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Center for Chemical Engineering Technical Activities Fiscal Year 1987

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J. Hord, Editor

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Technical research activities performed by the Center for Chemical Engineering during the Fiscal Year 1987 are summarized herein. These activities fall within the general categories of process measurement, thermophysical properties data, and chemical engineering science. They embody: development and improvement of measurement principles, measurement standards, and calibration services such as volumetric and mass flow rates, liquid volume, liquid density, and humidity; generation (via accurate measurements and advanced predictive models) of reliable reference data for thermophysical properties of pure fluids, fluid mixtures, and solids of vital interest to industry; 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.

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INTRODUCTION

This document summarizes technical research activities of the Center for Chemical Engineering (CCE) during Fiscal Year 1987 (October 1, 1986 through September 30, 1987). This Center is one of six such units that compose the National Engineering Laboratory of the National Bureau of Standards. A brief summary of the structure and technical activities of the National Bureau of Standards is given in the introductory portion of this report, along with organizational information on the Center for Chemical Engineering.

The activities of the Center are focused on 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 fundamental scientific framework for reliable measurement and data bases that assure equity in domestic and international trade, and enable innovation as well as improved design and control of chemical 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 three sections, one for each participating division in the Center: Chemical Engineering Science, Thermophysics, and Chemical Process Metrology. Each division summary is related in the same format but with individual style and emphasis. These summaries lead off with an introduction; state the division goal; outline division subelement (group) functions; summarize project activities; cite primary publications; and close with lists of conferences and workshops hosted, sponsored, or organized by the division or Center.

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 Engineering, National Bureau of Standards, 325 Broadway, Boulder, CO 80303.

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o Chemical Engineering

INSTITUTE FOR MATERIALS SCIENCE & ENGINEERING

* Ceramics
* Fracture & Deformation
* Polymers
* Metallurgy
* Reactor Radiation

INSTITUTE FOR COMPUTER SCIENCES & TECHNOLOGY

* Information Systems Engineering
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* Systems and Network Architecture
* Advanced Systems

NATIONAL MEASUREMENT LABORATORY

o Basic Standards
o Radiation Research
o Chemical Physics
o Analytical Chemistry

o Denotes Center
* Denotes Division

ORGANIZATION OF THE CENTER FOR CHEMICAL ENGINEERING

CENTER FOR CHEMICAL ENGINEERING
*J. Hord, Director
H. Semerjian, Act. Deputy Director
J. Ulbrecht, Senior Consultant
Optical Diagnostics Group
A. Macek, Acting Group Leader

***CHEMICAL ENGINEERING SCIENCE DIVISION**
V. Schrodt, Chief

- Transport Processes (S. Sikdar)
- System Dynamics (J. Brennan)
- Properties of Solids (L. Sparks)

THERMOPHYSICS DIVISION
*N. Olien, Chief

- Equation of State & Statistical Physics (R. Kayser)
- *Properties of Fluids (W. Haynes)
- Dynamic Measurements (A. Cezairliyan)

CHEMICAL PROCESS METROLOGY DIVISION
H. Semerjian, Chief

- Fluid Flow (G. Mattingly)
- Multiphase Reacting Flow (A. Gaigalas)
- High Temperature Reacting Flow (A. Macek)
- Process Sensing (K. Kreider)

*Located in Boulder

MISSION OF THE NATIONAL BUREAU OF STANDARDS (NBS)

The basic mission of the National Bureau of Standards is to provide for the Nation's measurements and standards needs. NBS applies its expertise in science and engineering to foster the attainment of such national goals as: economic growth through innovation and productivity growth in industry and commerce, and through optimal utilization of labor, energy and material resources; reasonable and equitable regulatory decision-making with maximum benefit and minimum economic impact and uncertainty; equity in U.S. commerce through mutual understanding and acceptance of recognized transfer standards; and accuracy and compatibility in scientific communications and technology transfer among industry, government and academia, including the ability to make meaningful comparisons between the theoretical predictions and empirical data used in developing scientific knowledge.

Through performance of the functions set forth in the NBS Organic Act of 1901 and subsequent revisions, and through numerous other statutes, the Bureau pursues its mission by fulfilling three major roles. The Bureau of Standards: (1) is the Nation's central reference laboratory and lead agency for the development and provision of measurement standards, measurement methods and techniques, and standard reference materials and data essential for the resolution of Federal, State, and local scientific and technical measurement issues; (2) addresses technological problems for the Nation through the application of basic physical, chemical, mathematical, and engineering science by providing traceability of measurements to national standards essential for ensuring measurement comparability, by uniform determination of the physical, chemical, and engineering properties of matter, and by provision of uniform methods for measuring the performance of materials, products, and engineered systems products; and (3) enhances the technological and scientific base of the Nation's productive sectors by developing basic technologies and information that underlie product and process development and innovation.

As a major operational unit of the Department of Commerce, NBS also contributes significantly to fulfilling the Department's mission to promote trade and commerce and to ensure the smooth and orderly working of our economy.

NATIONAL MEASUREMENT LABORATORY: Provides the national system of physical and chemical measurement; coordinates the system with measurement systems of other nations and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; provides advisory and research services to other Government agencies; conducts physical and chemical research; develops, produces, and distributes standard reference materials; provides standard reference data; provides calibration services; and collaborates with the Bureau's major organizational units in carrying out its responsibilities.

INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY: Provides scientific and technical services to the central management agencies (e.g., the Office of Management and Budget and the General Services Administration) to support the formulation of Federal automatic data processing (ADP) policies, the selection and direction of Federally sponsored computer research and development, and the resolution of policy issues affecting computer use; develop and recommend Federal Information Processing Standards; participate in the development of voluntary industry ADP standards in both national and international organizations; conduct research in the science and technologies of automatic data processing, computers, and networks; provide direct technical assistance to other Federal agencies in solving specific computer applications problems; cooperate with private sector users in determining standards requirements; cooperate with users in industry to test standards and develop certification techniques; conduct information exchange activities in the areas of computer and networking technologies; provide technical leadership for the development of national and international standards for ADP products to enhance the international trade position of the U.S. computer industry and to ensure that international standards do not form trade barriers; cooperate with representatives of foreign governments and organizations in research and testing activities; and monitor Federal Government participation in voluntary commercial standards development efforts.

INSTITUTE FOR MATERIALS SCIENCE AND ENGINEERING: Develops and maintains the scientific competences and experimental facilities necessary to provide the Nation with a central basis for uniform physical measurements, measurement methodology, and measurement services fundamental to the processing, characterization, properties and performance of materials, and to other essential areas in materials science; provides government, industry, universities, and consumers with standards, measurement methods, data, and quantitative understanding concerning metals, polymers, ceramics, composites, and glasses; characterizes the structure of materials, chemical reactions, and physical properties which lead to the safest, most efficient uses of materials, improve materials technologies, provide the bases for advanced material technologies in basic and high-technology industries, and encourage recycling; obtains accurate experimental data on behavior and properties of materials under service conditions to assure effective use of raw and manufactured materials, provides technical information such as reference data, materials measurement methods, and standards to processors, designers, and users for selection of cost-effective combinations of materials, processes, designs, and service conditions; uses the unique NBS reactor facilities to develop neutron measurement methodology, develop sophisticated structure characterization techniques, reference data, and standards; participates in collaborative efforts with other NBS organizational units in the interdisciplinary developments in materials science; and disseminates generic technical information from the Divisions to private and public sector scientific organizations through special cooperative institutional arrangements and through conventional distribution mechanisms.

NATIONAL ENGINEERING LABORATORY: Provides technology and technical services to users in the public and private sectors to address national needs and to solve national problems in the public interest; conducts research in engineering and applied science in support of objectives in these efforts; builds and maintains competence in the necessary disciplines required to carry out this research and technical service; develops engineering data and measurement capabilities; provides engineering measurement traceability services; develops test methods and proposes engineering standards and code changes; develops and proposes new engineering practices; develops and improves mechanisms to transfer results of its research to the ultimate user; develops and demonstrates new institutional practices to stimulate use of technology; and collaborates with the National Measurement Laboratory in conducting its assigned responsibilities.

CENTER FOR CHEMICAL ENGINEERING: Performs research in process metrology, thermophysical properties of fluids and solids, and unit operations and processes; provides measurement practices and standards, fundamental engineering data, calibration and measurement services, and engineering science for the chemical and related industries, academe, and Government.

CHEMICAL ENGINEERING SCIENCE DIVISION: Develops and maintains competence to provide essential engineering measurement and data bases that underlie the design and performance of chemical engineering processes and the behavior of solid materials of importance to the chemical and related industries; performs basic and applied research in unit operations (heat and mass transfer, and separations including membranes, chemical complexation, crystallization, selective adsorption, and liquid-liquid extraction), systems engineering, thermodynamic analyses of subprocesses, and scale-up; performs thermal and related properties measurements research to develop data-predictive models and reference materials for solid feedstocks and fuels (coal and gas hydrates) and for technical solids (insulating materials, metals, alloys, polymers, composites, and ceramics); provides critically evaluated data, measurement standards, predictive models, and engineering correlations in these research activities.

THERMOPHYSICS DIVISION: Develops new measurement techniques, thermodynamic models, and molecular theories to describe the thermophysical behavior of condensed matter ranging from classical fluids and solids to highly complex fluid mixtures containing molecules of varying size, polarity, and chemical nature. Research includes multicomponent-multiphase fluid mixtures, interfacial phase transitions, nucleation, computer simulation of fluid behavior, critical point phenomena and properties, properties of supercritical fluids, phase separation, equations of state, and transport processes in fluids and high-melting temperature metals. Results include: theoretically-based predictive models and correlations that use transportable computer codes to predict thermophysical properties of condensed substances; state-of-the-art experimental measurements; and critically evaluated properties data.

CHEMICAL PROCESS METROLOGY DIVISION: Develops improved measurement techniques, theoretical and computational models to describe and qualify the performance of laboratory and process plant instruments, and complementary advanced fluid dynamics analyses/models to explain the behavior of fundamental fluid flows; develops experimental and theoretical means to characterize fluid behavior (solid-fluid slurry flow modes, fluidized beds, chemically reacting flows, etc.) and to evaluate the performance of combusting flows (gaseous, liquid, solid and slurry fuels) with emphasis on high temperature, corrosive and erosive exhaust streams; develops measurement standards and provides measurement services for flow (volume and mass rates), fluid density, fluid volume, and humidity; and provides advanced measurement techniques, standard measurement practices, and technical data (experimental, theory and computer models) for measurement, analysis and control of chemical processes.

TECHNICAL ACTIVITIES
OF THE
CHEMICAL ENGINEERING SCIENCE DIVISION

V.N. Schrodt, Chief

1. INTRODUCTION

Efficient design and operation of plants and facilities in the chemical, biochemical, petrochemical, petroleum, gas and other processing industries are strongly dependent on reliable engineering data and well-documented characterization of process mechanisms. Efficient design and operation enable U.S. industry to compete more effectively in the world marketplace, where intense international competition has focused efforts to improve manufacturing equipment and processes. Furthermore, an increased emphasis on environmental protection has created a need for alternative processes operating with closer tolerances, emphasizing higher yields and internal recycling with separation, so that fewer pollutants are produced. 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. The work of the Chemical Engineering Science Division is focused on providing the knowledge and understanding needed for the elemental processes, and on advancing the state of the art for transport phenomena models and theory. The key ingredients 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 related to process design and operation, the work of the Division is involved in measurements and data necessary for accurate and verifiable custody transfer of chemicals and fuels.

In specific areas that relate to the research of the other CCE 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 new ones are being explored.

