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

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Annual Report

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

Introduction

This report describes the progress during the third year of this five-year project, which began on December 1, 1990. The objectives of the 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 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 shape (methane + neopentane) and polarity (methane + ammonia) that are important for the development of predictive models for energy-related fluids.

The following reports summarize the status of each of the individual apparatus development and measurement projects. The work is progressing well in all areas.

THERMAL CONDUCTIVITY APPARATUS

Richard A. Perkins

The new tantalum hot-wire cell is completed and can be used to measure the thermal conductivity and thermal diffusivity of electrically conducting fluids at temperatures from 220 to 500 K at pressures to 70 MPa. This is currently the only absolute transient hot-wire cell available in the United States for electrically conducting fluids, and it covers a wider temperature range than any tantalum hot-wire cell in the world. The temperature range will be extended to cover 80 to 500 K when a new cryostat is completed for the cell.

The cell is constructed from Hastelloy C-276 for good corrosion resistance in aqueous solutions containing halogen ions. The cell has 2 tantalum hot wires with 25 μm outside diameters. These wires are anodized to produce a thin (70 nm) film of tantalum pentoxide as an electrical insulation layer. The thickness of the oxide film can be controlled by the magnitude of the voltage used during the anodization process. Mechanical damage to the film (as evidenced by electrical leakage between the wires and the cell wall) can be repaired easily by re-anodizing the wire to the same voltage level. The chemical resistance of the oxide film can be increased by application of a polarization voltage between the hot wires and the cell wall. All other wetted materials in the cell are coated with polyamide and teflon for electrical insulation and improved corrosion resistance to 500 K.

Most researchers employing oxide-coated hot wires have first removed any atmospheric oxide film from the wire with a hydrofluoric acid solution and then immersed the wire in boiling water to remove any residual fluoride film which is left from this chemical polishing. We have found that this step is unnecessary since atmospheric oxide films are also strongly adherent and many researchers have reported that the properties of tantalum pentoxide films are not dependent on the history of the film. The chemical polishing step adds increased uncertainty in the wire diameter since the hydrofluoric acid solution also removes some of the tantalum hot wire while removing the oxide film. This added

uncertainty cannot be tolerated when the wires are used to measure the thermal diffusivity of fluids. Researchers have reported good quality tantalum pentoxide films using many different acids, and even bases, but films formed in dilute organic acids have been shown to tolerate larger applied voltages prior to electrical arcing across the thin oxide film. We have prepared test wire sections without the chemical polishing step and anodized them in dilute ascorbic acid using a maximum potential of 90 volts. These films have been heated in an oven to 600 K to verify that the film is strongly adherent. These test sections were placed in salt water to verify that differential thermal expansion did not damage the tantalum pentoxide film. No deterioration of the film has been detected after heating to 600 K.

Performance of the new tantalum hot wire cell is being verified with toluene and water. The NIST Thermophysics Division is also participating in an international round robin comparison of transport property measurements using a standardized sample of R134a. This round robin is organized by the International Union of Pure and Applied Chemistry (IUPAC) Subcommittee on Transport Properties; it will compare thermal conductivity data obtained by transient hot wire and light scattering instruments located in the United States, the United Kingdom, Germany, Japan, Portugal, and Greece. Performance of both the bare 12.7 μm platinum hot wires and the new coated 25 μm tantalum hot wires will be verified during this IUPAC round robin. The results of our initial verification measurements will be reported at the 22nd International Thermal Conductivity Conference in November 1993. We are continuing to experiment with other wire materials, such as 25 μm platinum wire coated with polyamide, which are potential alternatives for fluid systems that corrode the tantalum pentoxide thin film.

VIBRATING WIRE VISCOMETER

Richard A. Perkins and William M. Haynes

The vibrating wire viscometer will be used to measure the viscosity of liquids and gases from 30 to 600 K at pressures to 70 MPa. Transverse vibrations of the wire are driven by an ac current in the wire in the presence of a permanent magnetic field. The vibrations are monitored using the induced voltage from the wire as it moves in the permanent magnetic field. The frequency of the principal

vibration mode is primarily a function of the tension, mechanical properties, and dimensions of the wire. Damping of the wire vibrations is due to the internal mechanical losses and the external viscous drag of any fluid surrounding the wire. At any given temperature, the internal damping can be measured by evacuating the cavity surrounding the wire and characterizing the wire vibration. The wire can be driven in a steady-state mode where the tension of the wire can be determined from the resonant frequency and the viscosity of the fluid can be determined from the bandwidth of the resonance curve. Alternatively, the wire can be driven into transverse vibrations near its resonant frequency, and the transient vibrations can be measured as a function of elapsed time after the drive voltage is turned off. In this case, variations in the tension of the wire can be determined from the vibration frequency, and the viscosity can be determined from the logarithmic decrement of the magnitude of the vibrations.

