrounding vortex structures. These interactions are poorly understood at present and they strongly influence the basic physics involved in these flames. The types of interactions predicted by the computations compare well with those observed experimentally. The model provides a complete description of the flow, species, and thermophysical properties fields and permits rapid assessment of the effects of parameter variations. Continued close cooperation between the numerical and experimental efforts is planned to provide guidance to the experimentalists and to ensure that the model remains firmly grounded in reality.

**High-Speed Laser Tomography**

R.G. Joklik, D.R.F. Burgess, R.E. Snyder, H.G. Semerjian

The technique of high speed laser tomography is under development to allow rapid measurements of temperature and chemical species concentration distributions throughout a two-dimensional "slice" within time varying
chemically reacting flow fields. Work has progressed from time averaged measurements of steady phenomena, such as laminar diffusion flames and gaseous jets, to real time measurements in sodium-seeded flames. Using the experience gained, the temperature and OH concentration field were measured in a premixed methane flame in a 5 ms period. This was achieved by sweeping an ultraviolet laser beam through the field every millisecond while tuning the laser frequency over an OH absorption line. The experiment used an axially symmetric flame, requiring only a single measurement angle. The temperature was determined from the measured absorption line width.

Current work has focused on two main areas. To improve the sensitivity of the temperature measurements, particularly in zones of low OH concentrations, a two-line ratio technique is being implemented. The frequency scanning range and speed of the dye laser used for the OH measurements has been extended to allow temperature measurements of this type at a rate greater than 1 kHz. Also, a new multiangular tomographic system has been developed for rapid measurements in assymmetric fields at repetition rates up to 10 kHz. This six-angle system has been used to measure the soot concentration field in rapidly fluctuating ethene-air jet diffusion flames with a time resolution of better than 1 ms. Future experiments will measure mixture fraction, temperature, and OH concentration in these flames. Comparison of these data with concurrent modeling results is aimed at understanding the dynamics of flame-flow field interactions, which control the processes of vortex formation, shedding, and break-up. Details of eddy formation in the jet have also been observed using a laser sheet imaging technique in a plane intersecting the centerline of the jet. In this technique, titanium chloride is seeded into the fuel jet, and titanium oxide particles are formed in a narrow zone by reaction with combustion generated water. Scattered laser light from the particles is then used for flow visualization.

**Flame Temperature Measurements by Laser Excited Fluorescence**

J.J. Horvath, R.G. Joklik, H.G. Semerjian

A new nonintrusive temperature measurement technique, thermally assisted laser induced fluorescence (TALIF), is being developed for measurements in high-temperature chemically reacting flows. In this method, an upper electronic state is populated from the ground state by means of laser excitation. The population in this excited level is collisionally redistributed, then radiatively decays, and the resultant fluorescence is detected as a function of energy level. The temperature can be obtained by plotting the observed fluorescence intensities as a function of the upper energy level. This distribution could also be used to ascertain the presence of a Boltzmann distribution throughout the higher energy levels. One can also measure two wavelengths simultaneously and obtain a temperature from a single laser pulse. The fluorescence observed is from the anti-Stokes line of the excitation pulse, hence this method is applicable to high luminosity flames and conditions of high background Stokes fluorescence.

Initial experiments have used gallium as the seeding species in premixed flames. A tunable dye laser, pumped by a nitrogen laser, was used to excite
the $4p_{1/2}-5s_{1/2}$ transition of Ga at 403.3 nm, and the resultant fluorescence from upper levels was observed. Premixed $\text{CH}_4/\text{Ar}/\text{O}_2$, $\text{CH}_4/\text{Air}$, $\text{C}_2\text{H}_4/\text{Ar}/\text{O}_2$, and $\text{C}_2\text{H}_4/\text{Air}$ flames were studied to determine the useful temperature range of this technique. Temperatures of these flames could be varied from approximately 1950 to 2500 K depending on flow conditions. Measured temperatures were about 100-150 K below the adiabatic flame temperature. Fluorescence signals were also obtained in an ethylene diffusion flame, but an unexpected broad band fluorescence was observed which yielded abnormally high temperatures. To correct for this broad band fluorescence interference, computerized data reduction schemes have been developed.

Recent work has used an Nd-YAG pumped dye laser for greater spectral coverage of the useful wavelengths. This work has focussed on determining the temperature range of useful thermometric species. Time-resolved fluorescence measurements indicated that upward collisional transfer rates are faster than the downward rates, as predicted by theory. Current work involves using a wavelength modulation technique to perform sodium line reversal temperature measurements on various flames to compare with the fluorescence values. Future studies will include substitution of nitrogen in the flame by argon to evaluate quenching effects and the use of naturally occurring molecular species ($\text{OH}$, $\text{CH}$, $\text{C}_2$) for fluorescence studies. The ultimate goal is the development of single laser pulse temperature measurement techniques for use in industrial and scientific applications over a wide range of temperatures.

**Fluorescence Spectroscopy for Control of Paper Pulping Processes**

J.J. Horvath, H.G. Semerjian

There is an increasing need for the development of measurement science and technology for on-line measurement of process variables in the pulp and paper industry. Current process techniques for measurement of delignification rates in the pulping process are based on sampling and off-line analysis systems. The resultant delay prevents the on-line control of the digester and pulping processes, and results in less than optimum operating conditions. The ideal process monitoring technique would be both an in-situ and real-time measurement system, so that important variables of the digestion process can be monitored and corrections applied before a cook is completed. The goal of this project is to develop in-situ techniques, based on fluorescence spectroscopy, for monitoring pulping processes.

In these studies, laser excited fluorescence of black liquor was investigated as a possible monitoring technique for pulping processes. A pulsed dye laser was used to examine the fluorescence spectrum of black liquor solutions. Various excitation wavelengths between 280 and 403 nm were used. Black liquor fluorescence spectra were found to vary with both excitation wavelength and black liquor concentration, providing good detection limits and linear response over a large dynamic range. Recently, measurements have also been made on optically dense pulping liquors, obtained from a paper mill, using a backscatter configuration without any sample dilution. The fluorescence spectra obtained from these samples were found to vary with processing time, indicating a good possibility of using
fluorescence for process control and monitoring. In order to quantify these measurements, additional experiments were performed with well characterized pulp liquor samples of known composition. The results with these samples showed the fluorescence intensity to vary linearly with lignin concentration up to 1 g/l dissolved lignin. The fluorescence spectrum also indicated a chemical change occurring near the end of a cook, something speculated upon in the literature. Fluorescence from paper pulp streams and paper fibers has also been investigated; results indicate the fluorescence signal to be related to the lignin content.

**Optical Diagnostics for Investigation of CVD Processes**

D.R.F. Burgess, M.R. Zachariah

The development of microscopic descriptions of chemical vapor deposition (CVD) processes has been hampered by the difficult task of detecting small concentrations of gas-phase reactive species. Most investigations have focused on macroscopic observables, such as pressure and temperature effects. By providing selectivity in the creation and detection of reactive species in CVD, one can identify the reactions and species which are critical to deposition processes and, consequently, be able to control the uniformity and quality of epitaxial growths. Our approach to this problem is to employ optical techniques, which are highly species specific, to create, detect, and measure the reactivity of important gas phase intermediates in CVD processes. Currently the focus is on the gas phase chemistry of silane and ammonia fragments relevant to silicon nitride deposition.

The experiments are carried out using pre-mixed gases in a windowed cell with a reactive flow of a mixture of silane and ammonia in argon surrounded by an argon shroud flow. The flow rate, concentrations, and total pressure are controlled using electronic flow controllers and a vacuum pump. UV light from an excimer laser is used to photolyze silane and ammonia, creating reactive fragments, and initiating gas phase chemistry. The photolysis process is monitored via emission from excited photofragments. Reactivities of fragments with silane and ammonia are determined by measuring their time dependent concentrations using laser-induced fluorescence (LIF). Silane and ammonia photolysis processes have been characterized using emission spectroscopy under a range of conditions, from concentrations where fragments are rapidly quenched to regions where particles are formed in the gas phase. Future studies will include investigation of the kinetics of the chemical processes important in CVD systems using LIF techniques.

**Optical Sensing in Bioreactors**

J.J. Horvath, A. Enriquez,* H.G. Semerjian, A.E. Humphrey*

Implementation of new biochemical processes for production of new drugs and chemicals, conversion of biomass, etc., requires new measurement capabilities. Bioprocesses require very closely controlled environments, normally realizable only in batch processes. This is mainly due to the complex kinetics of most bioreactions, separate periods of growth and product
formation, biocatalyst degeneration, contaminant risks, and mechanical difficulties of handling a rheologically complex material. Therefore, development of new on-line measurement techniques is critical for future implementation of bioprocesses. Furthermore, nonintrusive measurement methods are desirable to avoid difficulties associated with sampling, contamination, long response time, etc. Optical techniques provide the best potential for making nonintrusive, rapid, and selective measurements. Use of fiber optics can also enable the development of probes which are sterilizable, can provide measurements with good spatial resolution, and can be multiplexed to provide multipoint monitoring capability. Laser-induced fluorescence (LIF), Raman scattering, and infrared absorption techniques will be utilized for measurement of key process variables such as cell mass activity, cell concentration, and concentration of substrates and products.