One of the primary research efforts of the Division is focused on industries related to the new 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 biosubstances. 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 separations 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 NBS 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 are developed for selected thermal properties of certain 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) use 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 NBS as an impartial national laboratory excelling in measurements and their interpretation. During the past year, the effort in two-phase aqueous extraction research has been expanded to include a project on bioseparations using new polymers and affinity ligands. Work was continued on heat transfer in supercritical extraction processes and on the use of reaction systems at supercritical conditions to treat hazardous wastes. A new project has been funded, initiating research on flow through porous beds. An effort to involve the Division in research related to Computer Integrated Processing is being considered.

In addition, the Chemical Engineering Science Division serves other government agencies, trade associations, etc., by providing research appropriate to the mission of the National Bureau of Standards and consistent with the goals of the Center for Chemical Engineering and the Division. This externally supported research constitutes a major part of the planned effort in achieving the goals of the Division.

2. GOAL

The goal of the Division is to provide evaluated generic engineering design data and elemental process engineering models; standard measurement procedures and test methods; predictive techniques, correlations, computer codes, and underlying theories needed by the chemical and related industries to design, control, and develop new manufacturing processes.

The output of this program assists these industries in maintaining and enhancing their competitiveness in the international marketplace. 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, new ideas and phenomena, and predictive models in synergism with experimental programs. These efforts 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, leading 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.

- 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 agencies and industrial trade organizations and to promote efficiency and measurement accuracy in the chemical and allied 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: ceramics, composites, polymers, foams, fibers, fiberboards, aggregates, metals, and solid fuels (e.g. coal, oil shale, and gas hydrates). Work is performed on the ignition and combustion characteristics and rapid oxidation of metal alloys, in an oxygen environment, at pressures up to 20 MPa. Efficiencies and new concepts of refrigeration are studied.

4. SELECTED PROJECT SUMMARIES

TRANSPORT PROCESSES GROUP

Separation by Reversible Chemical Complexation: Data, Mechanisms and Modeling

R.D. Noble, J.J. Pellegrino, R.D. Nassimbene,
D. Randolph, M.-F. Jin, S.K. Sikdar

Reversible chemical complexation offers important advantages over conventional methods for separating species from gases and liquids. The objectives of this research are to develop basic measurement techniques and standards, provide a body of high quality experimental data, and develop predictive models and computer codes for the use of this facilitated transport technique in separation processes. The fundamental characteristics of this separation technique are being studied by performing experimental work on two applications: 1) selective separation of gases by an immobilized liquid membrane consisting of an ion exchange membrane neutralized by an organic base carrier, and 2) selective separation of carboxylic and amino acids by acid and salt-forms of ion exchange membranes.

The experimental part of the program includes measurement of mass transfer fluxes and determination of the mechanisms of transport. Mathematical modeling is employed to develop equations to predict species fluxes and separation factors of one species over another. Gases which have been successfully separated using ethylene diamine-mediated perfluorinated ion exchange membranes are CO_2 and H_2S. Current efforts are being directed toward hydrogen. In liquids, transport data are being collected on some carboxylic and amino acids, and the mechanism of transport is being established. The gas separation work is funded by DoE.

Biochemical Separation

B.R. Bateman, D. Szlag, K. Giuliano, R.A. Perkins,
M. Scurry, D. Steward, H. Cabezas, B. Dale, S.K. Sikdar

The major objective of the biochemical separation program is to provide data and understanding necessary for the design of industrial bioseparation processes. Current research activities are focused on the technique of two-phase aqueous extraction as a means of separating proteins from aqueous solutions.

Aqueous two-phase extraction has the potential of being a dominant factor in the downstream processing of bioproducts. Used in the early part of a multi-step multi-technique bioseparation train, this technique can greatly concentrate proteins. However, the cost of dextran, a constituent of the polyethylene glycol (PEG)-dextran two-polymer system used in this technique, remains an impediment to the commercial exploitation of the two-phase aqueous extraction method. Finding an inexpensive substitute for dextran, and characterizing the phase and protein partition behavior is an important goal of this research.

The PEG-maltodextrin system has been identified as a promising low cost two-phase system with significant advantages over the conventional PEG-dextran system. Apart from the cost advantage of maltodextrins (less than 1% of the cost of dextran), the low viscosity of the maltodextrin phase greatly speeds phase disengagement without the use of centrifugation. Protein partition and the separation factor of the desired protein can be greatly enhanced by attaching common textile dye ligands to PEG. The dye ligand-PEG-maltodextrin system has been demonstrated to work efficiently for model proteins such as bovine serum albumin and alcohol dehydrogenase, as well as on cell lysates. We have collected protein partition coefficient and phase diagram data on the PEG-maltodextrin system. Comparable data sets on the conventional PEG-dextran systems have also been collected.

On the theoretical side, a statistical thermodynamic approach is being investigated as a tool to predict protein partition coefficients. In the fist phase of this activity, the technique of direct correlation function integrals (DCFI) has been successfully applied to accurately predict phase diagrams of the PEG-water-salt system. Future activity will include the study of dye-ligand partition and protein partition in the PEG-maltodextrin systems. The bioseparation program is collaborative with the University of Arizona and the University of Bombay.

In a related study on the thermodynamics of protein unfolding, we have found that the enthalpy and heat capacity changes on protein denaturation correlated quite well with the transfer free energies of the constituent amino acids, regardless of the sequence. Thus it has been found possible to predict the free energy of denaturation from literature data on transfer free energy of amino acids.

Plans are in place to initiate research in other areas of bioseparation, such as affinity membrane, affinity chromatography and electrophoresis.

Heat and Mass Transfer to Supercritical Fluid Mixtures

M.C. Jones, P.J. Giarratano, L.A. Powers, S.M. Selim

In this project, transport rates are investigated for supercritical gas and liquid mixtures in the region of the solution critical point and, in particular, the retrograde condensation region. This condensation process is of industrial importance for supercritical extraction as one means of separating solvent from extract. Despite the fact that the thermodynamics of the process are well known, very little has been done on the study of transport rates. The approach is to apply fundamental principles of transport mechanisms to precise measurements made on mixtures with well-documented thermophysical properties.

To date, measurements have been made on the n-decane-carbon dioxide system at two pressures and five compositions in the region of the critical solution locus. Heat transfer rates have been obtained for a heated horizontal cylinder with crossflow and under natural convection conditions. Several facts have been established. First, heat transfer rates in crossflow are indistinguishable from those in natural convection when the wall temperature rise is above about 10 K. This is expected on the basis of the high Rayleigh number achievable in natural convection for supercritical fluids. Second, it has been established that heat transfer rates on the condensation side of the critical locus are larger than on the evaporation side and, further, that the condensation heat transfer rates are a factor of two greater than can be accounted for by classical film condensation theory using the best available estimates of mixture properties. Finally, at high condensation heat transfer rates, wall temperatures become unstable in a region where multiple steady states have been observed.

The variation in the interfacial tension along the phase boundary may be responsible for some of these results and future experiments are planned to make direct visual observations of the phase change mechanisms. Future work is also planned to extend the observations to other solutes and geometries and to construct a mathematical framework for the correlation of experimental results.

SYSTEMS DYNAMICS GROUP

Superfluid Helium Transport in Zero Gravity

D.E. Daney, P.R. Ludtke

Transferring cryogens in space is an integral part of NASA's space program. For cooling and maintenance of expensive equipment in space, superfluid helium needs to be transferred in a microgravity environment. The NBS approach is to use a centrifugal pump, free of cavitation problems. The objective of this program is to support the NASA mission by providing a data base on superfluid helium pumping characteristics, and to aid in the fabrication of a prototype pump for tests onboard a space shuttle.

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 liquid nitrogen 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 3 and 4-inch 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 uses the flow facility to evaluate new measurement techniques and to perform special tests on meters to provide measurement traceability to NBS. These tests are performed with liquid nitrogen. The third area of flow research is concerned with high velocity flows (over 50 m/s) and uses water from a local hydroelectric plant since such velocities are well beyond the range readily 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, M.J. Hiza, 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 is concerned with 1) reviewing and evaluating thermodynamic modeling of cryogenic systems in support of high energy physics experiments at the National Accelerator Laboratory; 2) analyzing the fluid mechanics, thermodynamics, and phase equilibria, and assessing the applicability of measurement methodology in the production, transfer, and storage of liquid-solid mixtures of hydrogen; and 3) performing experiments and analyzing the fluid mechanics and thermodynamics related to 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, in area 2) by the Defense Advanced Research Projects Administration, and in area 3) by the National Aeronautics and Space Administration.

PROPERTIES OF SOLIDS GROUP

Cryocooler Studies

R. Radebaugh, P. Bradley, J. O'Keefe, V. Arp, J. Gary*

A pulse tube refrigerator was built under a NASA-Ames contract and reached a record low temperature of 60 K in one stage. The lowest temperature previously reached with a pulse tube refrigerator was 105 K. This new work has led to the device becoming a serious alternative to other refrigeration schemes that have more moving parts. The pulse tube refrigerator has only one moving part. A test apparatus to measure the efficiency and refrigeration power per unit mass flow has been constructed under the same program. Measurements of efficiency and refrigeration power have been made on four different pulse tubes. The results show intrinsic cooling efficiencies as high as 50 to 90 percent of Carnot in some cases and large refrigeration powers.

Under a five-year Air Force (AF) contract, the regenerator test apparatus was modified to make tests in the presence of pressure waves to simulate the environment seen by regenerators in an actual refrigerator. A high specific heat material, GdRh, has been formed into powder for testing as a regenerator. This material was sent to an AF contractor for tests in an actual refrigerator. It increased the refrigeration power by 23 percent and decreased the low temperature limit from 7.1 K to 6.2 K. This material is now being tested in the NBS apparatus. Theoretical and experimental studies of the effect of the phase angle between compressor and expander pistons on regenerator performance are in progress and indicate overall refrigerator improvements can be made by a proper choice of phase angle. A computer program for the first step, optimization of regenerators, has been developed and the floppy disk for use on a personal computer is available upon request to the U.S. Air Force.

The least reliable component of present cryocoolers is the mechanical compressor. A proposed alternative uses a thermal compressor in which the gas to be compressed is first adsorbed on charcoal at a low pressure. The charcoal is then heated slightly and the adsorbed gas is driven off at some higher pressure. Only slow-moving check valves are needed to provide continuous flow in one direction. The necessary data to design a helium-charcoal compressor is lacking, but a program funded by the Air Force Space Technology Center has allowed us to measure the adsorption characteristics of helium on charcoal in the temperature range 10 to 77 K. These results will be published in the journal Cryogenics. Measurements on other charcoals as well as measurements of heats of adsorption are in progress.

Refrigeration reliability can be improved by the use of redundant cryocoolers. This approach requires the use of heat switches between the cryocoolers and the sensor to be cooled. One technique uses pressure contact between two metals. Required forces are about 13 000 N (3 000 lb). No data existed on the thermal conductance of such contacts at cryogenic temperatures. With funding from the Air Force Space Technology Center, we have made measurements on three pairs of metal samples, at temperatures from 10 K to room temperature and with forces from 45 N (10 lb) to 27 000 N (6 000 lb). The data have been used by an AF contractor for the design of heat switches.

*NBS Center for Applied Mathematics

Metal Combustion in High Pressure Oxygen

J.W. Bransford, K.M. McDermott

A program to study the ignition and combustion characteristics of a number of metals and alloys in high pressure oxygen, at pressures to 14 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 industrial users of liquid and gaseous oxygen.

The top surface of a cylindrical sample is heated by a focused CO_2 laser beam. Interior and exterior temperatures are measured before, during, and after ignition. High-speed movies of the ignition and 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.

