1 of 1

DOE/ER/13823--T2

DEVELOPMENT OF MEASUREMENT CAPABILITIES
FOR THE THERMOPHYSICAL PROPERTIES OF ENERGY-RELATED FLUIDS

DE-AI05-88ER13823

Annual Report

December 1, 1990 - November 30, 1991

Prepared for

Dr. Oscar P. Manley, ER-15
Division of Engineering and Geosciences
Office of Basic Energy Sciences
U.S. Department of Energy
Germantown, MD 20545

Prepared By

Thermophysics Division
Chemical Science and Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899

For additional information, contact

Dr. Richard F. Kayser, Chief
Thermophysics Division
Room A105 Physics
National Institute of Standards and Technology
Gaithersburg, MD 20899

301-975-2483

September 23, 1989

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

872

CONTENTS

Introduction	3
Thermal Conductivity Apparatus	4
Vibrating Wire Viscometer	4
Dual-Sinker Densimeter	5
High-Temperature Vibrating Tube Densimeter	6
Dynamic Phase Equilibria Apparatus	7
Apparatus for Dilute Solutions	7
Total-Enthalpy Flow Calorimeter	7
Dielectric Constant Apparatus	8
Benchmark Measurements	8
Brief Statement of Work for the Period	
December 1, 1991 to November 30, 1992	10
Budget for the Period	
December 1, 1991 to November 30, 1992	11
Original Budget for the Period	
December 1, 1990 to November 30, 1995	12

removed

DEVELOPMENT OF MEASUREMENT CAPABILITIES
FOR THE THERMOPHYSICAL PROPERTIES OF ENERGY-RELATED FLUIDS

Introduction

The objectives of this project are to develop state-of-the-art experimental apparatus that can be used to measure the thermophysical properties of a wide range of fluids and fluid mixtures important to the energy, chemical, and energy-related industries and to carry out carefully selected benchmark measurements on key systems. The research is being done by two groups within the Thermophysics Division of the Chemical Science and Technology Laboratory of the National Institute of Standards and Technology (NIST). One group is located in NIST's laboratories in Gaithersburg, Maryland, the other in Boulder, Colorado. The measurement capabilities to be developed include new apparatus for transport properties, thermodynamic properties, phase equilibria properties, and dielectric properties. These new apparatus will extend the existing state of the art for properties measurements and make it possible to study a wide range of complex fluid systems (including highly polar, electrically conducting, and reactive fluids) under conditions that have been previously inaccessible.

The specific measurement capabilities to be developed are:

1. Thermal Conductivity Apparatus
2. Vibrating Wire Viscometer
3. Dual-Sinker Densimeter
4. High-Temperature Vibrating Tube Densimeter
5. Dynamic Phase Equilibria Apparatus
6. Apparatus for Dilute Solutions
7. Total-Enthalpy Flow Calorimeter
8. Dielectric Constant Apparatus

The research also includes benchmark experimental measurements on pure and mixed alternative refrigerants and their mixtures with lubricants, on aqueous solutions, and on carefully selected systems consisting of species of diverse size (methane + neopentane) and polarity (methane + ammonia) that are important for the development of predictive models for energy-related fluids.

THERMAL CONDUCTIVITY APPARATUS

Richard A. Perkins

The tantalum hot-wire cell will allow us to study the thermal conductivity and thermal diffusivity of electrically conducting fluids such as aqueous solutions and highly polar liquids such as refrigerants. This new thermal conductivity cell uses a tantalum hot wire that has been electrically insulated with a thin tantalum pentoxide layer. Accurate measurements of thermal conductivity and thermal diffusivity will require careful characterization of the diameter and electrical resistance of the wire after electrocleaning and after the electrolytic deposition of the tantalum pentoxide layer. The existing high-temperature and low-temperature thermal conductivity instruments have been relocated next to each other. This move provides room for the new tantalum hot-wire cell and allows use of the existing diffusion pumping system of the low-temperature cryostat to evacuate the new cryostat for the tantalum hot-wire cell. A reference platinum resistance thermometer, quartz pressure transducer, and high pressure cell have been purchased. The remaining components for the interior of the thermal conductivity cell have been designed and are being purchased or fabricated. The initial testing of the tantalum hot-wire cell will begin in October, 1991 using the furnace of the high-temperature instrument for temperature control. The design of the cryostat, which will ultimately contain the new cell, will be finalized when proper operation of the new cell has been demonstrated. The new cryostat for the tantalum hot-wire cell will be completed during the second year of the project to allow studies of conducting fluids at low temperatures.