Experiments have been carried out on fluorescence characteristics of aromatic amino acids and a series of dipeptides and polypeptides to determine the effects of amino acid sequence and various chemical functional groups on the observed fluorescence spectra. Preliminary results with dipeptides of phenylalanine (Phe) and glycine (Gly) have demonstrated significant sensitivity to sequencing. Further studies are underway with dipeptides of tyrosine and tryptophan. The fluorescence spectra of commercially produced biomolecules, such as antibiotics and artificial sweeteners, have also been investigated. Spectra of the components of a typical fermentation, i.e., yeast, nutrient, and the product enzyme, have been examined and characterized as a function of excitation wavelength. Present work involves use of these spectra for on-line monitoring of fermentation using a flow-through cuvette. The characteristic fluorescence spectra from the yeast and nutrients are used to monitor the state of the fermentation, nutrient uptake, and the growth rate of yeast. Good correlation has been obtained between the fluorescence and dry cell weight measurements. A new microbial fermentation system to produce the antibiotic bacitracin is currently being set up; it will be monitored using fluorescence techniques.

Work is also under way with the University of Maryland to develop deconvolution techniques for determining the concentration of single components in complex multicomponent mixtures. Several other approaches are being explored to improve the selectivity of fluorescence measurements. Preliminary measurements performed using two-photon fluorescence and fluorescence lifetimes indicate good promise for improving selectivity. The recently acquired scanning spectrofluorometer has been used to obtain excitation/emission spectra which can be displayed as 3-D plots or contour plots. Data processing techniques are being developed for using these data to determine single components in multicomponent mixtures. In the future, other techniques such as synchronous scanning fluorescence spectroscopy, and Raman and resonance Raman scattering will be used to provide improved species selectivity. Fluorescence techniques are also expected to provide a powerful tool for cell activity and intracellular kinetics measurements.

*Lehigh University
Humidity Calibration

S. Hasegawa, P. Huang, G. Scace

To date, humidity calibrations have been provided using the two-pressure humidity generator which operates over the dew-point range of -60°C to 30°C. In response to an increasing demand, especially from the microelectronics industry, for calibration standards below 1 ppm, a new low-frost point generator facility is under development. This generator will be capable of producing gas streams having moisture concentrations of approximately 15 ppb to above 2 ppm (dew points from -100°C to above -60°C). The system is currently operational and efforts on the low frost point generator have concentrated on (1) continued development of proper operating procedures, e.g., methods to obtain reliable ice coating of the saturator section, and (2) the use of a primary electrolytic moisture concentration measurement method for validation of proper operation.

Thin Film Thermocouples for Heat Engines

K.G. Kreider

A cooperative effort with the Office of Transportation Systems of DoE, NASA-Lewis, a commercial firm, and Purdue University has been used to demonstrate the feasibility of measuring the interior temperatures of ceramic-lined diesel engines. The NIST role was to sputter-deposit the thin film platinum and gold based thermocouples on the sensor plugs used to acquire heat transfer and real time thermal histories of diesel engines. The adhesion technology developed previously at NIST was used to obtain suitable durability and performance on the partially stabilized, plasma sprayed zirconia cylinder liners. Engine tests performed at Purdue University on a diesel engine verified the theoretical predictions made in the DoE programs and corrected earlier misleading results obtained with inferior probes. Thus the advantages of ceramic insulation in these diesel engines were verified.

A patent application has been submitted to the Department of Commerce and the DoE on the use of sputtered ultrathin bonding layers of reactive metals between the ceramic and the noble metal sputtered thin film thermocouples. Continuing effort in this area is planned to assist the DoE engine test program and to develop high temperature (up to 1750°C) sputtered thin film thermocouples.

Solid State Gas Sensors

S. Semancik, T.B. Fryberger

Experimental research has been done on semiconducting oxide materials to examine the mechanistic processes at work in conductance-type gas sensors. The ultimate goal of this work is to improve the sensing properties of such solid state materials by understanding how adsorbed gases modify their
electrical properties. Tin oxide (SnO₂) has been the focus of these studies since it is capable of responding to both oxidizing and reducing gases, and is already used as the base material in some gas sensors.

Results obtained thus far, in model studies on SnO₂ crystals, have demonstrated the key role of oxygen vacancies and structural defects in determining the conductivity level for this n-type semiconductor. We have also shown that vacancy concentration changes can occur primarily in the outermost portion (~5 nm) of SnO₂(110) crystallites; thereby dominating the electrical behavior of the entire crystallite. These findings are very important since they indicate that future sensors may take advantage of the surface sensitive response in materials like tin oxide to minimize undesirable sensor characteristics (e.g., slow response, drift, hysteresis) by suppressing bulk diffusional processes.

We are also developing an increased understanding of the action of metal additives for producing enhanced and more selective sensor response. Experimental work on the Pd/SnO₂ system has shown that the chemical interaction between palladium and the base oxide is relatively weak, and that the Pd tends to cluster when it is surface-dispersed on various types of SnO₂ specimens. These island-like overlayers produce a composite metal/oxide system with semiconducting characteristics that are desirable for gas sensing applications. When tested as a hydrogen sensor, our Pd/SnO₂ prototype specimen exhibited a 16-fold enhancement over pure SnO₂. These results, if compared to those for bulk-loaded Pd in SnO₂, suggest that higher detection efficiencies can be attained using surface-dispersed additives.

Continued work in this project will involve investigating response modifications produced by other selectivity enhancing metals including silver, platinum, and tin. We will also study the temperature and pressure dependence of gas-induced conductivity changes in metal/SnO₂ systems, as well as sensing interference effects that develop in gas mixtures.

**Ultrathin Chemical Sensors**

S. Semancik, M.J. Tarlov, T.B. Fryberger

This new project will expand upon findings from our earlier work on gas sensing materials to develop the scientific base for an advanced generation of detection elements for use in gaseous and liquid environments. The fundamental idea is that sensing processes can be limited to the surface regions of certain materials, thereby eliminating measurement problems that can originate in the bulk, e.g., drift and hysteresis.

Oxide films, having thicknesses of 1 to 10 nm, will be deposited and characterized (interactively) in order to optimize their sensing capabilities. A primary objective of this project will be to determine the ultimate effectiveness for (ultra)thin oxide films when used in multisensor arrays. Efforts will concentrate on ultrathin forms of two proven sensing oxides: tin oxide (SnO₂) and iridium oxide (IrO₂). Bulk and thick film forms of these oxides have already been used successfully in gas sensing and
pH sensing applications, respectively. We will consider pure SnO$_2$ and IrO$_2$ as well as purposely modified forms produced by the introduction of various "dopants" (including catalytic metals).

In the initial stages of work, which took place during FY 88, plans were developed for a special ultrahigh vacuum facility where oxide films can be deposited, characterized, and tested. Construction of this equipment will take place in FY 89. Two aspects which will be investigated first are the type of oxidation procedure to be used for forming the films and the nature of the epitaxy that occurs on various substrates. Preliminary results for SnO$_2$ have indicated difficulties with thermal fabrication procedures; therefore, we expect to move next to reactive deposition processing. While early parts of the research will focus on fabrication techniques and microstructural characterization, the later efforts will be concerned with response behavior and material stability in operation. New electrical measurement capabilities will also need to be developed in the course of the project.

The study of these novel sensing elements is expected to have a major impact on the development of improved thin film forms of solid state materials for gaseous and aqueous composition sensing. Successes in this research program would also point the way for using planar technology to manufacture multicomponent, selective sensor arrays.

**Superconducting Sensors**

K.G. Kreider

Thin film YBa$_2$Cu$_7$O$_{7-x}$ superconductors were produced by magnetron sputtering from a single target followed by crystallization and oxidation in oxygen. These films were produced on monolithic substrates including MgO single crystals and yttria-stabilized ZrO$_2$ and were produced on silicon wafers and alumina substrates using magnetron sputtered ZrO$_2$ as a chemical diffusion barrier during the 900°C heat treatment. Two areas of interest to CCT are the development of sensors for the chemical industries, based on superconducting quantized interference devices (SQUIDS), for detection of charge exchange reactions, and the chemical reactivity of the films to H$_2$O and CO$_2$ in air. Early studies have focussed on the relationship between film stoichiometry and fabrication parameters. It was found that controlling the oxygen partial pressure during sputtering was extremely critical to obtain 1:2:3 stoichiometry and sharp high temperature superconducting transitions.

**IrO$_2$ Ionic Sensors**

M.J. Tarlov, K.G. Kreider, P.H. Huang, S. Semancik

Reactively sputtered iridium oxide (IrO$_2$) is being investigated as a pH sensing material. The pH sensitive iridium oxide films offer several advantages over conventional glass pH electrodes: (1) iridium oxide films are stable in aqueous solutions of extreme pH and temperature whereas glass electrodes tend to dissolve, (2) iridium oxide thin films can be readily
deposited on probes that are smaller and more mechanically rigid than glass electrodes, and (3) iridium oxide films have a much lower impedance than glass membranes. During the past year, we have been evaluating the pH sensing performance of DC magnetron reactively sputtered iridium oxide films relative to that of the glass electrode. In addition, ultrahigh vacuum electron and ion spectroscopies have been used to examine the composition and structure of model iridium oxide sensor surfaces. It is expected that this will provide an improved microscopic understanding of the pH sensing mechanism and the cause of electrode instability.