Thermal Properties of Advanced High-Temperature Materials

L.L. Sparks

Ceramics and ceramic based composites continue to develop as replacements for metals and plastics in electronic components and high performance engines and structures. 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. Knowledge of these properties is required to allow ceramics to be used in applications such as unlubricated bearings, high-temperature reactors, turbine rotors, adiabatic diesel engines, turbo compressors, thermal barriers, electrical components, and substrates for electronic components.

Three projects to address these needs are active within the group: (1) continued development of a steady-state thermal conductivity apparatus to allow ceramics and ceramic composites to be studied to 1270 K; (2) completion of a guarded-hot-plate thermal conductivity apparatus to allow ceramic fiber insulation to be studied to 800 K; and (3) alteration of the existing optical dilatometer to study foamed ceramics at low temperatures.

Oxidation of Metals in High Pressure/High Temperature Oxygen

J.W. Bransford, J.A. Hurley

A program to design and operate a Thermogravimetric/Differential Thermal Analysis (TGA/DTA) apparatus has been undertaken. The TGA/DTA apparatus, now in the design and construction stage, will be used to directly determine the oxidation rate of various metal alloys in high-temperature and/or high-pressure oxygen. The data generated by these studies will be of interest to all users of oxygen at high temperature and elevated pressure.

Development of SRM's

J.G. Hust, J.E. Callanan, 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 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 and related industries. Microporous and ceramic fibers are currently being developed as SRM candidates.

Potassium nitrate has been certified as a temperature and enthalpy of fusion standard for differential scanning calorimetry (DSC). Auxiliary measurements have shown it to be useful as a reference material.

A supply of anthraquinone has been obtained and purified for development as an SRM. The anthraquinone and high-purity cadmium foil are being sampled for certification.

Test samples of organics and inorganic salts over the higher temperature range 400-1000 K have been obtained for evaluation as potential standard reference materials.

Studies of 1) the capability of DSC for development of heat capacity standards and 2) the energy calibration procedures for DSC have been completed. Final statistical analysis of these data is being completed in collaboration with the NBS Statistical Engineering Division.

A statistical study of the ASTM calibration procedures, and variants of those procedures, resulted in improved estimates of uncertainty limits for certification. From consideration of the results of this study and the energy calibration study, improved calibration (correction) procedures are being developed.

Research leading to the development of measurement procedures for heat capacity and heat of vaporization of volatile liquids and to the potential development of standard reference materials has been undertaken.

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6. CONFERENCES

CONFERENCES

The Calorimetry Conference, 42nd Annual Meeting at Boulder, CO, July 26-30, 1987 (local arrangements Chairman, J.E. Callanan).

An international conference on Frontiers in Bioprocessing, Boulder, CO, June 28-July 2, 1987. S.K. Sikdar, chaired program committee and co-organized conference with J. Hord, V. Schrodt, P. Todd (Univ. City Sci. Center) and M. Bier (U. AZ).

Session [71] on Safety and Reliability of Cryogenic Systems, AIChE Annual Meeting, Miami, FL, Nov. 5, 1986. Co-organized and co-chaired by J. Hord.

TECHNICAL ACTIVITIES
OF THE
THERMOPHYSICS DIVISION

N.A. Olien, Chief

1. INTRODUCTION

The research of the Thermophysics Division focuses on the thermodynamic properties and dynamic behavior of fluids and solids, with particular emphasis on properties and substances of current and future importance in chemical engineering.

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 the above efforts is the critical evaluation and correlation of data leading to the publication of Standard Reference Data. Standard Reference Data often take the form of conventional correlations and tables, but more recently the preferred form is that of predictive models as computer codes.

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 NBS 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 the conversion and utilization of coal, oil shale, heavy oils, and tar sands to gaseous and liquid feedstocks and fuels which, in turn, contain substantial amounts of aromatic organics and associating compounds (containing N, O, S); 2) fluid mixtures encountered in bioprocess engineering, which are essentially aqeuous 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 NBS 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 NBS 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 NBS 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, 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 to 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)-
  R.F. Kayser, 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; 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-CCE sponsors of the work of this Group include the DoE, NASA, and the NBS 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, coal conversion products, heavy oils, and biochemical solutions. Principal non-CCE sponsors of the work of this Group include the DoE, the Gas Research Institute, the DoD, industrial consortia, and the OSRD.

DIVISION OFFICE PROGRAM

- Dynamic Measurements (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, G. Morrison, M.L. Japas (Guest Scientist). Collaborator: P. Schiebener (Technical Univ. of Munich)

One group of activities in the past year was related to the interests of the International Association for Properties of Steam, with Levelt Sengers chairing Working Group A on pure steam and aqueous systems. With IAPS-sponsored visitor Schiebener, a new correlation of the refractive index of water and steam was completed as a function of pressure, temperature, and wavelength, and compared with all literature data of the past 100 years. A report was prepared for IAPS and is being shaped into a publication for J. Phys. Chem. Ref. Data. With Japas and Garvin (Chemical Thermodynamics Division of NBS) a beginning was made with reformulation of the dielectric constant of water, a property whose derivatives enter all correlations of aqueous electrolyte properties. A one-day seminar on properties and industrial problems of solutions in high-temperature steam was coorganized by Levelt Sengers at the IAPS meeting, September 1987, Reading, UK.

Another group of activities continued to center around aqueous mixtures. With Gallagher, the apparent molar properties and phase boundaries of dilute

NaCl in high temperature water are being mapped onto the known properties of pure water. With Japas, the anomalous solubility of gases in high-temperature water is being formulated.

An invited talk was given by Levelt Sengers at the Airlie House Conference on the Thermodynamics of Aqueous Systems, May 1987, and a paper is being finalized for the proceedings of the meeting. Morrison spoke at the BYU Symposium on Chemistry in High Temperature Solutions, August 1987, and has finished a first draft for the Proceedings.

Thermodynamic Properties of Fluid Mixtures

L.A. Weber, E.J. Clark, G. Morrison, J.S. Gallagher, J.L. Manley, J.M.H. Levelt Sengers, M. Patron (Guest Scientist).
Collaborator: C. Peters (Univ. of Delft)

The work on characterization of the system isobutane-isopentane, a geothermal working fluid mixture, was completed, and several publications (including an article in the Review of Scientific Instruments) and presentations at AIChE meetings resulted.

The PVT apparatus was dismantled, repaired, and modified for study of the mixture CO_2-C_2H_6. The VLE apparatus was thoroughly cleaned and a large number of improvements were made in the hardware and in the interface with the computer.

In a NATO collaboration with Peters, the Donohue perturbed-hard-sphere model has been successfully applied to mixtures of small and long n-alkanes. A paper was written for presentation at the New York AIChE meeting. Work is ongoing on the calculation of critical curves and three-phase boundaries.

With scientists at the University of Maryland, collaborative programs have been set up on crossover in pure fluids and mixtures. A large number of joint tutorials have been held. Work has begun on crossover in refrigerants.

New work is starting on the development of a high-pressure dilatometer; also, we are studying the feasibility of preparing extended-chain polymer fibers from pressurized solutions.

Electrophoretic Light Scattering From Macromolecular Solutions and Colloidal Dispersions

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

The analysis of quasielasticly 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. 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 simultaneously monitor 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, NBS/CCE

Computer Simulation Studies of Liquids and Solids

R.D. Mountain, J.G. Amar

The molecular level computer simulation of the properties of liquids has proven to be an essential technique for utilizing formal, statistical mechanics-based models of condensed matter. We have an active program which both develops and utilizes simulation methods to model thermal properties in terms of the molecular level interactions. The NBS supercomputer is an essential resource for this work. During the past year, our efforts have been directed towards various aspects of supercooled liquids, towards the simulation of molecular fluids, and towards the study of the growth of particulates by aggregation of matter. The work on molecular fluids ties in closely with Thermophysics Division work on refrigerant mixtures and on properties of dilute water mixtures at elevated temperatures. The aggregation study is a collaborative effort with the NBS Center for Fire Research.

An extensive study of the supercooled liquid state of a simple model system was undertaken to identify those features which would distinguish the supercooled liquid from the equilibrium liquid. Some atomic-level properties associated with shear were found to do this. We also made a start on the study of glass formation using a simple model of a binary mixture. The objective is to guide the development of dynamical theories of glass formation. Another project studied the time-development of composition domains in a phase separating mixture. The results clarified the theoretical picture and indicated that the existing phenomenological theory is adequate. Work has continued on the study of infrared absorption in liquid mixtures. Some experimentally observed features continue to not be described by the models studied, indicating the need for some careful thought about the physical processes being modeled. We have developed a set of effective potential functions for two refrigerants, dicholordifluoromethane (R12) and chlorodifluoromethane (R22). These potentials will be used to model the thermal properties of mixtures of these liquids. Particulates, such as soot particles, grow through the aggregation of other particles. Our modeling of this process is being used to study the kinetics of the growth process and to aid in the development of light scattering as a diagnostic probe of particulate size and structure. The structure is characterized by a "fractal" or Hausdorf dimension on the order of 1.8.

Low-Frequency, Low-Shear Rate Viscosity Measurements

R.F. Berg, M.R. Moldover
Collaborators: A. Voronel (Univ. of Tel Aviv), J.S. Huang (Exxon)

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 Hz) and a low shear rate (0.05 s^{-1}). The viscometer has extremely precise temperature control in the range (-100°C to +100°C) and has been used with fluids at pressures up to 10 MPa. As part of the NASA project, we have measured the viscosity of four binary mixtures near their consolute points. These mixtures have viscosity enhancements that, according to theory, should be of the same form in liquid-vapor systems near critical points. In the past year we have exploited the viscometer for two other projects. (1) We measured the viscosity of two liquid alkali metal alloys which freeze at temperatures near -80°C. This work was directed toward testing a theory of glass formation in alloys. (2) In collaboration with J.S. Huang, we measured the viscosity enhancements found in a microemulsion in association with a critical point and with a percolation transition. The measurements showed that most of the viscosity increase is related to the percolation transition. Microemulsions are under study in industry for their application to enhanced oil recovery, delivery of pharmaceuticals, and advanced separation processes. The unique capabilities of our instrument are ideal for this and any other shear sensitive system.

Spherical Acoustic Resonators for Thermophysical Properties and Standards Measurements

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

A new determination of the universal gas constant, R, has led to the value: $R = (8.314471 \pm 0.000014)$ J mol^{-1} K^{-1}. The standard error of this result, 1.7 parts per million, is 5 times smaller than that of the best previous value of R. The new value of R leads to a 5-fold improvement in the values of the Boltzmann constant, $k = (1.3806513 \pm 0.0000025) \times 10^{-23}$ J K^{-1}, and the Stefan-Boltzmann constant, $\sigma = (5.670399 \pm 0.000038) \pm 10^{-8}$ W m^{-2} K^{-4}. The more accurate values of R, k, and σ will be most useful for primary thermometry (e.g. gas, noise, acoustic, and radiation thermometry) with thermometers whose design does not permit them to be used at the temperature of the triple point of water, 273.16 K, where the thermodynamic temperature scale is defined.

We have compared the 1/8-liter spherical acoustic resonator which had been transferred from Gaithersburg to Boulder in March 1986 with the cylindrical resonator that was used for speed of sound measurements in

Boulder. We conducted the comparison with a methane-ethane mixture in the pressure range 0-3.4 MPa and in the temperature range 300 K-350 K. The speed of sound determined by the two independent measuring systems differed by 0.02% at the lowest pressures and 0.05% at the highest pressures. Such small differences between independent measurements are rare. This comparison was part of a DoE-sponsored project to develop techniques to measure the speed of sound in industrially important gases at high temperatures.