VIBRATING WIRE VISCOMETER

Richard A. Perkins and William M. Haynes

The transducer for the vibrating wire viscometer will use a tungsten wire, 0.01 cm diameter by 2 cm long, immersed in the fluid of interest. The wire will be clamped at both ends and driven by passing an electrical current through the wire in the presence of a fixed magnetic field. Theory is available in the literature to extract the fluid viscosity from a vibrating wire in either the steady state or transient mode of operation. Our existing torsionally oscillating quartz-crystal viscometers use the steady-state mode of operation where the vibration

frequency is scanned to characterize the resonance curve of the viscometer. Alternatively, the vibrating wire viscometer can be operated in a transient mode where the wire is initially set into vibration at time zero and the magnitude of the vibrations are recorded as a function of elapsed time. The design for the benchtop demonstration transducer will be completed this year. The electronics will be set up so that the transducer can be driven in either a steady-state or a transient mode. During the next year, we will construct the benchtop transducer and begin testing it in both the steady state and transient modes of operation. This testing will allow us to verify the proper design of the transducer and to select the preferred mode of operation. The wire will be bare during the initial transducer development and the testing will be done on a well-characterized nonpolar fluid such as argon. When the transducer design has been verified with a nonpolar fluid, a coated wire will be tested with argon and a polar fluid such as water.

DUAL-SINKER DENSIMETER

Mark O. McLinden

During the current reporting period, the design and fabrication of the various elements of the dual-sinker densimeter have proceeded in parallel. The support frame for the entire instrument has been completed; it incorporates two levels of vibration isolation to shield the central measuring instrument (an analytical balance) from external disturbances. The vacuum-insulated isothermal enclosure incorporates three parallel cooling circuits (using either liquid nitrogen or an external circulating bath fluid) and several independently controlled electric heater circuits; apart from simple electrical plumbing connections, it is also complete. The analytical balance was successfully tested in vacuum (operation of the balance in vacuum is desired to avoid problems with convection currents when the cell is operating at above ambient temperatures). Development of the two most difficult and unique elements of the instrument, the magnetic-suspension coupling and the sinker changing mechanism, has also progressed well, resulting in successful mock-up tests of both. The coupling transmits the weight of the sinkers (which are immersed in the fluid of interest) to the analytical balance via two permanent magnets held in an equilibrium position by a feedback control circuit. The two magnets are on opposite sides of a pressure separating wall. This wall must be constructed of an absolutely nonmagnetic material;

numerous materials were screened before finding a beryllium copper alloy that was satisfactory. Three distinct approaches to switching between the sinkers were tried and discarded before arriving at the current design which incorporates a simple mechanism requiring only a vertical movement of the lower magnet of the coupling to effect the change. With the successful tests of the coupling and sinker changing mechanisms, the design of the sinkers and the pressure vessel have been finalized and fabrication begun. The final elements of the system, including the vacuum system, filling manifold, and instrumentation, are also under development.

HIGH-TEMPERATURE VIBRATING TUBE DENSIMETER

Ren Fang Chang and Michael R. Moldover

A prototype vibrating tube densimeter for measuring fluid densities with a precision of 100 g/m^3 at temperatures up to 400°C has been designed and fabricated and is now undergoing "shake-down" tests. In common with commercially available vibrating tube densimeters, the sample is confined to the interior of a continuous, stainless-steel tube. The tube is caused to oscillate in a bending mode and the density of the sample is determined by the change that it causes in the resonance frequency of the mode under study. However, in contrast to the commercial densimeters, the prototype does not use cements, glues, or polymer insulations of any kind. Our current design also has the following unique features: (1) the use of a current passing through the tube to cause the tube to oscillate in the field of a permanent magnet, (2) the use of the voltage induced in the tube by its oscillation in the field to detect the oscillation, (3) the optional use of higher frequency modes of oscillation than the lowest bending mode of the tube, and (4) the optional use of a bridge arrangement in the detection circuitry that incorporates a non-oscillating portion of the tube to compensate for the temperature dependence of the electrical impedance of the tube. These features have been demonstrated with the prototype; the main problems have been filling the tube without introducing bubbles and understanding the pressure dependences of the modes. During the next year, we will test the room-temperature stability of the densimeter (using test fluids such as argon, xenon, water, cyclohexane, and ethanol) and design and fabricate an oven to accommodate the prototype so that tests at higher temperatures may begin.

DYNAMIC PHASE EQUILIBRIA APPARATUS

William M. Haynes

Work on this apparatus will begin in the second year.

APPARATUS FOR DILUTE SOLUTIONS

Lloyd A. Weber and Graham Morrison

Systems of mixed refrigerants offer the good possibility of being desirable substitutes, possibly even "drop-in" replacements, for the recently outlawed CFC's. Ebulliometry offers a convenient method for studying the thermodynamics of such mixtures. It provides a direct determination of the infinite dilution activity coefficients, γ_1^∞ and γ_2^∞ , which can be used to calculate the parameters that appear in common thermodynamic models such as those of van Laar and Wilson. During the past year we have built and tested two ebulliometers, a low-pressure comparative ebulliometer made of glass, and a high-pressure simple ebulliometer made of sapphire and metal. The first model operates from temperatures of 253 to 373 K and pressures from 20 to 150 kPa, and the second model operates from 273 to 373 K and 100 to 2000 kPa. Both instruments incorporate modern instrumentation and computer data acquisition and control features (including platinum resistance thermometers and quartz pressure gages). Both models have been used to measure the vapor pressures of pure refrigerants, including HCFC-123 and HCFC-141b. In the coming year, we will extend this work to binary mixtures by building several new boilers designed for work on mixtures.