A number of criteria have been used to evaluate the performance of iridium oxide as a pH probe. Iridium oxide films deposited on a variety of substrates have shown near-Nernstian behavior in the pH range of 2 to 12. Also, the sensitivity of the films to ionic interferences has been relatively low in comparison to the glass electrode. Preliminary work has indicated that dissolved redox and gas species may represent the most serious interferences for iridium oxide electrodes. This is not surprising in light of iridium oxide's electronic conductivity. Electrode potential drift (instability) has been another problem, and slow hydroxylation reactions at the electrode/solution interface are thought to be responsible. A systematic study of the relationship between IrO₂ film crystallinity (film structure may be controlled from amorphous to polycrystalline) and electrode response is underway.

To understand the fundamental reactions occurring at the IrO₂/solution interface that determine electrode behavior, model IrO₂ sensor surfaces were examined with x-ray and ultraviolet photoemission, and ion scattering spectroscopy. Surprisingly, little or no reaction was observed between large doses of gas-phase water and clean IrO₂ surfaces prepared by ion bombardment and annealing in oxygen. However, it was found that adsorption could be activated by rf plasma excitation. The results obtained from these model surfaces will greatly aid in the interpretation of data obtained from "real" IrO₂ sensor surfaces.

The combination of electrochemical and surface analytical techniques are the basis for a research strategy directed toward the development of improved ionic sensing materials. An understanding of the fundamental principles of electrode operation is a necessary step in the logical design of more selective and specialized ionic sensors.

5. PUBLICATIONS


Fryberger, T.B., Erickson, J.W. and Semancik, S., Chemical and electronic properties of Pd/SnO2(110) model gas sensors, Surface and Interface Analysis (in press).


Robertson, J.L., Moss, S.C. and Kreider, K.G., Comparison of sputtered amorphous and quasicrystalline films of Al.72Mn.22Si.06, Phys. Rev. Let., Vol. 60, No. 20 (May 1988).


Tsong, T.Y., Lin, D.S., Chauvin, F., Gaigalas, A. and Astumian, R.D., Resonance electroconformational coupling: an electric field induced enzyme oscillation for cellular energy and signal transduction, Bioelectrochemistry and Bioenergetics (submitted).


6. CONFERENCES AND WORKSHOPS

CONFERENCES

Session on Flame Models at the 1987 Fall Technical Meeting of the Eastern Section of the Combustion Institute, Gaithersburg, MD, Nov. 2, 1987. Chaired by R.W. Davis.

Session on Sprays at the 1987 Fall Technical Meeting of the Eastern Section of the Combustion Institute, Gaithersburg, MD, Nov. 2, 1987. Chaired by C. Presser.


WORKSHOPS


Sponsored Workshop on the Role of Cooperative Phenomena in Understanding Electromagnetic Field Effects in Biological Membranes, held on Sept. 7-8, 1988, at Bethesda, MD.

TECHNICAL ACTIVITIES
OF THE
TEMPERATURE AND PRESSURE DIVISION

A.O. McCoubrey, Acting Chief

1. INTRODUCTION

The need that is addressed by the Division is accurate measurement of temperature and pressure throughout the United States on a basis that is consistent with measurements of these quantities in other industrial nations of the world. National reference standards for temperature and pressure are necessary for accurate measurement of these quantities; the program of the Division is part of the statutory responsibility of NIST to provide the U.S. national reference standards for measurements and to provide related services to make such reference standards useful in industry, science, and government. The CCT/NIST approach to meeting the need for accurate measurements of temperature and pressure is based upon research to establish the scientific basis for temperature and pressure reference standards, technical development to implement such reference standards, delivery of services derived from the operation of these reference standards, the development of technology to assist users in the realization of benefits from the services, and publication of related information.

More specifically, the program of the Temperature and Pressure Division is focussed upon temperature measurement technology below the pyrometric range, and pressure measurement technology from pressure levels of several hundred atmospheres to those that prevail in the most modern state-of-the-art vacuum systems. The activities within the present program include:

- research directed toward new optical methods for the accurate measurement of temperature and pressure under dynamic conditions (millisecond time resolution) and within small volumes (millimeter dimensional resolution);

- research directed toward the evaluation of the optical fiber thermometer as an absolute thermodynamic standard thermometer, and the use of this thermometer as a means to link the pyrometric temperature scale with the practical temperature scales [IPTS-68(75) and the pending ITS-90] at the gold point, the silver point and, possibly, the aluminum point;

- research to advance the technologies for realizing or maintaining accurate temperature and pressure scales;
• research and development to refine the U.S. National reference standards for temperature and pressure;

• development to improve the methods for transferring the values of NIST standards for temperature and pressure to users in industry, science, and government;

• calibration services and measurement assurance program (MAP) services to transfer the values of NIST units and scales for temperature and pressure to users in industry, science and government;

• special test services to support temperature and pressure measurement needs for which calibration or MAP services are not established;

• participation in the temperature and pressure related work of the Consultative Committees of the International Committee of Weights and Measures;

• participation in the temperature and pressure related work of domestic standards committees;

• development to improve quality control and reduce uncertainties in pressure calibration services based on dead weight piston gages;

• documentation and publication of research results, methods for calibration services, and methods for special test services.

Important changes in the thrust of the Division activities related to temperature scale research have been made during the past year. In October, 1987, the research project to establish a millikelvin temperature scale was terminated, and the available staff effort was redirected toward noise thermometry within the range of the new international temperature scale, ITS-90, and the production of a standard reference material device, SRM-768, for temperatures from 0.01 K to 0.5 K. In the fall of 1988, very-low temperature research (noise thermometry and the improvement of SRM-768) was also terminated, and the resources were again redirected to the development of facilities for the realization of the new international temperature scale, for temperatures below the triple point of water. The possibility of producing a revised version of SRM-768 (relaxed specifications for W and Be superconducting fixed points) will be considered in the future; the decision will depend upon user needs for the technology at the present state of development.

2. GOAL

The goal of the Temperature and Pressure Division is to provide the required NIST services to support measurements of temperature and pressure at necessary levels of accuracy in industry, science, and government throughout the United States. This goal is addressed by:
• the conduct of research to provide an up to date scientific basis for national reference standards for temperature and pressure;

• the development and dissemination of efficient and effective services based upon these reference standards and incorporating advanced technology as required to minimize cost to users, optimize quality, and increase accessibility;

• the conduct of research and development to anticipate future needs in industry, science, and government growing out of emerging and advancing technologies;

• the conduct of research and development to advance temperature and pressure measurement technology for the benefit of U.S. industry, science, and government;

• the production of scientific publications and technical reports to optimize the availability to users of technical results and methods from Division programs.

3. GROUP AND PROGRAM FUNCTIONS

The technical activities of the Division are carried out in five groups and one Division Office program.

GROUPS

• Thermometry Research and Calibration Services - B.W. Mangum, Group Leader

The program of this Group includes calibrations and related services for resistance thermometers, thermocouples, thermistors, laboratory thermometers (mercury in glass), and digital thermometers. The Group also conducts research and development leading to new thermometric fixed points and improvements (including automation) of the facilities for the maintenance of the International Practical Temperature Scale [IPTS-68(75), to be replaced by ITS-90].

• Temperature Scale Development - J.F. Schooley, Group Leader

This Group is responsible for studying optical fiber thermometry as a metrological tool; for completing the NIST gas thermometry contribution to the 1990 International Temperature Scale; for assessing the prospects for utilizing noise thermometry for metrological and industrial measurements above 0.5 K; and for the preparation and calibration of SRM 767A and 768. Outputs include data, physical theories and descriptions, and devices. Principal non-CCT sponsors of the work of this Group include the DoD and the NIST Office of Standard Reference Materials (OSRM).
• Optical Measurements of Temperature and Pressure - G.J. Rosasco, Group Leader

The Optical Measurements of Temperature and Pressure (T and P) Group conducts fundamental research into the process of spectral line formation in order to provide a basis for accuracy in the use of nonlinear Raman spectroscopies for the determination of T and P. Accurately known conditions of T, P, and species concentration are established in gas phase systems significant for diagnostic applications. Reference spectra are measured and analyzed in terms of line formation theory to determine the limits of accuracy for T and P measurements. The physical phenomena important in determining the lineshape function are investigated both experimentally and theoretically. Lineshape functions are tested and the molecular parameters which specify these functions are determined. Theories which describe these molecular parameters as functions of T, P, and composition are developed and tested. Measurement accuracy is provided in the form of validated, predictive expressions for the spectral distribution as a function of T, P, and composition.