*NBS Center for Basic Standards

Refrigerant Mixtures - Measurement and Modeling

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

The use of refrigerants, chlorofluorinated hydrocarbons (CFC's), has an economic and ecological dilemma of millennial proportions. The use of CFC's profoundly influences our lives, from "comfort" uses, to climate control for the electronic equipment that characterizes our technological age, to the storage of food and temperature sensitive materials such as medicines, blood products, and organs for surgical transplants. There is evidence that the leakage of two major refrigerants, R11 and R12, beyond the tropopause could lead to the eventual destruction of the ozone layer, which removes the high-energy component of the ultraviolet part of the solar spectrum. The presence of these wavelengths in ambient sunlight would increase the incidence of skin cancers, affect plant growth, and modify lower atmospheric chemistry. In recognition of the importance of room-temperature working fluids and the consequences of the continued use of R11 and R12, an international treaty to reduce their use has recently been signed by the U.S.

A satisfactory substitute must meet a variety of criteria. In addition to the appropriate thermophysical properties, it must be non-toxic, non-combustible, non-corrosive, and stable at elevated temperatures in the presence of traces of water, and in the presence of high electric fields. An analysis of over 800 compounds, indicates, ironically, that the only satisfactory substitutes will likely be fluorinated hydrocarbons.
G. Morrison has made a survey of silicon compounds; there were no obvious candidates from that group. Despite the relative simplicity of CFC's and their economic significance, there is little experimental information about all but a few of them; information about their mixtures is even more meager.

The cooperative program with the NBS Center for Building Technology is making a two-front attack on this problem. We have used a modified Carnahan-Starling equation of state to generate accurate thermodynamic surfaces for the pure materials. The modified equation is simple and has a firm physical foundation. M. Patron and J.V. Sengers have begun the application of a cross-over algorithm to the equation of state. This modification would compensate for the shortcomings of a classical equation in the critical region, and it would be the first application of the recently developed Albright/Sengers prescription to a practical equation of state. The same equation of state has been modified for mixtures. Considerable progress has been made in predicting the properties of mixtures. The mixture equation of state and the phase diagram algorithms and equation of state parameters published in the Morrison/McLinden NBS Technical Note of 1986 have been used by J. Gallagher to produce a set of 17 thermodynamic charts of 3 pure materials and 7 mixtures. In addition, measurements are being made on both pure and mixed refrigerant materials to check older data and to expand the data base. Work has begun on materials, both pure and mixed, that are likely candidates to replace R11, R12, and R22 as working fluids.

*NBS Center for Building Technology

The Langmuir Film Balance

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

The Langmuir film balance measures the surface tension of water-insoluble surfactant monolayers. It can also be used to prepare monolayers in well characterized states for a variety of optical, mechanical, and chemical experiments. The surfactants typically studied with this instrument, molecules that contain one or more highly polar groups attached to large apolar moieties, are characteristic of the species encountered in cell membranes, micellar systems, certain classes of emulsions, and liquid membranes, systems that have obvious biological functions as well as industrial applications. Although these systems are often multilayer in structure, measurements on the monolayer provide a means of making direct measurements of molecular, mechanical, and phase properties that can only be inferred from measurements on the more complex system in-situ.

The film balance developed and constructed at NBS is a computer interfaced instrument in which many of the problems associated with older instruments - surface active contamination, temperature gradients, saturation of the vapor above the film, and tedium of measurement - have been substantially minimized. The instrument also has a robust semiconductor sensor that allows surface tensions to be measured over nearly five orders of magnitude. Measurements made on this instrument during its development have verified recent measurements on the nature of certain phase transitions in the liquid phase of the monolayer - a discovery that has eluded researchers for nearly eighty years. Other measurements on this instrument have shown that the classic studies of liquid-vapor equilibrium in the monolayer were seriously compromised by surface active contamination. Both these measurements were done as a matter of the normal operation of the instrument and without the excessive and distracting precautions needed on older style instruments.

The NBS Langmuir balance offers the opportunity to study phenomena in detail that has not been possible in the past and to measure fundamental thermophysical properties of pure and mixed monolayers without being compromised by uncontrolled artifacts. Any fine measurement has the merit that it will lead to a better quantitative understanding of a material or phenomenon; the understanding of these monolayers is presently not well established. In addition, however, the measurements offer the opportunity of establishing a set of standard reference data on an important class of materials.

Interfacial Phenomena

M.R. Moldover, J.W. Schmidt, R.F. Kayser, J.C. Rainwater

The program on interfacial phenomena addresses industrially important problems in liquid-solid, liquid-liquid, and liquid-vapor interfaces using modeling, theory, and experiment. The work has led to 14 publications and 25 invitations to speak within the past year.

In the area of modeling, the theoretically motivated Rainwater-Moldover-Gallagher correlation of VLE data for binary mixtures was extended to include interfacial tension. The extended VLE correlation was shown to predict the interfacial tension in mixtures of CO_2 + butane within experimental accuracy. The method is applicable immediately to the 27 binary mixtures, including refrigerants, for which Rainwater has correlated VLE surfaces in the extended critical region. The interfacial tensions of refrigerants are used to predict heat transfer in heating and air conditioning equipment; the interfacial tensions of mixtures such as CO_2 + butane are used to model petroleum reservoirs.

Theoretical efforts have focused on general mechanisms for stabilizing thin liquid films against external fields such as gravity. Much progress has been made in understanding the role of dispersion forces quantitatively, and the work has expanded to include the effects of electrical double layer forces. New results include a calculation of the thickness of high-dielectric-constant wetting layers that form on solids immersed in electrolyte solutions and a calculation of the difference between the surface tension of a charged interface and of the same interface when uncharged. The results apply to mixtures of polar and nonpolar molecules in contact with technologically important substrates such as glass.

A state-of-the-art ellipsometer has been used to study the interface between the liquid phases of two binary mixtures (CS_2 + CH_3OH and C_6H_{12} + CH_3OH), the goal being to distinguish between two schools of thought concerning fluid interfaces. One class of theories predicts that the interfacial tension is not a strong function of the area of the interface, whereas another predicts substantial increases in the interfacial tension when an interface is confined to a small area, as in a pore. The predicted increase depends upon the smallest possible length of capillary waves. A preliminary analysis of our data shows that capillary waves can be defined to a length scale that is approximately twice the bulk correlation length. If this result is sustained by a more sophisticated analysis, it implies that an interface confined to a very small pore or nucleating droplet could have an interfacial tension as much as 8 times that of the macroscopic interface.

PROPERTIES OF FLUIDS GROUP

Corresponding States Theories of Fluid Mixtures

J.F. Ely, J.R. Fox, R.D. McCarty, M.L. Huber, T.S. Storvick (Guest Scientist)
Collaborators: D. Erickson (Rice Univ.), R.T. Jacobsen (Univ. of Idaho)

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 two. Current work involves extending these results to real fluids.

An original and radically new approach to the improvement of corresponding states methods is being developed. The resulting "field space" transformations 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 pure fluid correlations. This is corrected in the new structure. 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

J.F. Ely, J.W. Magee, M.L. Huber, T.J. Bruno, W.M. Haynes
Collaborators: J. Sherman*, L. Chu*, R. Baldwin*, D. Erickson (Rice Univ.)

Industrial interest in enhanced oil recovery using near-critical carbon dioxide, in supercritical fluid extraction of fuel materials and foodstuffs, 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 four projects are underway which address various aspects of supercritical fluid properties.

The first project, which is sponsored by a consortium of four companies, one trade organization and NBS, deals with the measurement and correlation of PVTx data for carbon dioxide-rich mixtures. Thus far, experimental data have been obtained for one ternary and three 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.

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, n-pentane and carbon dioxide have been obtained. In the near future rescaled 32-term BWR equations will also be available for normal and isobutane.

In the third project, supercritical solubility data for high value coal liquids such as creosols have been obtained in a flow equilibrium apparatus. Various solvents (and co-solvents) have been investigated as to their value in extracting these materials. Work is currently underway to model this equilibrium data with an equation of state designed for polar fluids.

Finally, 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, solubilities, and partial molar volumes.

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Predictive Computer Packages

J.F. Ely, R.D. McCarty
Collaborator: R.T. Jacobsen (Univ. 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 useable 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 NBS 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 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

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T.J. Bruno, R.D. Goodwin
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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.

*Chemical Engineering Science Division, NBS/CCE

PVT Measurements and Correlation

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Collaborators: R. Masui (Nat. Research Lab. of Metrology, Japan), J. Sherman (Colorado School of Mines)

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 CO_2, $CO_2 + N_2$, $CO_2 + CH_4$, $CO_2 + N_2 + CH_4$, $CO_2 + C_2H_6$, R-13, methanol, benzene, and toluene. Planned measurements include carbon dioxide plus hydrocarbons, $N_2 + O_2 + Ar$ (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, is currently being applied to monomethylhydrazine.

Phase Equilibria Studies

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

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/cm^3, 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. Future measurements will include binary mixtures of nitrogen and normal butane, and then ternary mixtures of nitrogen, carbon dioxide, and normal butane.

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. Construction of a differential refractometer cell for use at high pressures (70 MPa) and high temperatures (800 K) has been initiated. This technique will provide a real time, non-destructive means for the determination of binary mixture compositions at extreme conditions encountered in new technologies in the energy industry.

An apparatus is available for measurement 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, CO_2, and CO. Measurements are now in progress for hydrogen and ethylene; a study of the hydrogen and ammonia system 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 a ternary mixture of ethane, n-butane, and n-pentane and has been used to predict interfacial tension. A mathematically complex model has been derived to accomodate VLE in the presence of liquid-liquid equilibria (LLE). 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

J.W. Magee, B.A. Younglove, J.E. Mayrath, H.M. Roder, R.D. McCarty, N.V. Frederick, M.R. Moldover

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 data have been obtained for three mixtures of CH_4 and C_2H_6 from 100 K to 320 K at pressures to 35 MPa. When combined with previous data on pure CH_4 and C_2H_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_2H_6 binary system is the most important binary system in the natural gas industry. C_V measurements on air and mixtures of CO_2 and C_2H_6 will be initiated in the near future. We will also soon have the transient hot-wire apparatus 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 similiar 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 capabilites, 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

D.E. Diller, H.M. Roder, D.G. Friend, J.C. Rainwater
Collaborators: C.A. Nieto de Castro (Lisbon Univ.), W.A. Wakeham (Imperial 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, theoretical 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 on compressed gaseous argon and methane at temperatures to 500 K and pressures to 50 MPa. Measurements on ethane, carbon dioxide, and their mixtures are scheduled next with this apparatus. The low temperature viscometer has recently been used to obtain viscosity data for liquid toluene at temperatures from 185 K to 320 K. 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 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 error 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 is nearing completion. It will operate 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 have recently completed new correlations for the thermal conductivity and viscosity of methane 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 progess. The transport properties of binary mixtures of methane and ethane have been studied experimentallly in this laboratory; a correlation of the thermal conductivity surface was published during 1987, and a study of the mixture viscosity surface has now 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.

Neutron Scattering

H.J.M. Hanley, G.C. Straty
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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 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 fluids for the past year were glycerol and a suspension of latex spheres in water. Glycerol was selected because it can be made to behave as a simple or a complex liquid by varying the temperature. The latex spheres--since they make a well-defined system--were used to get benchmark data.

Specific tasks carried out during the past year were: (a) measurement of S(Q) for glycerol in the temperature range 175 K to 300 K on the NBS SANS (small angle neutron scattering) and NBS BT6 spectrometers; (b) measurement of S(Q) for the latex suspensions on the NBS SANS at very high concentrations--information on polydispersivity and "glass" formation resulted; and (c) design and partial testing of a cell to study glycerol under shear via neutrons, and design and partial testing of a shearing cell for use with colloids and/or polymers. With regard to (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 NBS reactor facility to handle fluids in nonequilibrium. There is strong industrial and biological interest in shearing equipment.