TOTAL-ENTHALPY FLOW CALORIMETER

Joseph W. Magee

The constant-pressure flow calorimeter will operate between 200 and 700 K at pressures to 20 MPa, and it will be well-suited for a variety of measurements, especially total enthalpy. It will produce benchmark-quality data whose uncertainties will be approximately $\pm 0.2\%$ at temperatures to 500 K. During the first year, the overall design has been finalized. Next year, the work of acquiring and constructing parts will go into full swing. In particular, the materials for the calorimeter and connecting tube sections will be ordered, along with heaters, thermoelectric coolers, thermopiles, and thermistors. After the

calorimeter section has been machined, it will be performance tested with its associated instrumentation.

DIELECTRIC CONSTANT APPARATUS

Christopher W. Meyer and Graham Morrison

Measurements of dielectric constant yield two of the most important parameters for predicting the properties of polar fluids, namely, the dipole moment and the molecular polarizability. To obtain data needed for alternative refrigerants, an apparatus was assembled from existing components and used to measure the dipole moments of a number of refrigerants. However, this instrument needs improvement. The capacitor has a hysteresis with pressure that is on the margin of being a problem. The capacitance bridge is temperamental and has a range that is just adequate for the measurement. A 3 ppm measurement of the capacitance was easily achieved. While that capability is satisfactory for species with large dipole moments, it presents problems for species with temperature dependent dipole moments. During the second year, we will develop a better instrument with a capacitance cell designed along the lines of that of Younglove and Straty.

BENCHMARK MEASUREMENTS

The vapor-liquid boundary is a "benchmark" for the initial comparison of two materials as working fluids. The accurate location of this boundary is an essential input for developing accurate thermodynamic tables on which any detailed analysis and evaluation for applications is based. With the two ebulliometers described above, we have measured the vapor pressures of several promising alternative refrigerants, including HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), HCFC-141b (1,1-dichloro-1-fluoroethane), and HCFC-124 (1-chloro-1,1,1,2-tetrafluoroethane). The first two of these materials are promising replacements for R-11 (trichlorofluoromethane), the working fluid in large chilled water systems. There is a large body of information on R123 but little information on R141b. R-124 is one of the components of a three-component mixture that has been proposed as an alternative for R-12 (dichlorodifluoromethane), the working fluid in automotive air conditioners and domestic refrigerators. There is little information on the properties of R-124.

In our search for correlations between the properties of mixtures and the molecular properties of the species in the mixtures, we have found that the permanent dipole moment is a strong indicator of mixture properties. The dipole moment is also a valuable parameter in fundamental physical models for mixtures. In that connection, we have measured the dielectric constant of a number of alternative refrigerants, and from these measurements we have obtained their dipole moments. In particular, we have measured the dipole moments of the following fluids:

1. pentafluoroethane (R125)
2. 1,1,1,2-tetrafluoroethane (R134a)
3. 1,1,1-trifluoroethane (R143a)
4. 1,1-difluoroethane (R152a)
5. 2-chloro-1,1,1,2-tetrafluoroethane (R124)
- 6a. 1,1,2,2-tetrafluoroethane - trans conformer - (R134)
- 6b. 1,1,2,2-tetrafluoroethane - gauche conformer - (R134)
- 7a. 1,1,2-trifluoroethane - C₁ conformer - (R143)
- 7b. 1,1,2-trifluoroethane - C₂ conformer - (R143)
8. 1,1-dichloro-2,2,2-trifluoroethane (R123)
9. 1,2-dichloro-1,1,2-trifluoroethane (R123a)
10. 1,1-dichloro-1-fluoroethane (R141b)

BRIEF WORK STATEMENT FOR THE PERIOD
DECEMBER 1, 1991 - NOVEMBER 30, 1992

We plan to complete the development of the Thermal Conductivity Apparatus and the Dielectric Constant Apparatus. We plan to continue the development of the Vibrating Wire Viscometer, the Dual-Sinker Densimeter, the High-Temperature Vibrating Tube Densimeter, the Apparatus for Dilute Solutions, and the Total-Enthalpy Flow Calorimeter. We plan to initiate the development of the Dynamic Phase Equilibria Apparatus. We plan to continue the Benchmark Measurements related to CFC Alternatives.

**DATE
FILMED**

2 / 7 / 94

END