A long range objective for this group is the development of a means to assure the accuracy of measurements of time varying T and P. The approach is to develop at NIST an accurately characterized source of T(t) and P(t). The values of these time varying quantities will be determined by use of the optical diagnostic technique whose accuracy was established from the research described above. The dynamic source can serve as the basis of a calibration service and will allow the measurement of the temporal response of sensors.

• Piston Gage - C.D. Ehrlich, Group Leader

The piston gage is the standard instrument for precise pressure measurements in the range above the limits of manometry. The instrument consists of a carefully made piston fitted into a matching cylinder which is, in turn, connected to a pressure generating system. The piston is loaded with measured weights, floated by adjusting the cylinder pressure using a transmitting fluid, and rotated to help attain concentricity of the piston in the cylinder. This rotation both minimizes the possibility of and aids in the detection of metal-to-metal contact, which causes unwanted frictional forces. The pressure is calculated as the ratio of the downward force due to the weights and the piston, and the 'effective area' of the piston-cylinder combination. The goal of the Piston Gage Group is to determine the effective area at atmospheric pressure, (A₀), and the change in the effective area with pressure, with an accuracy sufficient to: (a) provide U.S. piston gage manufacturers with the needed calibration services to keep their products competitive in the world market; (b) meet the need for increased accuracy requested by our calibration service customers, such as the DoE and DoD laboratories; and (c) participate effectively with other national standards laboratories in setting international standards for pressure calibrations.

• Low Pressure, Vacuum and Leak Rate - C.R. Tilford, Group Leader

This group develops standards, provides calibration services, and characterizes instrumentation over twelve decades of pressure from above
atmospheric to ultra-high vacuum. Similarly, leak rate (very low flow rate) standards are maintained and used for the calibration of helium leaks between $10^{-8}$ and $10^{-11}$ mol/s. The specialized measurement capabilities of the Group are used in the development of new measurement techniques and, to a limited extent, in the determination of material properties. This work has enjoyed outside support from the DoE Office of Fusion Energy, the Department of Defense, Sandia National Laboratories, and the NIST Office of Nondestructive Evaluation.

DIVISION OFFICE PROGRAM

- Nuclear Magnetism - H. Marshak, Research Scientist

This project is concerned with nuclear orientation thermometry for the realization of a temperature scale in the millikelvin temperature region. The past year has been devoted to the reduction of experimental data and writing a number of publications. This work will be completed during the first quarter of FY89, reflecting the decision to terminate research on the millikelvin temperature scale.

4. SELECTED PROJECT SUMMARIES

THERMOMETRY RESEARCH AND CALIBRATION SERVICES GROUP

Calibration Services

B.W. Mangum, W. R. Bigge, G. W. Burns, E.R. Pfeiffer, M.G. Scroger, G.F. Strouse, J.A. Wise

The objectives of this program are (1) to maintain the IPTS-68(75) in the range 13 K to 1337 K [the region of the scale in which the standard instruments are the standard platinum resistance thermometer (SPRT) and the Pt-10%Rh/Pt thermocouple (t/c)]; (2) to make improvements in the realization of that scale; (3) to disseminate the scale (through calibrations, precision measurement seminars, MAPs, lectures, publications, interactions with standards-writing organizations, etc.); and (4) to prepare for implementation of a new International Temperature Scale. Also, an additional objective is to maintain the Provisional 0.5 K to 30 K Temperature Scale (EPT-76) and to provide calibration services based on that scale.

133
The following table outlines the calibration procedures.

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Calibration Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 K to 500 K</td>
<td>Capsule SPRTs</td>
</tr>
<tr>
<td>78 K to 904 K</td>
<td>Long-stem SPRTs</td>
</tr>
<tr>
<td>904 K to 1337 K</td>
<td>Type S t/c</td>
</tr>
<tr>
<td>273 K to 2373 K</td>
<td>Noble, base, and refractory metal t/c</td>
</tr>
<tr>
<td>100 K to 815 K</td>
<td>Liquid-in-glass thermometers, low temperature thermocouples, thermistors, IPRTs,* digital thermometers</td>
</tr>
</tbody>
</table>

*Industrial Platinum Resistance Thermometer

During the past year, the Temperature Calibration Group performed many precision calibrations for domestic industrial and governmental users and a few for foreign users. Those calibrations provide traceability to the IPTS-68(75) maintained at the NIST. The following calibrations were performed:

<table>
<thead>
<tr>
<th>Service</th>
<th>Number of Items</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 33010C, long-stem SPRT</td>
<td>30</td>
</tr>
<tr>
<td>Type 33020C, long-stem SPRT</td>
<td>52</td>
</tr>
<tr>
<td>Type 33050C, capsule SPRT</td>
<td>11</td>
</tr>
<tr>
<td>Type 33040C, capsule SPRT</td>
<td>2</td>
</tr>
<tr>
<td>Type 33120M, SPRT MAP</td>
<td>1, 8 SPRTs</td>
</tr>
<tr>
<td>Type 33060C, Rhodium-Iron RT</td>
<td>7</td>
</tr>
<tr>
<td>Type 33060C, Germanium RT</td>
<td>3</td>
</tr>
<tr>
<td>Thermocouples</td>
<td>240</td>
</tr>
<tr>
<td>Liquid-in-glass thermometers</td>
<td>600</td>
</tr>
<tr>
<td>Low-temperature thermocouples</td>
<td>22</td>
</tr>
<tr>
<td>Thermistors; IPRTs; digital thermometers</td>
<td>50</td>
</tr>
</tbody>
</table>
In conjunction with the rhodium-iron (RIRT) calibrations, it was found that results on the NIST reference RIRTs over a six-year period indicate that our original two rhodium-iron reference standards for EPT-76 are stable within about 0.1 mK with respect to each other and with respect to stable platinum reference standards. This stability is better than that reported by most other national standards laboratories.

**Thermometric Fixed Point Development**


During the past year, considerable effort has gone into constructing, assembling, and evaluating temperature fixed-point cells for use in calibrating SPRTs, on both the IPTS-68(75) and the soon-to-be-adopted ITS-90. Experimental problems associated with realizations of some of the new fixed points of the ITS-90 were addressed also. The work on the fixed points included:

1. Completed initial testing of five (5) Sn freezing-point cells (constructed previously) containing 99.9999+% pure metal of SRM 741 and seven cells of zinc filled with 99.9999+% pure metal of SRM 740.

2. Constructed and tested two Sn and two Zn freezing-point cells containing 99.9999+% pure Zn in shot form from commercial sources and compared results with Sn and Zn freezing-point cells containing SRM metals. The Zn in shot form was being evaluated in anticipation of purchasing and certifying new metal for SRM 740. These four freezing-point cells of tin and zinc were constructed for commercial firms.

3. Samples of 99.9999+% pure Al and Ag and other freezing-point cell components were purchased for the construction of cells to be used in an international comparison with similar cells from the IMGC (Italy) and INM (France).

4. Two large cells, filled with 1500 g of 99.9999% pure indium in a Teflon inner container located in a stainless steel outer container, were investigated and put into use in a new furnace in our PRT Calibration Laboratory to provide a freezing point to be used as a check point in the routine calibration of SPRTs. Data obtained on these cells were analyzed and a paper describing the results of the investigation was written. The pressure dependence of indium was found to be 48.9 ± 0.5 mK/MPa and the freezing-point temperature to be 156.6341°C.

5. Freezing and melting curves of eleven borosilicate and two stainless steel and mercury cells were investigated at their triple points. Seven borosilicate cells and the two stainless steel cells were sealed over thirteen years ago. One borosilicate cell was capped but not sealed over the same period. Three borosilicate cells were recently prepared by vacuum distilling samples which were stored in capped soft glass bottles. The earlier measurements on the ten cells, when they were freshly made, showed freezing ranges of less than 0.1 mK for up to 80% of their freezes. The freezing ranges of recent measurements on them were 0.1 to 0.2 to over 0.5 mK. The newly made cells also exhibited these broad freezing ranges. Soda
lime glass contains Na₂, CaO, MgO, and Al₂O₃ in addition to SiO₂; borosilicate glass contains Na₂O₃, B₂O₃, and Al₂O₃ in addition to SiO₂. Any free metals formed by chemical reaction would dissolve in mercury. Although from the standpoint of chemical equilibria, small amounts of free metals could form, such reaction seems unlikely since mercury is far below the metals in the electromotive force series. In the case of the stainless steel cells, small amounts of nickel are expected to have dissolved in the mercury. Further analysis of the assembled data is in process. For the mercury triple point or freezing point, cells of Teflon or other suitable plastics, that are free of metals, should be tried.

6. A furnace, electronic control, and power supply for realizing the freezing point of indium was designed, constructed, and assembled. Tests on an existing indium cell showed that the freezing point can be reproduced within 0.1 to 0.2 mK. In a single freeze, the calibration of six SPRTs has been demonstrated to be repeatable to within about 0.1 mK.

7. Some furnaces used for pre-heating SPRTs close to the temperatures of calibration prior to their insertion into freezing-point cells were constructed and additional ones are currently under construction.