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Non-Newtonian Fluid Behavior

H.J.M. Hanley, J.C. Rainwater, M.L. Huber
Collaborators: D.J. Evans (Australian Nat. Univ.), S. Hess (Berlin Tech. Univ.)

This program addresses some of the theoretical problems related to the overall goal of studying complex liquids. The work is carried out in conjunction with 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 1s 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.

Specific tasks include: (a) the differences between 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; (b) work on the rheological characteristics of simple fluids is continuing with a reexamination of earlier Weissenberg effect calculations from a reassessment of the importance of shear dilatancy and finite compressibility; (c) the radial distribution function and structure factor have been calculated as explicit 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 used 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 those measured in light scattering experiments on sheared colloidal suspensions, and the essential qualitative features of those experiments are reproduced correctly.

Other recent work includes: (d) 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; (e) continued work on the development of computer programs to simulate liquids under shear and to show their relationship to experiment; and (f) continued study of an exactly solvable weak potential model under a flow field more general than planar Couette flow.

DYNAMIC MEASUREMENTS PROGRAM

Thermophysical Measurements by Dynamic Methods

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

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 liquid electrically conducting substances 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. This new technique will be further explored during the coming year.

A system for high-temperature thermal diffusivity measurements has become operational. The system utilizes the laser-pulse technique for measuring thermal diffusivity of substances at temperatures above 1500 K. The system was tested for temperatures up to about 2200 K and is capable of going up to 3000 K. Preliminary measurements on graphite in the range 1500-2200 K were performed. The results indicated a reproducibility of better than 1%, which is considered extremely good at these temperatures. The system can be used for measurements on both conducting and nonconducting materials.

The microsecond-resolution pulse heating system, which became operational a year ago, was used to conduct feasibility studies on rapid heating of graphite to high temperatures. The objectives were to reach the triple point of graphite (about 4500 K) and to investigate the possibility of excursions in the liquid phase of graphite. The initial results are promising; however, a considerable amount of additional work is required to attain the objective.

As an integral part of the dynamic measurements program, effort was exerted on the development of rapid temperature measurement techniques. The research was concentrated on the development of multiwavelength pyrometry as well as spatial-scanning pyrometers. When completed, these will be unique instruments capable of performing accurate temperature measurements, with millisecond resolution, either at six wavelengths or over a 2-cm long linear target.

Work has begun in connection with the accurate measurement of thermal expansion of tungsten above 1500 K and up to near the melting point (about 3700 K). This work is in connection with the establishment of tungsten as a standard reference material for thermal expansion.

Theoretical studies in support of the Dynamic Measurements Program are continuing in two areas: (1) stability of a liquid cylindrical specimen under high electromagnetic fields and (2) transient temperature distribution in a rapidly cooling spherical specimen.

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6. CONFERENCES AND WORKSHOPS

CONFERENCES

A Symposium consisting of four sessions and twenty-two papers in honor of Thomas W. Leland, 1987 Spring National Meeting of AIChE, Houston, TX. Organized and chaired by James Ely.

A Symposium on Thermodynamics for Bioseparations, November 1987 AIChE National Meeting, New York, NY. Organized and chaired by Professor Carol Hall, Department of Chemical Engineering, North Carolina State University, Raleigh, NC and Neil Olien.

WORKSHOPS

Working Group A, International Association for Properties of Steam, held at Reading, UK, Sept. 13-18, 1987. Chaired by J.M.H. Levelt Sengers, who also coorganized a one-day workshop on Solutions in High-Pressure Steam and High-Temperature Water.

Workshop on Thermophysical Properties for Bioprocess Engineering, Gaithersburg, MD, March 16, 1987. Organized and chaired by Neil Olien. Report of Meeting published in Chemical Engineering Progress, Vol. 83, pp. 45-48 (Oct. 1987).

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 used 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 U.S. industry and the scientific research community. These measurements include temperature, pressure, velocity, flow rate, humidity, composition and concentration, pH, particle size and number density, volume fraction and other quantities of interest in multiphase reacting and non-reacting 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 beds, plug flow reactors 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 separation processes; magnetic resonance techniques are expected to provide critically needed data on compositional distribution and transport rates in bioreactors. Techniques developed for particulate measurements in flames are being extended to study formation of silica particles, in order to 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 toward optimization of powder atomization processes, one of the most promising processes in metals processing and for production of high temperature ceramics. Finally, currently available high temperature reactor facilities (FBR, PFR) are being 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. The results 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 industrial and public clients across the country. The recent upgrading of these facilities will make it possible to serve U.S. industry even better.

2. GOAL

Within the framework of the Center for Chemical Engineering, the 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.

It is further recognized that 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 U.S. industry in domestic as well as foreign markets.

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

3. GROUP FUNCTIONS

The research activities of the Division are performed 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 applying these principles toward improving and expanding the NBS 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 confined flows 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 NBS 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 to public institutions.

- Multiphase Reacting Flows Group - A.K. Gaigalas, Group Leader

The mission of the Multiphase Reacting Flows Group is to perform research on multiphase flows at ambient and near-ambient temperatures with and without chemical reactions. The ultimate purposes of this activity are 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.

The Multiphase Reacting Flows Group bears the responsibility for NBS 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 non-intrusive optical 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 measurement, laser induced fluorescence (LIF), 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. Some of the research in this group will be assigned to the Optical Diagnostics Group, in the Center Office, in fiscal year 1988.

- 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 form films and a comprehensive surface analytical facility is used to characterize the surfaces of these films where the chemical reaction takes 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. Further, thin film thermocouples deposited on metal, ceramic and polymer substrates are subjects of study.

A study to develop optimum and standardized methods for collection of samples of water, air, and soil is an integral part of the research effort in this group.

The Process Sensing Group is responsible for providing the NBS calibration services for 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 CCE 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 quantified and reported for publication in the appropriate literature. In the specific calibration services offered to U.S. industry, activities are summarized as follows:

Service	Number of Items Calibrated
Flowrate	58 (40 for industry)
Volumetric Containers	88 (81 for industry)
Aerodynamic Devices	85 (59 for industry)
Reference Standard Hydrometers	73 (73 for industry)
Humidity	81 (78 for industry)

These calibrations generally establish a traceability link between the respective calibration requester and NBS. In this way, these calibrations form a basis for the assurance of all measurements produced in the requester's laboratories.

Besides these services, a number of in-situ calibrations were performed by NBS personnel in the customers' laboratories. In this way, improved measurement assurance was provided to strengthen the traceability links between actual, installed instrumentation and the national standards for these measurements.

Round-Robin Flow Measurement Assurance Program

G.E. Mattingly

In the last year, the Fluid Flow Group has continued the DoD-requested program to conduct a round-robin flow measurement assurance program to check flowmeter calibration facility performances in Army, Navy, and Air Force labs. This program, requested for hydrocarbon liquids, has been designed for several sets of tandem turbine meters. Specific test procedures are being used in the DoD labs to quantify lab performances to make satisfactory flow measurements. This program will be used on a continuing basis to maintain desired control of these measurement processes. At the request of these DoD labs, this testing program is being expanded to include industrial laboratories. In this manner, realistic flow measurement traceability will be established and maintained for the participating laboratories.

Also, in the last year, the Fluid Flow Group has responded to a Navy request to assess the flowrate measurement accuracy of a Navy selected flowmeter calibration facility. The results of this project will be two-fold: (1) to produce a quantified evaluation of the facility's performance in actual dynamic conditions of use, and (2) to provide direct traceability to NBS flow standards for this facility.

Flowmeter Installation-Effects Consortium Research

G.E. Mattingly, T.T. Yeh

The NBS flowmeter research program on installation-effects continues to attract participation of industry through a consortium that has been formed to assist in supporting this program. Benefits to consortium participants include guiding current and future phases of the work and receiving results on a timely basis. The consortium currently includes some 15 meter manufacturers and users, U.S. and foreign. Research results will provide, for the first time, qualitative and quantitative descriptions of the distorted pipeflows produced by piping configurations. These results are used to upgrade or to initiate useful installation specifications for flowmetering standards by implementing a new strategy to achieve this goal.

The strategy adopted for this program contrasts markedly with that used in the past. Conventionally, it has been the practice to conduct considerable numbers of specific meter calibrations to determine the minimal distances (between meter and specific upstream piping configuration) for which uncertainty levels on meter factors are to be increased by specified amounts. Through this conventional approach, little was learned or understood of the salient features of the pipeflow profiles involved. The currently adopted strategy focuses on these profiles; specifically, it measures them using Laser Doppler Velocimetry (LDV), and characterizes them and their changes with distance from the piping configuration.

With these results, and the associated understanding of these pipeflows, a number of limited, informed calibration tests can be carried out by meter manufacturers and others so that specific results, i.e., discharge coefficients, meter factors, etc., are related to pertinent pipeflow characteristics. In this way, meters can be installed in any locations where their performance is satisfactorily stable, and meter factors or discharge coefficients are satisfactorily predicted for the installation. It is expected that this strategy will produce installation specifications for metering standards which will enable satisfactory flow measurements to be made in installations previously considered non-ideal and for which no current standards are applicable.

In the past year, extensive LDV profiling has been done in two-inch (50 mm) diameter, cylindrical pipeline water flows. Results for diametral Reynolds numbers of 10^4 and 10^5, and a relative roughness of 0.0005, show that the second elbow-out-of-plane configuration generates severe and complex swirl. This second elbow arrangement has a short (2.4D) length of straight pipe placed between the elbows. This short length of pipe produces considerable changes in the outflow compared to the closely coupled elbows tested previously.

As was done with the previous configuration using different types of flowmeters (a turbine and three sizes of orifice meter), the methodology of our research was demonstrated. The level of success varied for the different types of flowmeter.

It is concluded that this strategy for producing improved flowmeter installation specifications can be very effective. The current phase of this research continues to produce analogous results for the single elbow piping configuration so ubiquitous in actual metering practice and so disruptive of meter performance. It is also concluded that results of this program can be very useful in designing and installing efficient flow conditioners for reducing or eliminating such anomalous pipeflows.

High Pressure Inert Gas Atomization

G.E. Mattingly, P.I. Espina

Metal atomization--the production of fine powders through the interactions of high pressure gas jets and liquid metal streams--is an emerging technology that offers considerable promise for industrial productivity in the metallurgical industries. To assist U.S. industry in this area, the NBS Office of Non-Destructive Evaluation (NDE) has formed an industry-government consortium to produce and demonstrate the measurement methods needed to automate and optimize the productivity of this process. To attain this objective an NBS team has been formed which brings together four different capabilities--metallurgy, fluid flow, optical particle measurement, and automation.

In the past year, the Fluid Flow Group has conducted a range of experiments on gas-liquid interactions. The strategy is to begin with the gas-only flow field and determine the characteristics of this flow as conditions are changed toward the harsh, hostile pressures and temperatures 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. The salient features of these flowfields are then correlated with pertinent parameters.

Our efforts continue to generate measurement techniques capable of sensing critical flow features. These sensors will then provide input for other sensors or for automated control so that the desired powder product is made. This project is viewed as a continuing one in which a wide range of conditions--metal alloys, powder sizes, geometrical arrangements of gas-liquid interactions, stimulation techniques, ultrasonics, etc.--can be tested to determine effects upon the process productivity.

Vortex Shedding Flowmeter Research

G.E. Mattingly, T.T. Yeh

The industry-government consortium sponsored project on vortex shedding flowmeter performance successfully completed its two year effort to characterize "jitter" and "fade" effects. The final report of the experiments has been sent to the sponsors (14 vortex meter manufacturers and users). With the final report was sent a survey questionnaire to suggest topics for a follow-on second phase of this program and to indicate industry interest in continuing research.