8. The construction of a new apparatus, incorporating an argon triple-point cell, that is to be used in the calibration of long-stem and capsule SPRTs nearing completion. This apparatus will accommodate seven long-stem SPRTs and six capsule SPRTs. The external reservoirs (52 l total) for containing the argon sample were cleaned, assembled, and tested to contain the gas at 900 kPa without leaks. The sample cell proper was assembled with the thermometer wells and tested for vacuum and pressure (900 kPa) after thermal cycling three times between room temperature and the liquid nitrogen temperature. Two of the flanges, where the long-stem SPRTs will be tempered, have been assembled, and heaters for their respective "cans" have been wound. The "vacuum flange" was just assembled. Preparations are being made to test the vacuum containment of the argon triple-point cell and temperature control shield system. This will be followed with the assembly of the helium heat exchange manifold for the long-stem SPRT wells. Then, the coupling to the top flange, from which the entire argon triple-point assembly will be suspended inside the liquid nitrogen Dewar, will be assembled. When construction of this apparatus is completed, it will be tested and installed in the PRT Laboratory, replacing the comparison apparatus currently used at the oxygen point.

9. Thirteen SPRTs that were found to contain excessive moisture were examined for possible repair. Eleven were selected for repairs by opening their hermetic seals, baking, pumping dry, and resealing with dry argon/5% oxygen gas mixture. Nine of these SPRTs were found unexpectedly to leak. The leaks were repaired and the external platinum leads were replaced on some of the SPRTs. The repaired SPRTs were tested to be adequately dry. The repair process and testing showed that the manufacturers should follow more stringent quality control. As found in prior work, it was shown that the annealing process can generate enough water to make the SPRT contain excessive moisture.
Automation, Modernization and Upgrading of the Calibration Laboratories


The temperature related calibration laboratories in which the NIST maintains and disseminates the IPTS-68(75) are being modernized, upgraded, and semi-automated; this is long overdue. Most of the instrumentation required for this work has been purchased, but only in the PRT Calibration Laboratory has any of it been installed and some of the programming done. The upgrading and automation of the PRT Calibration Laboratory are nearing completion, but those for the Thermocouple and Liquid-in-Glass Calibration Laboratories are just beginning.

During calibrations of SPRTs, comparisons have been made between a manually-operated DC current comparator bridge and an automatic DC pulse bridge in preparation for automation of the measurement and analysis processes in the calibration of SPRTs.

Thermocouple Research for the DOD Combined Calibration Group

G.W. Burns, M.L. Reilly

With support from the U.S. Navy Metrology Engineering Center, work continued on the development of a calibration procedure for a commercial heater probe. This probe was specifically designed to test the thermocouple harness of specific jet engines. The engines are used in the Navy's VH-IN helicopter. The heater probe had been previously designated by the Navy as "difficult to calibrate," due to the lack of a reliable standard.

Extensive tests to develop suitable calibration standards and procedures for the heater probes were conducted during FY88. The calibration stability and repeatability of several heater probes and of specially manufactured Type N and Type K thermocouples were evaluated. The studies included determining the effects of cycling the heater probes between room temperature and 800°C, and of heating the heater probes for prolonged periods of time at 800°C. In addition, the effects on the emf-temperature relationships of Type N and Type K thermocouples after isothermally annealing them at 750 and 800°C for periods up to 200 h were measured both in the heater probes and in a laboratory calibration furnace.

One heater probe, which was manufactured in March 1988 and had not been used previously, was tested over a four month period during which time it was cycled 59 times between room temperature and 800°C and was heated for approximately 500 h at 800°C. The change in its calibration at 800°C did not exceed 1°C during the test period. Another heater probe, manufactured in October 1974 and having considerable use since its manufacture, exhibited a calibration change of about 3°C after four test cycles and about 47 h of heating at 800°C.

Sheathed Type N thermocouples that had been isothermally annealed for 8 h at 800°C exhibited emf changes equivalent to about 0.6°C after 200 h of heating at 800°C at fixed immersions. The results showed that the
calibrations of such thermocouples performed by comparison with Type S reference thermocouples in a laboratory calibration furnace could be transferred to the heater probes with a total uncertainty of 1.5 to 2°C.

Medical Thermometry

B.W. Mangum, G.A. Evans, Jr.

The goal of this program is to develop a set of fixed temperature points and a means of using them to calibrate transfer standards for the temperature region of interest (0 to 200°C) to the medical community.
The following table outlines the temperature fixed point program:

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_f$ (°C)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>156.635 ± 0.002</td>
<td>SRM 1971, 100 cells tested.</td>
</tr>
<tr>
<td>Succinonitrile</td>
<td>58.0805 ± 0.0015</td>
<td>SRM 1970, 115 cells tested, RSI article published, NBS J.Res. paper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SP 260-101 published.</td>
</tr>
<tr>
<td>Phenol</td>
<td>40.922</td>
<td>Investigated; good point, but not SRM.</td>
</tr>
<tr>
<td>n-Lauric acid</td>
<td>43.95</td>
<td>Investigated; rejected.</td>
</tr>
<tr>
<td>n-Docosane</td>
<td>43.8905</td>
<td>Investigated; to be SRM.</td>
</tr>
<tr>
<td>Rubidium</td>
<td>39.303 ± 0.005</td>
<td>SRM 1969, article published in TMCSI, SP 260-87 published.</td>
</tr>
<tr>
<td>Ethylene carbonate</td>
<td>36.3238 ± 0.0004</td>
<td>Alternative to Rb; paper published in Metrologia.</td>
</tr>
<tr>
<td>Gallium</td>
<td>29.772 ± 0.001</td>
<td>SRM 1968, several papers published.</td>
</tr>
</tbody>
</table>

Since there was a special (even critical) need for two temperature fixed points, at about 41 or 42°C and 44 or 45°C, bracketing the hyperthermia range used in cancer therapy, an investigation to find and develop such fixed points was continued. In the NIST study, the freezing/melting behavior of small cells of phenol, n-lauric acid, and n-docosane was investigated. Results of that investigation led to the selection of phenol and n-docosane as the materials for the two fixed points. Based on that investigation, n-docosane will be produced at the NIST as SRM 1973. The National Cancer Institute funded some of this work; the NIST Office of Standard Reference Materials (OSRM) funded the remainder.
TEMPERATURE SCALE DEVELOPMENT GROUP

Noise Thermometry Above 0.5 K

W.E. Fogle, J.H. Colwell, R.J. Soulen, Jr. (Guest Researcher), W.E. Bowers

The capability to realize the EPT-76 (0.5 K to 30 K) temperature scale in the Noise Thermometry Lab was implemented through the introduction of calibrated thermometers and the SRM 767A device and the associated hardware and software. The noise thermometer hardware was updated with the installation of a new data acquisition system, a new frequency counter, and an uninterruptible power supply. A paramagnetic Curie-law thermometer capable of use up to 3.5 K was designed and built, along with a specially designed mutual inductance bridge. These steps will permit the evaluation of noise temperatures to considerably higher temperatures than before, with faster data rates and more reliable results.

SRM 768 Production and Calibration


The $^3$He melting-curve apparatus used for precise temperature registry has been improved in order to facilitate its use in determining the absolute values of temperature for the superconducting transitions of the SRM 768. The existence of proximity effects in the beryllium transitions has been pursued as a means of providing the user with a better technique for their employment in precision thermometry. The international intercomparison of SRM 768 devices with Dutch and West German laboratories as a means of intercomparing their present realizations of temperature scales in the range 0.01 K to 0.5 K has progressed to the point of exchanging specially-prepared devices.

Installation of User-Facility Dilution Refrigerator

J.H. Colwell, W.E. Bowers

A surplus $^3$He-$^4$He dilution refrigerator has been installed. The apparatus, capable of maintaining temperatures as low as 0.015 K on a continuing basis, has been utilized by guest workers from MIT and elsewhere (A. Drukier, T. Girard, and their collaborators) for the study of massive-particle detectors based upon superconductivity.

Analysis of Sapphire Optical Fiber Probes

M.L. Reilly, S.J. Pang (Guest Researcher)

Careful study of three commercial sapphire optical fiber probes has elucidated the problems in their use in metrological-quality radiation thermometry. Experiments performed include light scattering and absorption. Both properties are temperature dependent. Further studies show unexpected reactivity of sapphire with the constituents of Inconel protective sheaths,
forming islands of Cr, Ni, and Fe oxides on the fiber surfaces. Talks on optical fiber thermometry were presented to the ASTM E-20 Committee and to an ASTM Workshop on Temperature Measurement.

Analysis of Thermocouple Test Units

M.L. Reilly, G.W. Burns

Automated data acquisition and analysis techniques were perfected and utilized for the study of thermocouple-based test harnesses on behalf of the U.S. Navy.

Thermodynamic Temperatures in the Range 0°C to 660°C By Gas Thermometry

J.F. Schooley, R.E. Edsinger (Guest Researcher)

Thermal expansion measurements were made and analyzed on several samples of the NBS Gas Thermometer working bulb, permitting the final calculation of kelvin thermodynamic temperatures in the range 230°C to 660°C. These were compared to the values obtained on the 1968 International Practical Temperature Scale. The results were presented in a paper submitted to the journal "Metrologia" and in a talk before the National Conference of Standards Laboratories.

Production and Calibration of SRM 767A Devices

J.F. Schooley, G.A. Evans, Jr., R.J. Soulen, Jr. (Guest Researcher)

With support from the NIST OSRM, a fresh supply of SRM 767A devices was prepared and calibrated. In addition, the first experiments were performed to study the suitability of several types of high transition-temperature superconductors for the 767A device.

OPTICAL MEASUREMENTS OF TEMPERATURE AND PRESSURE GROUP

G.J. Rosasco, W.S. Hurst, J.P. Looney, W.J. Bowers

The determination of the temperature and J dependence of the line broadening coefficients for CO:CO has been completed. A modified exponential gap (MEG) law has been shown to account for these data. This law is being tested against our recent measurements of the collisional collapse of the Q-branch in the range 0.1 to 1 MPa and 295-1000 K. Line shifting as a function of J and T has been determined for CO:CO (and additionally for N2:N2) over this same range of T and P. The latter data are necessary in order to accurately model the collisional collapse. A reliable predictive basis should be completely specified by the end of FY89.

A paper describing the spectral lineshapes for simultaneous forward-backward scattering in a multipass cell has been prepared. In the course of these studies, evidence for the applicability of the soft collision model for describing the combined effects of velocity and phase changing collisions in D2:D2 and D2:He has been obtained. Similar measurements of D2:Ar have revealed new features not predicted by any known theory for the spectral
distribution arising from the combination of velocity and phase changing collisions. Theoretical investigation and further experimentation are planned for this important and novel system.

Experiments and preliminary analysis of the temperature (300-1000 K) and pressure (0.1 to 5 MPa) dependence of the self-broadened H₂ Q-branch have been completed. Both phase and velocity changing collisions play an important role in this spectrum. The temperature and J dependence of the line shifting also has been determined. The analysis to this point has shown that the line broadening can be explained by a combination of a temperature dependent vibrational dephasing contribution and a MEG law based description of the rotationally inelastic portion of the linewidth. The velocity changing collisions in the pressure regime of interest are typically described by an effective optical diffusion coefficient. At room temperature this coefficient is almost equal (within 3%) to the mass (self) diffusion coefficient. Preliminary indications from our measurements are that the optical diffusion coefficient deviates markedly from the mass diffusion coefficient at elevated temperatures. Verification and further elucidation of the temperature dependence of this important contribution to the linewidth will be concluded in FY89. In addition to their importance in propellant diagnostic studies, we are interested in the pure hydrogenic and hydrogenic mixed gas systems because of their potential use as working media in generators of rapidly varying temperature and pressure.

PISTON GAGE GROUP

Piston Gage Calibration Services


The Piston Gage Calibration Service has significantly increased its workload (and income) for the second straight year; it is up 43% in workload over the previous year's comparable increase. These increases are largely due to our accommodating the major U.S. manufacturer of piston gages and the U.S. Air Force by providing approximately 100 additional gas-operated piston/cylinder calibrations from June 1987 to June 1988. Fortunately this workload has now been reduced by demonstrating that the quality control of the manufacturer is quite good, thereby eliminating the need by the Air Force for 100% NIST calibration. We will be looking to reduce our calibration workload even further by encouraging users to go to secondary calibration sources whenever feasible, perhaps by participating in MAP programs with selected laboratories. This will free up NIST personnel to spend more time recalibrating our own primary and secondary standards, training new personnel, and bringing newly acquired primary standards on-line. However, this will have the drawback of reducing calibration income, and perhaps tying up a significant amount of staff time in the MAP program itself.
A breakdown of FY88 calibrations is given in the following Table:

<table>
<thead>
<tr>
<th>Service</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas piston gages</td>
<td>36</td>
</tr>
<tr>
<td>Gas piston gages (special)</td>
<td>80</td>
</tr>
<tr>
<td>Gas transducers</td>
<td>2</td>
</tr>
<tr>
<td>Oil piston gages</td>
<td>35</td>
</tr>
<tr>
<td>Controlled-clearance piston gages</td>
<td>1</td>
</tr>
<tr>
<td>Bourdon tubes</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>155</strong></td>
</tr>
</tbody>
</table>

**Transfer of Gas Piston Gage Calibration Service**

*Primary Standard Support to Manometry*

V.E. Bean, R.G. Driver, C.D. Ehrlich, B.E. Welch, J.C. Houck (Contractor)
Collaborators: R.E. Edsinger, L.A. Guildner

Significant progress was made toward reducing the reported uncertainties and refining the effective area values associated with the gas piston gage calibration service. Work reported in the past concerning the calibration of four gas piston gages against the Gas Thermometer Manometer was carefully evaluated, and uncertainty estimates were derived. As this work was performed in the absolute mode of operation (the region above the piston is evacuated), and whereas most of the gas piston gage calibration work is performed in the gage mode of operation (the region above the piston is at nominal atmospheric pressure), it was necessary to obtain information concerning the additional uncertainty in going from the absolute to the gage mode. An upper bound on this uncertainty was obtained as a result of calibration of two gages against the Ultrasonic Interferometer Manometer, coupled with cross-floats of pairs of the original piston gages, which demonstrated differences in effective area as a function of mode of operation and gas species. Combining this upper bound with the absolute mode uncertainties, it was then possible to establish gage mode uncertainties for the original set of piston gages.

The transfer of these effective areas and uncertainties to the new gas piston gage calibration bench has begun. J. Houck and G. Driver have performed calibrations and intercomparisons between several of the new and old gages and one of the gages recently calibrated against the NIST Gas Thermometer Manometer. Using two nominally identical gages in each pressure range allows these calibrations to continue in a ladder-like fashion, so that uncertainties can be assessed at higher gas pressures as time goes on. The goal here is to have new effective areas and uncertainties in place, at least to 4 MPa, in FY89.
Piston Gage Quality Control Initiative


With increased customer demands for lower uncertainties, more overlap of calibration ranges, and improved documentation in the Piston Gage Calibration Service, several steps were taken to address these issues. Reducing uncertainties for the gas service is discussed above, while some comments concerning the oil service will be addressed below in the section on Distortion. In addition, however, as part of an effort both for ourselves and our customers, and aimed at reducing uncertainties and providing better overlap and quality control, two sets (from different manufacturers) of "simple" piston gages have been ordered. These gages can be treated as either primary standards or secondary standards, and when used in conjunction with controlled-clearance piston gages will provide a means of evaluating the uncertainties associated with the calculation of distortion coefficients. They will also provide an additional means of verifying the stability of our own working standards.

Other efforts in the area of quality control include instituting a program to routinely calibrate the masses used in the calibration services, putting a large amount of information pertaining to calibration of our own instruments into spreadsheet files for ease in evaluation and access, and upgrading our own documentation. The spreadsheet files will aid in our ability to generate control charts of various sorts in a more efficient manner. The goal is to eventually computerize the entire piston gage data base. We are also working to bring the program that is used to analyze the raw data from a cross-float over from the NIST mainframe computer to a PC. Difficulties have been encountered in getting parts of the statistical program to run satisfactorily on the PC, but the NIST Statistics Division is working with us and we will hopefully overcome this difficulty soon. Our recently developed calibration documentation is being upgraded to include a section outlining the quality-control steps indicated here, as well as a section that provides more detail about the analysis that goes into a NIST piston gage calibration report. We are still reviewing this report and may soon switch to a new data reduction technique.

BIPM Gage Intercomparison

V.E. Bean, C.D. Ehrlich, B.E. Welch

A major effort this year has been the calibration of a piston gage to be used in an international round robin organized by the BIPM (International Bureau of Weights and Measures) Consultative Committee for Mass and Related Quantities Working Group on Medium Pressure. This gage was calibrated in both the gage and absolute modes over the pressure range 11 kPa to 131 kPa both by the Pressure Group and the Vacuum Group, giving an excellent opportunity for absolute comparison between the two groups. Although all of the data are not fully evaluated, initial indications are that the agreement is well within the combined uncertainties of the two sets of measurements.
Distortion of Piston Gages at High Pressure

V.E. Bean, C.D. Ehrlich, D.B. Ward

As pressure increases, the leading source of uncertainty in pressure measurement is a lack of knowledge of how the effective area of the piston gage changes with pressure. Published results of a piston gage intercomparison in the pressure range of 20 to 100 MPa, with LNE, PTB, IMGC, NPL, and NIST participating, demonstrated a lack of agreement among these national laboratories in determining the pressure coefficient of the effective area of the transfer-standard piston gage used in the intercomparison. PTB, IMGC, NPL and NIST have initiated research programs to re-examine piston gage distortion. In brief, the NIST program is to:

(1) Develop the capability of calculating the distortion from theory that is amenable to a satisfactory error analysis.
(2) As a test of the calculations:
   a) Measure the change with pressure of the outer diameter of the cylinders for two piston gages which are made of different materials and compare with the calculations;
   b) Cross-float these two piston gages and compare the ratios of the effective areas with the calculations.