MULTIPHASE REACTING FLOWS GROUP

Measurement of the Solids Fraction in Two-phase Flows

W.G. Cleveland, 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 can act as a waveguide for radio waves. By measuring the speed of radio waves propagating in the flowing slurry and by comparing the measured speed to the value for pure water, it is possible to infer the amount of solid material carried by the water stream. Tests of the meter in the laboratory have demonstrated a high degree of accuracy. Attempts to adapt the meter to the factory environment are in progress. The major problem is the high conductivity of the process stream and the necessity to use non-intrusive antennas.

The operation of the meter has been investigated in solutions with sodium sulfate concentration up to 10 mM. The major contribution of the conductivity to the value of the extracted dielectric constant was as required by Maxwell's equations. Small discrepancies between the expected and measured dielectric constant were most likely due to the nature of the parameter fitting algorithm. The small instability in the convergence of the algorithm is under investigation. It was also found that the addition of a small amount of the second mode improved the correspondence between the expected and measured response of the detector array.

The conductivity studies were performed with an intrusive antenna consisting of a loop in the middle of the pipe with its plane aligned with the axis of the pipe. Further effort is being made to make the antenna less intrusive and thus acceptable to the factory environment.

Electrophoretic Light Scattering (ELS)

S. Woo, A.K. Gaigalas, J.J. Ulbrecht

The object of this study is to develop a technique to monitor the protein separation process. 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 electric fields. ELS also utilizes the variability of the surface charge of proteins to detect differences in electrophoretic velocity. The major difference is that ELS occurs in-situ and is orders of magnitude faster then the gel method.

The initial effort consisted of setting up the apparatus for measurement of diffusion of latex spheres in solutions of different ionic strength. This effort has resulted in a working system which can measure the diffusion of latex particles using photon correlation techniques. The initial measurement of the change of diffusion coefficient with changing ionic strength has been successful. Besides its intrinsic merit, this measurement serves as a foundation for extending the work to electric field effects. Another effort in that direction has been the measurement of diffusion in low molecular weight acrilamide solutions. These solutions can support large electric fields and thus will be very useful for the initial ELS measurements. At this time two sets of ELS scattering cells are being developed.

Electrochemical Study of Mass Transfer in Porous Media

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

A project has been initiated to measure, as a function of frequency, the ac electrochemical impedance of a porous medium saturated with an aqueous salt solution. The impedance at low frequencies depends on the mass transport of the 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 magnetic resonance imaging measurements.

Electrochemical Measurement of Diffusion Coefficients

B. Robertson

The electrohydrodynamic (EHD) method of measuring the Schmidt number has been compared carefully with the older dc method of Levich using 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, or the concentration of the limiting reactant, as does the dc method. The two methods agree within 1 per cent when the EHD measurement is done at a low disk velocity. A knowledge of the diffusion coefficient in the pure liquid is necessary for studying the effect of a porous media on mass transfer. This work has been done in collaboration with B. Tribollet and C. Deslouis of the University of Pierre and Marie Curie in Paris.

Studies of Flow in the Vicinity of a Mixer Blade

R.C. Calabrese, B.J. Sadoff

A liquid-liquid drop dispersion flow loop facility has been used, in collaboration with the University of Maryland, to study flow in the vicinity of sharp-edged bodies which simulate real mixing elements. The facility uses laser velocimetry, high speed photography, and hydrogen-bubble techniques to characterize flow fields. The experimental work has led to the following conclusions. Trailing vortices extend to about 2 blade widths beyond the point of formation. The turbulent kinetic energy peaks at about one blade width beyond the tip, and it is highest on the outer edges of the vortices. In the vortex, the magnitude of the rms turbulent velocity is greater than that of the mean. At the blade tip, mean deformation rates on the vortex edge are about 100 times the impeller speed, peaking at about 190. These values become more uniform and decrease with distance from the point of vortex breakdown. The mean velocity field is equally rotational and deformational. At the blade tip, about 10% of the energy dissipated is due to mean gradients. The viscous contribution decreases rapidly to about 1%. On the vortex outer edges, energy dissipation rates can be one to two orders of magnitude greater than the mean for an equivalent stirred tank. The peak value in the channel is about 250 times the mean.

Corrosion of Nuclear Waste Containers

A. Van Orden

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. Since there are no data for this or any other alloy under repository conditions for hundreds or thousands of years, this project seeks to use ancient metals as analogues for these waste containers. The abundance of metal archaeological artifacts found under many conditions makes it possible to use these to test mathematical models and draw general conclusions about the very long term corrosion behavior and stability of modern iron objects. Nails and their surrounding soil were obtained for study from near Dorchester, which is a site of known Roman occupation. These artifacts, with their corrosion film coatings, have been examined using scanning electron microscopy, energy dispersive x-ray analysis, microprobe analysis, x-ray diffraction and Mossbauer spectroscopy to provide information on the composition of both the remaining metal and the corrosion film. These data can be compared with the theoretical models for corrosion of iron and may help in validation of these models. The chemistry of the soil, and the ground water interactions, are also being studied to provide information on the transport of metal ions away from the corroding interface and on transport of oxygen and other reactive species to the interface. The nature of the corrosive attack is being studied to evaluate parameters in the existing models such as localized attack.

Early results show that the corrosion film is composed of Fe_2O_3, Fe_3O_4, and non-stoichiometric FeO. The corrosion film has several layers, the origin of which is not yet known. There is also evidence of extensive localized corrosion, which must be considered in any model used to describe the development of oxides on low carbon steel. The microstructure of the nail itself gives data on the manufacturing techniques used at this time. By considering how the nails were made, information on subjects of modern interest such as decarburization of the surface is being obtained. Data from the analyses of the corrosion film and soil are being compared to short-term data on the corrosion of modern alloys. In addition to the experimental results, a database has been established for ancient metal artifacts with a particular emphasis on transport of metallic ions, in porous materials, over very long periods of time.

Application of Magnetic Resonance Imaging (MRI) Techniques to the Study of Mass Transfer in Porous Media

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

The flow of water in porous materials was visualized by using magnetic resonance imaging (MRI). For initially dry beds, the water gives a large signal that can be detected directly. For flow in a wet bed, a dilute solution of manganese ions in water was used to displace the pure water and quench the MRI signal. Thus, the flow could be visualized indirectly. For materials such as bentonite, which interact strongly with water, the MRI technique also shows the interface region in which the water-bentonite complex is formed. The technique is sensitive and can give accurate and quantitative results for flow with low Peclet number.

For the initial experiment, four materials were chosen to give a variety of properties and also be relevant for storing nuclear waste. The materials were cast rock, aluminum-oxide particles, purified bentonite, and kaolin. All samples were cylindrical, with diameters of about 10 cm and heights of 13 cm. In order to give a uniform signal intensity across the image plane, the receiver coil was made large enough to enclose the samples completely. Each sample was placed in the receiver coil with the long axis of the sample and coil oriented vertically and at right angles to the main field. The images were obtained for slices 1 cm thick and in-plane resolution of 1 mm by 2 mm.

HIGH TEMPERATURE REACTING FLOWS GROUP

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 counterflow and axisymmetric jet diffusion flames. Computer codes are currently being developed to model these two systems. Although flame sheet formulations are employed in these models, Lewis numbers can be arbitrary. This is particularly important in the effort to simulate the H_2-O_2 counterflow burner experiments being carried out at NBS, since Lewis numbers in these systems are much less than unity. The model being developed for the axisymmetric jet diffusion flame will include the effects of unsteadiness, particularly as related to pulsing of the fuel jet. Experiments are being carried out in a collaborative effort at Wright-Patterson AFB and at NBS. The computational models developed for these flames will provide complete descriptions of the flow, species and thermophysical properties fields, and will permit quick assessment of the effects of parameter variations. Rigorous comparisons between numerical and experimental results will be made at each level of code development to ensure that the models realistically simulate the actual physics.

Destruction of Hazardous Waste in Fluidized Beds

A. Macek, N.O. Spears*, R. Chawla*, H.G. Semerjian

Control of products of incomplete combustion, generated during incineration of hazardous wastes, requires an understanding of rates and mechanisms of oxidation and thermal decomposition of the 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 study, made earlier under the sponsorship of EPA, showed that at least three experimental research approaches should be considered: (a) laboratory burners or furnaces; (b) high-temperature flow reactors (providing they offer sufficient residence times for the reactant); and (c) fluidized beds. The first approach (flame destruction) is convenient, but it does not offer good control of three critical parameters for simulation of full-scale incineration systems: temperature, residence time, and oxygen concentration.

Therefore, a decision has been made to explore the other two approaches, starting with oxidation studies in fluidized beds.

So far, two studies were made in the NBS fluidized-bed reactor at high temperatures, based on a novel optical technique, allowing observations in the interior of the bed. The first of these, reported previously, was temperature measurement of burning char particles. The second study, including the determination of mixing regimes for bed particles and measurement of solids dispersion coefficients, has also been completed now and a comprehensive report was written.

The existing fluidized-bed reactor has been modified to allow the metering of gaseous reactants into the bed and on-line exhaust monitoring of CO, CO_2 and O_2, and a preliminary study of destruction of gas-phase reactants in the bed has been completed. The study comprised four sets of experiments in which chlorinated and non-chlorinated hydrocarbons (methyl chloride and propane) were oxidized, each in both catalytic and non-catalytic beds. The results show significant increase of oxidation rates in catalytic beds.

A new fluidized-bed reactor has been designed which will allow longer gas residence times in the bed. The new reactor will be served by the same instrumentation and data acquisition systems as the dilute-phase flow reactor which is currently used for black-liquor combustion studies: fiber-optic pyrometry, on-line gas monitoring, etc. Future plans include several possibilities: (a) parallel plug-flow and fluidized-bed oxidization and pyrolysis studies of chlorinated hydrocarbons; (b) retention of chlorine-containing reaction products in the fluidized bed by means of solid sorbents; and (c) fluidized-bed destruction of solid and liquid agents. In all cases, the emphasis will be on application of advanced measurement techniques (fiber optics and lasers) to elucidation of in-situ reaction parameters.

*Howard University

Particle Formation in High Temperature Reacting Flows

M.R. Zachariah, H.G. Semerjian, D. Chin*, J.L. Katz*

Investigations are underway to determine the feasibility of using flames as the reacting environment for the formation of refractory particles. The goals of the project are to investigate the underlying physical-chemical processes leading to particle formation and growth, and suggest ways one might control the underlying chemistry and physics through changes in process parameters, to affect the final product purity, particle size and polydispersity. Additionally, through the use of non-intrusive laser diagnostics applied to investigating these processes, it is hoped that the limitations and advantages of the various techniques will be clarified and refined.

Current efforts have focused on the formation of silicon dioxide particles in a counter-flow diffusion flame using a hydrogen-oxygen flame to provide the temperature field and the radical pool. This geometry has been shown to provide a flat, highly uniform environment suitable for optical probing. In these experiments silane is used as the source of silicon and is introduced in the fuel leg of the counter-flow reactor. Measurements are then made of the flame temperature field, particle diameters and particle number densities. Temperatures have been measured by both fine-wire thermocouples and OH absorption techniques. In-situ particle sizing is conducted by dynamic light scattering experiments and/or dissymmetry experiments. These two techniques were shown to give comparable results. Number density measurements have been made using static light scattering techniques in conjunction with Mie theory calculations.

The results to date suggest that by changing the silane loading one can greatly influence both the particle size and number density. Changes in the equivalence ratio result in shifts of the region where particles are formed, as well as their growth characteristics and final size. It has been shown that the temperature affects both particle shapes and sizes. The results suggest that particle formation and the eventual growth mechanism are highly coupled to the precursor gas kinetics and that particle size, number density and shape can be altered by changing process parameters.