There are two challenges in developing appropriate calculational methods:

(1) Existing theories do not have ways of estimating errors due to simplifying assumptions.
(2) Values for the pressure gradient in the annulus between the piston and cylinder are necessary input parameters for the calculations. We have demonstrated that the pressure gradient can be calculated from the dimensional clearance between the piston and the cylinder. However, obtaining adequate dimensional data is a nontrivial problem.

Obtaining the data to test the calculations is straightforward in that we have developed a very good method of measuring the change with pressure of cylinder outer diameters.

Currently we are examining the applicability of finite element analysis software to this problem. We are also collaborating with IMGC on both calculational and experimental methods.

High-Pressure Transducer Characterization

V.E. Bean

There is a need for a stable and sensitive pressure transducer capable of operating in the 700 MPa pressure range for experimentally determining the cylinder deformation coefficients for controlled-clearance primary standard piston gages and for pressure measurement intercomparisons among
laboratories. Transducers based on the electrical resistance of a length of commercial wire are used for intercomparisons, but lack the necessary sensitivity needed to characterize a controlled-clearance piston gage.

During this past year we have developed a new method of measuring this cylinder deformation coefficient using a transducer made of a single crystal of InSb. The calibration equation for the transducer is of the form

\[ P = A \ln\left(\frac{R}{R_0}\right), \]

where \( P \) is the pressure, \( A \) the calibration coefficient, \( R \) the resistance at pressure, and \( R_0 \) the resistance at atmospheric pressure. This transducer has the fortunate and unusual feature that the sensitivity increases as the pressure increases. At 700 MPa the sensitivity of the InSb transducer is 70 times that of the wire-transducer. During this year we have used this new InSb transducer to characterize five controlled-clearance primary standard piston gages including gages for India, Taiwan, DOE, and NIST.

We do not yet have enough long-term data to evaluate this transducer as a transfer standard, but this study is under way.

LOW PRESSURE, VACUUM AND LEAK RATE GROUP

Calibration and Test Services*

S. Dittmann, C.D. Ehrlich, R.W. Hyland

The number of calibrations and special tests increased significantly in all areas, and significant delays were encountered in completing this work. The calibration and test services within this Group are relatively new, some having been started or extended in scope last year, and many of the industries served are in rapidly changing fields where the instrumentation, process control requirements, and quality control procedures are in a state of flux. These factors make it difficult to predict demand for NIST services. At the same time, our primary standards and some of the transfer standards are still in a state of development, and staff and equipment must be shared between the calibration services, extension of range and improvement of accuracy of the standards, and research to understand the transfer standards that we and our customers rely on.

The NIST Ultrasonic Interferometer Manometer (UIM) was used in the low and medium vacuum range to calibrate 33 transducers (primarily capacitance diaphragm gages) for outside and internal use (major internal use is in our primary high vacuum and leak standards). Timely completion was frustrated by the delayed start of a major remodeling of the manometry laboratory.

Demand for the calibration of spinning rotor gages (SRG, a high vacuum molecular drag gage) increased to 28 units, and 3 ionization gages were calibrated below \(10^{-4}\) Pa. With the increased availability of calibrated SRG transfer standards, the demand for ion gage calibrations had almost disappeared. However, with the extension of our calibration range to \(10^{-6}\)
Pa, and the development of ultra-high vacuum processing techniques in the semiconductor industry, there appears to be an increased interest in low range ion gage calibrations. Unfortunately, in addition to the increased calibration load, a mechanical problem in part of our primary standard coincided with an unstable lot of SRG balls (sensors). Two months of additional data were required in order to separate the problems with the primary standard from those caused by the unstable SRGs and verify satisfactory operation of the primary standard.

Our new Special Test Service for helium leaks completed seven tests last year and ten this year. Most of these leaks were near the bottom end of our calibration range, $10^{-11}$ mol/s.

Progress was made in completion of the writing and editorial review of documentation for the low and medium vacuum and high vacuum calibration services.

* (Note: 1 atm = 100 kPa, 1 Torr = 133 Pa, 1 atm cc/sec = 5x10^{-5} mol/s)

**UIM Development and Evaluation**


The Ultrasonic Interferometer Manometer (UIM) was originally developed at NIST as a high-resolution low-range pressure standard. It is a mercury manometer utilizing an ultrasonic phase measurement technique to achieve a length resolution of $10^{-5}$ mm (one std. dev.). It proved to be flexible and easy to use, and demonstrated part per million (ppm) reproducibility at higher pressures. This prompted continued development to extend the range and reduce the uncertainty. In the latest phase of this development three new UIMs have been constructed, one with a range of 160 kPa for Sandia National Laboratories, and two with ranges of 350 kPa for NIST and the Navy Metrology Engineering Center. The three new instruments incorporate significant changes in the mechanical design, radio frequency electronics, and the computer control and data acquisition system. We are still experiencing mechanical noise problems with the 350 kPa design, which has a 2.8 m mercury column, but the new electronics, computer system, and Sandia manometer work very well and have been in daily use at NIST for over six months, with delivery awaiting preparation of new laboratory space at Sandia.

Completion of a measurement of the speed of sound in mercury two years ago allowed a major reduction in the uncertainty of the UIMs. This prompted a major reexamination of the possible errors this past year, including several experiments to evaluate random errors and systematic nonlinearities. We have concluded that a conservative estimate of the uncertainty at the three standard deviation level is 15 ppm. A major part of this uncertainty (6 ppm) accounts for systematic differences between different UIMs. We believe that these differences are due to diffraction of the ultrasonic beam propagating up the mercury column.
Our confidence in our uncertainty analysis has been bolstered by several comparisons of the UIM with standards in other national laboratories. In early 1988 we participated in an international comparison of pressure standards between 10 and 140 kPa, organized under the auspices of the BIPM. The UIM results were the seventh set to be submitted and agree well within combined uncertainties with results from The National Physical Laboratory, Teddington, The International Bureau of Weights and Measures (BIPM), Paris, and the National Institute of Metrology, Paris. The UIM results have the smallest random errors of any of the results yet submitted. Separate comparisons with the National Engineering Laboratory, Lower Hutt; the National Physical Laboratory, New Delhi; and the Institute of Metrology, Torino, have given similarly satisfying agreement.

Evaluation of gas-operated piston gages used as reference standards by our Pressure Group has also demonstrated agreement of the UIM and the independent piston gage standards to well within the combined uncertainties. However, results for different gases show small systematic differences that are within our total uncertainty, but larger than we would expect when only the operating gas is changed. This small discrepancy has yet to be resolved.

Triple Point Pressures

C.R. Tilford, C. Sutton (Guest Researcher)

The improved measurement of triple point pressures presents an opportunity to develop needed pressure fixed points and apply our pressure measurement expertise to the determination of thermodynamic properties. The primary limiting factor of existing triple point measurements is the correction for hydrostatic pressure differences between the cold triple point cell and the room temperature standard. A cryostat with a horizontal pressure line between the cell and the standard was designed and built. Argon was selected as the first material to be measured and preliminary measurements were made using an ultrasonic interferometer manometer as the standard. The measurements were in good agreement with the best of the published values, but were flawed by a significant change in the pressure with melt fraction. This change could be due to impurities, but most likely indicates excessive temperature gradients between the multiple heat shields required to achieve isothermal conditions at the triple point cell. Further work on this project has been deferred in favor of other priorities.

Gas-Operated Piston Gage Evaluation

R.W. Hyland, C.R. Tilford, R. Mangezhanì (Guest Researcher), Y.T. Sheng (Guest Researcher)

While liquid column manometers may be unexcelled for ultimate accuracy and ease of use, they are expensive and subject to environmental and operator perturbations. Piston gages, pressure balances, or deadweight testers are much simpler, cheaper, and less subject to external perturbations. They are generally used at higher pressures, but a program has been under way in the
Pressure Group to develop their use as part per million (ppm) transfer or reference standards for gas pressures in the range near atmospheric pressure. In the course of this work, B.E. Welch discovered that a common assumption, that the operation of these gages is independent of gas or mode of operation (gage or absolute), could be in error by as much as 30 ppm. Piston gage measurements made in the course of evaluating ultrasonic interferometer manometer (UIM) stability further gave the unexpected result that the effective area of a piston gage can change by up to 30 ppm at low pressures in the absolute mode of operation. Until the reasons for these effects are understood it will be very difficult to achieve the goal, desired by a number of users, of using these gages as transfer standards at the 5 to 10 ppm level.

We have used the UIM, which serves as a reference standard independent of gas species or mode of operation, to further investigate these effects. We have found systematic differences between the absolute and gage mode effective areas of up to 25 ppm, and have seen, as did Welch, dependencies on gas species of the effective area for stainless steel pistons and cylinders of up to 25 ppm. However, we have not seen dependencies on gas species for tungsten carbide pistons and cylinders greater than 2 or 3 ppm. These effects are clearly due to changes in the transfer of momentum or force between the gas flowing in the annular space between the piston and cylinder and the piston surface. The changes at low absolute pressures are probably due to the transition between molecular and viscous flow in the annular space. The dependencies on gas species may be due to surface roughness and different tangential momentum accommodation coefficients. However, at this time a consistent pattern in behavior from gage to gage is not apparent, and the way is not yet clear to the development of a first-principle theory.

**Development of Primary Vacuum Standards and Measurement Techniques**

S. Dittmann, A.R. Filippelli, F.G. Long, D.R. Martin

The operating range of our primary vacuum standard has been progressively extended to lower pressures by incremental improvements and the development of new operating procedures, followed by a careful uncertainty analysis. To date, this has extended the lower limit of routine measurements from $10^{-4}$ to $10^{-6}$ Pa. Analysis of a set of very low pressure ion gage measurements during this past year indicates that we can determine the sensitivity of vacuum gages with an adequate uncertainty (on the order of 5%) down to $10^{-7}$ Pa for nonreactive gases. However, significant problems were encountered with hydrogen due to the generation of atomic hydrogen at the hot filaments of the gages. Furthermore, at these pressures the determination of the sensitivity is of limited use for most gages unless we can also determine the gage’s residual current. Unfortunately, the base pressure of our calibration chamber is about $10^{-8}$ Pa, not adequate for residual current determination, and our efforts to reduce the base pressure have met with very limited success. We expect to build and evaluate a separate ultra-high vacuum system that we hope will reach $10^{-10}$ Pa. If this can be used to determine residual currents, then we will probably extend the range of our calibration service.
For several years we have granted modest support to a project in B.F. Kendall's laboratory at Penn State to develop a standard using the Brownian motion of a levitated particle. This work has recently taken a somewhat different direction, having successfully measured pressures in the high vacuum range using the decrement of vibration amplitude of small levitated metal spheres. Preliminary analysis indicates that this gage may be useful in the ultra-high vacuum range, where it would have the major advantage of not requiring a hot filament. This may provide an alternative method of extending the range of our standards to lower pressures.

Leak Rate Standards

While there is a definite demand for the extension of our leak rate standard to below our present limit of $10^{-11}$ mol/s, progress in this area has been greatly impeded by the assignment of major additional responsibilities to C. Ehrlich. Our present lower limit is set by the increase of our uncertainties to 10%. There is some possibility that as we gain experience in the calibration of slow leaks we can reduce this uncertainty and extend our range somewhat. In the interim, the Special Test Service is being maintained, we are building a quality control data base, and an experiment is proceeding to determine the linearity of our leak comparator system so that it can play a larger role in our calibration program.

There is also a demand for leak calibrations for gases other than helium, the only gas for which we presently calibrate. Extension to other gases requires increased confidence in capillary and orifice type leaks. We are starting to obtain a limited amount of performance data on such leaks.

Characterization of Vacuum Gages
S. Dittmann, A.R. Filippelli

In order to meet demands to extend the range to lower pressures and improve the accuracy of vacuum measurements, it is necessary to better understand the performance characteristics of vacuum gages. As part of this effort we continued to evaluate the performance of the Spinning Rotor Gage (SRG), a new commercial gage that utilizes the molecular drag on a levitated rotating ball. The SRG is finding increasing use as a high vacuum calibration or transfer standard, where long term stability is critical. Evidence to date had indicated that with proper care the balls would not change by more than 1 or 2% over a one to two year period. We were therefore surprised to see one group of balls, sent in for calibration by a gage manufacturer, change by 0.5 to 2% when they were baked.

At this time the only gage available for measurements below the high vacuum range is the workhorse ionization gage. We have previously documented significant performance differences in the high vacuum range between different ion gage designs, including significant nonlinearities in some
designs. If these nonlinearities extend into the ultra-high vacuum range, vacuum calibrations will be greatly complicated and accuracies reduced. This past year we experimentally evaluated the linearity of several different ion gage designs down to $10^{-8}$ Pa, where our measurements were limited by random errors in our primary standard and the ion current measurements. These indicate that for all but one of the 16 gages, the nitrogen and helium sensitivities were constant within 2 to 3% for pressures up to $10^{-3}$ Pa. Hydrogen data showed systematic trends at low pressures, but we believe these indicate pressure perturbations caused by chemical reactions with atomic hydrogen formed at the hot filaments, and do not indicate changes in the fundamental gage sensitivity.

**Partial Pressure Analyzer Calibration Techniques**

A.R. Filippelli, L.V. Lieszkovszky (Guest Researcher)

In many vacuum processes, particularly at lower pressures, a measurement or control of specific gas species is more important than that of the total pressure. Mass spectrometer instruments, generally known as residual gas or partial pressure analyzers, are widely used for vacuum system analysis and process control. With the increased emphasis on quality control there is a corresponding increase in calibration requirements for these instruments. In order to help determine how complicated the calibration procedures must be, we have been evaluating different commercial instruments for the dependence of their sensitivity on pressure, time, instrument operating parameters, and background gas. To date, this has been done only for helium, nitrogen, and argon. For the best of the instruments, the sensitivity is constant within 10% with reasonable variation of these parameters; for the worst, the changes are two to three orders of magnitude larger. There are indications that some of the problems with poorly performing instruments originate in the ion source. But we do not yet know how many of the problems are generic to a design and how many are specific to a particular instrument.

**DIVISION OFFICE PROGRAM**

**Nuclear Orientation Thermometry**

H. Marshak

This year was almost entirely devoted to finishing up the research work on the rare earth terbium. In addition to writing five papers, a considerable amount of time was spent analyzing data for these papers. Most of this data analysis was carried out using the NIST computing system. The last large paper should be completed soon. This work on terbium, which was an international collaboration between NIST, Freie Universitat Berlin, and Bonn Universitat was not only very productive, but also laid the ground work for further work on other rare-earth systems. In particular, the on-line low
temperature ion implantation groups (Leuven, Belgium; Daresbury, England; CERN-Geneva, Switzerland; and Oak Ridge, Tennessee) will no doubt do implantations on other rare earths.

In addition to the publications mentioned above and listed in "5. PUBLICATIONS" herein, some of this work was used in the Ph.D. thesis (Static and Dynamic Nuclear Orientation Studies on Rare-Earth Systems) of P. Roman (Freie Universitat Berlin). His thesis was graded magna cum laude and H. Marshak served as unofficial adviser.

Also this year, contributions were made to a final report prepared for NATO on our collaborative (NIST with Universitat Bayreuth, W. Germany; University of British Columbia, Canada; Kernforschungsanlage Julich, W. Germany) work to measure the $^3$He superfluid transition temperature ($T_{\pi}$) using nuclear orientation thermometry. NATO supplied travel funds to carry out this work. We hope to write a short paper on some of the results in the near future.

5. PUBLICATIONS


Bignell, N. and Bean, V.E., The H$_2$O(I)-H$_2$O(III)-H$_2$O(L) triple point of water as a fixed pressure point, Metrologia (submitted).


Brewer, W.D., Roman, P. and Marshak, H., Precision nuclear orientation measurements for determining mixed dipole magnetic/electric quadrupole hyperfine interactions, Hyp. Int. (in press).


Dittmann, S., NIST measurement services: The National Institute of Standards and Technology high vacuum standard and its use, NIST SP 250-34 (in press).


Hyland, R.W., NIST measurement services: pressure calibration in the range 1 to 150,000 Pa, NIST SP 250-35 (in press).


Marshak, H., Brewer, W.D. and Roman, P., Nuclear orientation of the rare-earth system $^{160}$Tb$^{27}$Sc, Hyp. Int. (in press).


6. CONFERENCES AND WORKSHOPS

CONFERENCES

Four Invited Sessions of the March, 1988, meeting of the American Physical Society, held in New Orleans, LA, were organized by the Executive Committee of the APS Instrument and Measurement Science Topical Group, J.F. Schooley Vice-Chairman. Schooley chaired one of the sessions.

WORKSHOPS

Two training workshops on the Calibration of Ionization Gages Using the Spinning Rotor Gage were held in Gaithersburg, MD, during the week of May 9, 1988. Both were organized by Sharrill Dittmann.

154
Center for Chemical Technology
1988 Technical Activities

J. Hord, Acting Director, CCT

National Institute of Standards and Technology
UNITED STATES DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

Technical research activities performed by the Center for Chemical Technology during the Fiscal Year 1988 are summarized herein. These activities include work in the general categories of measurements (standards, processes, and equipment design), properties (thermophysical, thermochemical, and kinetic), and biotechnology (protein engineering and separations). They embody: development and improvement of measurement standards, measurement principles, and calibration services for pressure, temperature, volumetric and mass flow rates, liquid volume and density, humidity, and airspeed; generation (via accurate measurements and advanced predictive models) of reliable reference data for thermophysical, thermochemical, and kinetic properties of pure fluids, fluid mixtures, and solids of industrial and environmental importance; provision of fundamental understanding of protein structure-function and advanced technology for commercial scale separation of proteins; and development of improved correlations, models, and measurement techniques for complex flows, heat and mass transport, mixing, and chemically reacting flows of interest in modern operations.

Biotechnology; calibrations; chemical engineering; chemistry; data; flow; fluid properties; kinetics; measurement standards; pressure; process measurement; sensors; separations; solid properties; temperature; thermochemistry; thermophysics; unit operations

162

Order From National Technical Information Service (NTIS), Springfield, VA. 22161