*Johns Hopkins University

Flame Temperature Measurements by Laser Excited Fluorescence

J.J. Horvath, H.G. Semerjian

A new nonintrusive temperature measurement technique, based on laser excited fluorescence, 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 vs the upper energy level that the transition originates from. All lines above the laser excited level will be found to fall on a straight line and the slope of this line will yield the temperature. This plot indicates the presence of a local 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 anti-Stokes of the excitation pulse, hence this method is applicable to high luminosity flames and conditions of high background Stokes fluorescence. This method is applicable to both naturally occurring species such as OH, CH and C_2 or atomic species seeded into the flame. Initial experiments have used gallium as the seeding species in premixed flames. A tunable dye laser, pumped by a nitrogen laser, is used to excite the $4P_{1/2}$-$5S_{1/2}$ transition of Ga at 403.3 nm and the resultant fluorescence from upper levels is observed. A wide variety of premixed flames were studied to determine the useful temperature range of this technique. Flames studied were $CH_4/Ar/O_2$, CH_4/Air, $C_2H_4/Ar/O_2$, and C_2H_4/Air. The temperature of these flames could be varied from approximately 1950 to 2500 K depending on flow conditions. Experimentally measured temperatures were found to be about 100-150 K below the adiabatic flame temperature calculated using the NASA computer program. 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 were developed.

Recent work has used an Nd-YAG pumped laser for greater spectral coverage of the useful wavelengths. This work has centered on determining the temperature range of useful thermometric species. We have also performed measurements using time resolved fluorescence to measure collisional transfer rates. We observed that the upward rates are faster than the downward as predicted by theory. Work will continue on both atomic and molecular seed species in order to develop single laser pulse temperature measurement techniques for use in industrial and scientific applications over a wide range of temperatures.

High Speed Laser Tomography for Measurement of Concentration and Temperature Distributions in Reacting Flows

H.G. Semerjian, D.R.F. Burgess

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 within five milliseconds. 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 frequency scanning range of the dye laser is currently being extended so that two OH lines can be scanned rapidly. This would enable the measurement of temperature using a two-line ratio technique.

Current work has focused on rapid measurements in non-symmetric fields at repetition rates up to 10 kHz, using a six-angle tomography approach. The new system has been used to measure the particle concentration field in rapidly fluctuating flames. Data have been obtained on the dynamics and three-dimensional structure of large eddies formed in an ethene-air turbulent diffusion flame. The frequency of eddy formation is controlled by introducing fluctuations into the fuel stream, using a loudspeaker. The formation, shedding, and break-up of eddies, marked by the soot particles formed in the flame, have been observed with a time resolution of 1 ms. Details of eddy formation in the jet have also been observed using a laser sheet beam located along the centerline of the jet. Titanium chloride is fed into the fuel jet, and when in contact with combustion generated water, it forms titanium oxide particles. Scattered light from the particles is used for flow visualization. As a parallel effort, a number of alternative reconstruction techniques have been investigated using computer simulations, to identify the approach ideally suited to this experiment. The maximum entropy method is found to be the most suitable, especially for reconstructing the field from a small number of projections (e.g. six angles).

Optical Sensing in Bioreactors

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

Recent advances in molecular biology have led industry and government agencies to recognize the economic potential for applying these advances in a diversity of industrial sectors, including the production of new drugs, food additives and chemicals, conversion of biomass, etc. However, implementation of these new technologies requires measurement capabilities which do not currently exist. Bioprocesses require very closely controlled environments, normally realizable only in batch processes. This is mainly because of 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, non-intrusive measurement methods are desirable to avoid difficulties associated with sampling, contamination, long response time, etc.

Optical techniques, especially with the use of tunable lasers, 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 the aromatic amino acids, indicating good sensitivity and selectivity. The fluorescence characteristics of a series of dipeptides and polypeptides were studied to determine the effects of amino acid sequence and various chemical functional groups on the observed fluorescence spectra. The spectra of commercially produced biomolecules, such as antibiotics and artificial sweeteners, were also observed. The fluorescence 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 using these spectra to monitor fermentation on-line using a flow-through cuvette. The fermentation broth is pumped through the cuvette where laser induced fluorescence spectra are measured, yielding information on the yeast and nutrient concentrations. The characteristic fluorescence spectra from the yeast and nutrients are used to monitor the state of the fermentation and the growth rate of yeast. The fluorescence can be correlated well with yeast dry weight as determined by withdrawing samples. Work is also under way with the University of Maryland, to understand the fluorescence of mixtures and to develop techniques for determining single components in complex mixtures. Groundwork has been laid for running a microbial fermentation to produce the antibiotic bacitracin which will also be monitored by on-line fluorescence. This is a completely different system which will demonstrate the applicability of LIF to on-line monitoring of various type bioreactors. We have also performed preliminary measurements using two-photon fluorescence and fluorescence lifetimes which indicate good promise for improving selectivity in the measurements. Fluorescence techniques are also expected to provide a powerful tool for cell activity and intracellular kinetics measurements. In the future, excitation/matrix, Raman and resonance Raman scattering will be used to provide improved species selectivity.

*Lehigh University

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 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 cooking process can be monitored and corrections applied before a cook is complete. 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. Laser excited fluorescence was found to be a sensitive technique for measurement of black liquor. The technique provides good detection limits and linear response over a large dynamic range. Measurements have recently been made on pulping liquors obtained from a paper mill. During the course of a 3 hour pulp cook, six or seven samples were obtained at various times from two separate runs. Laser excited fluorescence spectra were obtained, from these very optically dense liquors, using a backscatter configuration without any sample dilution. The fluorescence spectra obtained from these samples were found to vary during the cook, indicating good possibility of using fluorescence for a process control monitor. Even though we saw changes in the fluorescence intensity, the properties of these liquors were not well known. To relate fluorescence spectra to cooking liquors one should work with well characterized cooks whose properties are known. We are now working with a person at the Institute for Paper Chemistry who is providing us with liquors of known lignin concentrations made in a laboratory digester. The results in these samples have been good, where lignin concentrations were found to be linear in fluorescence intensity. The fluorescence spectrum also indicated a chemical change occurring near the end of a cook, something speculated on in the literature. We have also looked at the fluorescence of paper and paper fibers and found the signal to be related to the lignin content. Further studies will involve studying more laboratory pulp cooks to determine all parameters that affect fluorescence signals in order to develop a practical on-line measurement and control technique for the pulp and paper industry.

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 the above processes. The results of this study will provide an experimental data base, with well-defined boundary conditions, for the development and validation of spray combustion models being developed by the Jet Propulsion Laboratory, and Sandia and Los Alamos National Laboratories. The experiments are being carried out in a spray combustion facility, with a moveable-vane swirl burner, which simulates operating conditions found in practical combustion systems. A combination of non-intrusive 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, velocity and temperature fields.

Current efforts are focused on obtaining laser ensemble scattering and Doppler velocimetry measurements 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 flow rate; it thus allows one to study the effects of atomization on overall spray and spray flame structure. Flame characteristics are found to change dramatically as the atomizer air flow is increased, going from a sluggish flame (typical of pressure-atomized flames) to an intense fireball. This particular research nozzle is also being used by investigators at the University of California-Irvine and Carnegie-Mellon University, which will allow for direct comparison of our results and establish a broad experimental data base. In addition to the ensemble light scattering measurements, data will be compared 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 technique). Extinction data are being recorded with the air-assist atomizer to obtain information on the degree of light attenuation through the spray and spray flame. In an effort to significantly reduce the data acquisition time for the ensemble scattering measurements, a new detection system has been assembled in which two detectors are used to measure both scattering coefficients (Q_{HH} and Q_{VV}) simultaneously, thus determining the instantaneous values of the polarization ratio. This arrangement will avoid any measurement uncertainties associated with the averaging process, and may be applicable as a single particle counter. One of the topics of concern is the effect of fuel properties on spray and flame characteristics. Two sets of experiments are planned, one with heptane and the other with No. 6 residual oil as fuels. Heptane is a single-component fuel which will provide propitious 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.

*University of Maryland

Fundamental Studies of Black Liquor Combustion

A. Macek, N.D. Amin, S.R. Charagundla, H.G. Semerjian

Efficient operation of black liquor (BL) recovery boilers requires more fundamental information on combustion of BL droplets than is currently available. The problem of measurement of the pertinent combustion parameters is addressed by a joint project with the Institute of Paper Chemistry under DoE sponsorship. The NBS tasks of this joint project are directed toward studies of vaporization, pyrolysis, ignition, and combustion of dilute streams of BL droplets. This is currently being done in the high-temperature dilute-phase plug flow reactor (DPFR), specifically designed for such studies.

A positive-displacement technique, in which individual droplets are extruded from a hollow needle, was developed earlier in this project for on-demand generation of highly viscous droplets with diameters of the order of 1 mm. This technique is now being used for injection of BL droplets (with up to 65% solids) into high-temperature streams in the DPFR. High-speed photography has been used for: (a) observation of the processes of BL droplet formation and detachment from the needle tip, (b) measurement of diameters prior to detachment, (c) measurement of in-flight droplet diameters after detachment, and (d) measurement of velocities of droplets falling in a counterflowing hot gas stream. An extensive series of tests has been made, with droplet diameters ranging from 1.3 to 3.0 mm, gas temperatures from 700 to 875 °C, oxygen concentrations in the gas from 8 to 21%, and droplet residence times up to about 1 s. These in-flight studies are nearly complete and a new phase of studies is being planned, oriented toward measurement of particle sizes in fumes above char beds in recovery boilers by means of laser scattering.

The DPFR constructed in this project will also be used for investigation of pyrolysis and oxidation of other fuels (such as coal-water) as well as oxidative destruction (incineration) of hazardous wastes. The reactor is now being equipped for (a) ratio pyrometry measurements; (b) sample-extraction for gas-chromatographic analysis; (c) on-line monitoring of exhaust species (CO, CO_2, NO, SO_2, H_2S, O_2, and hydrocarbons); and (d) computerized data acquisition.

Optical Diagnostics for Metal Powder Atomization Systems

C. Presser, H.G. Semerjian

Rapidly solidified metal powders are important to systems requiring advanced materials. They provide the basis for alloys which exhibit, after consolidation, high strength-to-weight ratios, improved fracture toughness and fatigue resistance, unique magnetic properties, and high corrosion resistance. A collaborative research program has been initiated with the NBS Institute for Materials Science and Engineering, to apply laser diagnostic techniques, to investigate metal powder atomization and rapid solidification processes in the NBS metal powder atomization research facility. Liquid breakup processes of the molten metal in the vicinity of the injector are being investigated, in addition we apply sensors to monitor particle size in the atomizer exit passage for feedback and control purposes. Detailed process knowledge, along with an integrated system of sensors and expert systems for feedback and control, can then be used to monitor and control the atomization process, and to provide desired powder characteristics.

Particle size measurement techniques are currently being evaluated to determine their applicability to jet break-up and droplet formation processes in the metal powder atomization chamber. The techniques under consideration to measure particle size, number density and velocity include a) the ensemble light scattering technique, b) the phase/Doppler interferometer, and c) the scattering intensity deconvolution technique. One system 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 will also be implemented, along with a laser sheet beam, to illuminate the spray jet and provide qualitative data on the general features of the liquid jet and droplets. In addition, a second set of experiments is under way to obtain particle size measurements in the exit section of the atomizer facility. A laser light diffraction technique has been chosen to provide particle size distribution measurements along a line-of-sight. This particle size distribution, averaged along a cross section of the process stream, can then be used for process feedback and control. Restrictions on the degree of obscuration along the measurement path during an atomization run has to be considered. Therefore, to evaluate this problem under realistic conditions, the exit section of the atomizer chamber is being modified to incorporate two windows 180° apart. Transmission measurements and video movies, taken during several metal powder runs, have indicated the need for purging the windows in order to reduce deposition of particles and obscuration of the laser beam. Off-line measurements are planned so that the problem can be further studied in a more controlled environment.

Thin Film Thermocouples for Heat Engines

K.G. Kreider, S. Semancik

The goal of this project is to demonstrate the feasibility of a materials system and fabrication technique for measuring temperatures inside the combustion chamber of ceramic-insulated engines using thin film thermocouples. The ceramic insulating materials under investigation include partially stabilized zirconia (PSZ) in both monolithic and plasma sprayed forms and alumina (Al_2O_3). The thermocouple systems have included type E (chromel-constantan), type N (nisil-nicrosil), and platinum-platinum (with 6% rhodium).

Adhesion studies for these systems indicate that a reactive metal bond coat such as Cr or Ti is very useful in insuring a strong (70 MPa) bond between Pt and PSZ or Al_2O_3. This bond coat and its stability have been studied using X-ray photoemission spectroscopy and depth profiling using secondary ion mass spectroscopy. Scanning electron microscopy and electron microprobe analysis have indicated that the sputtered films were produced with the same composition as the target alloys, and continuous, strong, pore-free deposits can be sputtered 1-4 μm thick. Calibration, high temperature exposure, and flame testing of the sputtered thin film deposits indicate the sensitivity to the atmosphere and alloy changes by diffusion of the thin films. Type E and type N thermocouples are unstable at 1000 K and are not recommended. Type S thin film thermocouples, however, appear very promising and a project to evaluate thin film thermocouples in diesel engines is under way.

Small (1.0 cm) diameter plugs with NBS sputtered thin film type S thermocouples deposited on the plasma-sprayed partially-stabilized zirconia insulating layer are being used to monitor the surface temperature of a diesel engine. This plug sensor is inserted in the second intake valve port and is used to measure heat transfer and temperature excursion with 2-4 ms time resolution. This technology will provide the first accurate data of its type and should aid in the adiabatic engine design.

Chemical Gas Sensors

S. Semancik, T.B. Fryberger, J.W. Erickson

The electrical conductivity of tin oxide, SnO_2, can be altered by both oxidizing and reducing gases. This behavior makes SnO_2 suitable for use in a variety of solid state gas sensing applications. During the last year our studies have sought to provide detailed information on the ways in which oxygen vacancies affect the electrical properties of SnO_2 and related oxide materials. We have also been particularly interested in determining the extent to which surface phenomena dominate signal generation processes, and in studying the mechanisms by which metal overlayers can enhance the sensing performance and stability of tin oxide.

Experimental efforts have focused on SnO_2(110) single crystals (the most stable crystallite) that have been modified to examine effects that would occur in operating devices. Oxygen vacancy defects were investigated by first using oxidation procedures to form pure, nearly perfect SnO_2 surfaces, and then introducing oxygen vacancy defects by heating. The defect density, electronic structure and electrical conductivity at these surfaces were characterized using ion scattering, ultraviolet photoemission and an ultrahigh vacuum four-point probe developed in our laboratory. This work has shown that two distinct types of oxygen vacancies can develop at the SnO_2 surface, and that each has a different effect on the electrical conductivity. Such findings are of importance not only for understanding one class of solid state sensing materials, but can also impact our understanding of other key technological oxides (e.g. in microelectronics and superconductivity).

Metal overlayers have also been examined on SnO_2(110) as a way to enhance adsorption and selectivity in sensor response. Most of our work, thus far, has concentrated on palladium adlayers (which can be used to enhance hydrogen response), but preliminary work has also been done with silver and tin. Besides characterizing the additive-SnO_2 interactions, we were able to demonstrate increased efficiencies in model H_2 sensors containing monolayer coverages of Pd.

Our efforts on controlling surface defect concentrations and the dispersion of surface additives are aimed at developing improved materials for solid state gas composition measurements. Continuing studies in these areas are expected to further advance the gas sensing field toward a reliable thin film technology, ultimately capable of producing sensor arrays which could perform multiple gas analyses.

IrO_2 Ionic Sensors

K.G. Kreider, P.H. Huang, S. Semancik

Reactively sputtered iridium oxide is being considered as a pH sensing material. It has the advantage that thin films could be fabricated inexpensively on probes which would be smaller and more durable than presently used glass electrodes. The IrO_2 is not attacked at high temperatures and pH levels which would destroy the glass electrode. We have produced reactively sputtered iridium oxide pH sensing films (SIROF) on Al_2O_3 substrates. Long-term stability of the SIROF electrodes, hysteresis effects, and foreign ion interferences need to be investigated for practical pH sensing applications.

This research involves the understanding of the structure of IrO_2 and IrO_2-pH solution interfaces. For all oxides studied so far by other researchers including TiO_2, γ-Al_2O_3, σ-Fe_2O_3, SiO_2, and MnO_2, the slope of surface charge density versus pH increases with pH without any indication of reaching a plateau. In order to explain the phenomena associated with the very high surface charge densities observed at the oxide-solution interface, various theoretical models have been proposed. These models include the double layer model (GCSG), the porous double layer model, the gel layer model, the transition layer model, and the site-binding model. However, it appears that no satisfactory model for the oxide-solution interface has emerged to date. Hydration, hydroxylation, and acid-base properties are all factors which require special attention. Central to any model of the oxide-solution interface is the molecular structure of the layer of water at the oxide surface. The dielectric properties of water molecules, which are physisorbed or chemisorbed on the oxide surface in the compact layer need to be understood. For the IrO_2-solution interface, current efforts are underway to investigate adsorbed water in the electrochemical interface and the fundamental properties affecting the electrochemical behavior of hydrous IrO_2 films. Experimental techniques of open circuit potential measurement, dc and ac voltammetry, and impedance spectroscopy are being used to study IrO_2-solution interfaces for: (a) the long-term stability of the SIROF electrodes in the pH range 2 to 12 at temperatures up to 95°C; (b) the hydrated SIROF and the variation of its acidity with change in the iridium oxidation state; and (c) the reduced and oxidized form of the SIROF. These properties are strongly influenced by the hydrated nature of the IrO_2 layer.

Chemical changes produced at the solution-oxide interface are believed to be the origin of instabilities in the pH response of IrO_2-based sensors. Therefore, we have characterized the surface compositions of a number of iridium oxide-related materials using x-ray photoemission (XPS) and secondary ion mass spectrometry (SIMS). We have analyzed commercial powders, like $Ir_2O_3 \cdot xH_2O$ and $Ir(OH)_4$, as standards, and we have also studied IrO_2 films fabricated within our group. These films have been examined in "as fabricated" form, after baking or autoclaving, and following use of the films as electrodes (sensors) in pH-controlled solutions. Binding energy shifts of up to 2 eV have indicated significant differences in the chemistry at these film surfaces, and some of the results suggest that hydroxylation processes may be altering the performance of IrO_2 sensors.

The results of the electrochemical testing, surface analysis, and the study of the relationships between sputter fabrication and structure of the IrO_2 were presented in Tokyo, Japan at the 4th International Conference on Sensors and Actuators.

Humidity Calibration

S. Hasegawa

A new low frost point humidity generator was constructed during the last year. This new facility will enable us to calibrate precision humidity measurement instruments to below 1 ppm H_2O content. Low moisture content is particularly significant for carrier gases in the fabrication of integrated circuits.

Humidity Sensors

P.H. Huang

The material design for humidity sensing and measurement using halogenated organic polymer membranes has been granted a patent, #4,681,855. The invention is an improvement over existing devices because of its expected long life, lasting accuracy, and ability to be used at high temperatures and humidities. The membrane is a thin film of hygroscopic, fluorinated organic polymer having pendant functional groups of a relatively strong sulfonic acid type and groups of a relatively weak carboxylic acid type. Since the sulfonic acid functional group attracts water molecules more strongly than the one of carboxylic acid, the acidic functional group ratio determines the amount of water in the polymer. By varying the ratio of these acidic functional groups, a wide range of humidity can be measured accurately with low hysteresis. Potential applications are especially in the areas of controlling the drying processes that support industries such as textiles, paper, chemicals, and food. Meteorological and electronics applications are also feasible.

A new technique based on high frequency surface acoustic wave spectroscopy has also been investigated for humidity sensing. Polar water molecules in ambient moist air can be made to interact with the electric and acoustic fields of a surface acoustic wave (SAW) in a piezoelectric crystal surface. The interaction causes a change in the amplitude of the received surface wave which is proportional to the energy density of the wave. An amplitude-modulated SAW technique, which does not utilize adsorptive coatings, has been used to study this electro-acoustic interaction for humidity sensing in the range 90 to 98% RH. The sensor system consists of two identical high frequency, wide band SAW delay lines. One is used as a reference channel with shorted electric fields at the surface. The reference delay line is maintained in an environment of nearly zero percent relative humidity. The ratio of voltage output from the sensing channel to that of the reference channel has been measured. An experimental relationship exists between the measured voltage ratio and the relative humidity in the range from 90 to 98% for SAW frequencies in the range between 210 and 250 MHz. Several mechanisms are proposed for the electro-acoustic interactions between water molecules and high frequency surface acoustic waves.

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6. CONFERENCES AND WORKSHOPS

CONFERENCES

Sessions on Proving Devices and Laboratories (I and II) at the International Symposium on Fluid Flow Measurement, American Gas Association, Arlington, VA, Nov. 16-19, 1986. Organized and chaired by G.E. Mattingly.

Session on Spray Combustion at the Fall Technical Meeting of the Combustion Institute/Eastern Section, San Juan, PR, Dec. 15-17, 1986. Chaired by H.G. Semerjian.

Sessions on Combustion Fundamentals at the Second ASME/JSME Thermal Engineering Joint Conference, Honolulu, HI, Mar. 23-27, 1987. Three sessions organized and one session chaired by H.G. Semerjian.

DoE/NBS Black Liquor Research Review Meeting, Gaithersburg, MD, July 28-30, 1987. Organized by H.G. Semerjian.

Session on Heat Transfer in Furnaces at the ASME/AIChE/ANS 24th National Heat Transfer Conference, Pittsburgh, PA, Aug. 9-12, 1987. Chaired by C. Presser.

Session on Sprays at the Eastern Section Meeting of the Combustion Institute, Gaithersburg, MD, Nov. 2-5, 1987. Chaired by C. Presser.

Sessions on Reaction Engineering and Combustion Processes, and on New Experimental Techniques for High Temperature Reacting Flows at the AIChE 1987 Annual Meeting, New York, NY, Nov. 16-20, 1987. Organized and chaired by H.G. Semerjian.

WORKSHOPS

Hosted NBS Workshop on Optical Particle Sizing Techniques, held on Nov. 11, 1986 at NBS, Gaithersburg, MD. Organized and chaired by H.G. Semerjian.

Hosted Workshop for the Industry-Government Consortium on Flowmeter Installation Effects Research, held on June 1, 1987 at NBS, Gaithersburg, MD. Organized and chaired by G.E. Mattingly.

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Technical research activities performed by the Center for Chemical Engineering during the Fiscal Year 1987 are summarized herein. These activities fall within the general categories of process measurement, thermophysical properties data, and chemical engineering science. They embody: development and improvement of measurement principles, measurement standards, and calibration services such as volumetric and mass flow rates, liquid volume, liquid density, and humidity; generation (via accurate measurement and advanced predictive models) of reliable reference data for thermophysical properties of pure fluids, fluid mixtures, and solids of vital interest to industry; 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.

12. KEY WORDS (*Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons*)
calibrations; chemical engineering; data; fluid mechanics; fluid properties; process measurement; research; sensors; solid properties; thermophysics; unit operations.

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