Most vibrating wire viscometers are operated in a transient mode where the wire is driven initially by an ac current near its resonance frequency. The drive current is then turned off and the induced voltage is monitored as a function of elapsed time. The damping of the wire vibration is obtained from the logarithmic decrement of the induced voltage. The viscous damping is obtained by subtracting the internal damping measured with the wire in vacuum at the same temperature. In oscillating wire viscometers, it is desirable to have a constant wire tension over the entire temperature and fluid density range of interest so that the vibration frequency is constant. Oscillating wire viscometers measure the kinematic viscosity (η/ρ) of the fluid. Since the density of many fluids and fluid mixtures is not known with sufficient accuracy, it is useful to simultaneously measure the fluid density (ρ) to accurately determine the shear viscosity (η) of the fluid. It may be possible to use the same vibrating wire both as a densimeter and as a viscometer. If it is not optimal to use a single wire for both viscosity and density, a second vibrating densimeter wire can be located in the same pressure vessel with the vibrating viscometer wire.

The steady-state mode is most commonly used in vibrating wire densimeters, where the buoyancy of a well-characterized weight suspended from the wire is obtained from changes in the resonance frequency of the vibrating suspension wire relative to its vacuum resonance frequency. In this case, it is desirable to have the tension of the wire change significantly due to the buoyant forces on the weight.

If the buoyant forces are large enough, then there are relatively small contributions from the viscous drag of the fluid on the resonance frequency. Thus, it is desirable to have a weight with a relatively low but very well characterized density.

A prototype vibrating wire cell has been constructed and the initial testing has begun. The prototype cell consists of a 50 μm diameter tungsten wire which is 4 cm long. The prototype cell is tensioned with a single weight so we can explore its use both as a densimeter and as a viscometer. The wire is contained in a coaxial cylindrical cavity with a diameter of 8 mm. The permanent magnetic field is produced by 2 samarium-cobalt magnets located near the longitudinal center of the wire just outside the coaxial cylindrical cavity. The present cell is designed to operate at frequencies near 1 kHz. Holes are located near the ends of the vibrating wire for measurement of the wire length with a cathetometer. The data acquisition system used with the prototype cell includes a 80486 based personal computer with a data acquisition card, IEEE-488 interface, and an impedance analyzer. The data acquisition card has a 16-bit digital-to-analog converter to generate the wire excitation current and a multiplexed 16-bit analog-to-digital converter which can sample the induced wire voltage at frequencies to 100 kHz. The impedance analyzer is used to study the steady-state resonance curve of the vibrating wire in vacuum and in the fluid of interest.

Since the viscometer will be designed ultimately to operate in electrically conducting fluids, we have been examining alternatives for electrically insulating the wire. We have anodized tungsten wire to form an insulating layer of tungsten trioxide in a fashion similar to the tantalum hot wires used in the thermal conductivity instrument for conducting fluids. Anodic oxide films are much thinner and can tolerate higher temperatures than polymer films, such as polyamide and teflon. Thus, the anodized tungsten film has significant advantages for the vibrating wire viscometer where the diameter and density of the wire must be known very accurately.

During the next year, we will finalize the design for the vibrating wire viscometer. The design temperature limit for the viscometer is 600 K; thus, we will not be able to use polyamide or teflon for electrical insulation inside the temperature controlled region of the cell, but ceramics and anodic oxide films

should work well at these temperatures. The final cell and pressure vessel will be made of Hastelloy C-276 for good corrosion resistance in aqueous solutions containing halogen ions.

DUAL-SINKER DENSIMETER

Mark O. McLinden

This new apparatus will cover wide ranges of temperature, pressure, and density and will extend our accuracy for p-V-T measurements by nearly an order of magnitude. A variation on the simple, reliable buoyancy principle is employed: two sinkers of identical mass and surface area, but very different volumes, are weighed while immersed in the fluid of interest. The use of two sinkers leads to a cancelling of effects that would otherwise introduce errors.

The complete densimeter has been assembled during the current reporting period and system check-out tests have begun. A focus of the work has been on refining the control circuitry for the magnetic suspension coupling. The control circuit, suspension magnets, sinkers, etc. have been installed in the apparatus; while a stable suspension could be held for hours at a time in the initial tests, the resolution of the weighings with the analytical balance was lower than our goal. This problem was traced to electrical noise emanating from several components in the circuit and necessitated a significant redesign of the control circuit. The new circuit is now performing well -- that is, the resolution in the weighings is now sufficient to achieve our accuracy goal of 0.01% for liquid densities. The sinker changing mechanism also has been proven in the final assembly.

The entire apparatus is now being performance tested using sinkers fabricated from aluminum and stainless steel. The final sinkers will be fabricated from single-crystal silicon (tantalum coated) and tantalum. Measurements using the silicon and tantalum sinkers will be initiated by the end of 1993.

A paper entitled "Development of a dual-sinker densimeter for high accuracy fluid P-V-T measurements", was prepared by M.O. McLinden and N.V. Frederick and presented at the 11th Symposium on Energy Engineering Sciences at Argonne, IL, May 3-5, 1993. A copy of that paper is attached as Appendix A of this report.

HIGH-TEMPERATURE VIBRATING TUBE DENSIMETER

Ren Fang Chang and Michael R. Moldover

The objective of this project is to develop a vibrating-tube densimeter that operates at temperatures in the range from 300 to 670 K. The heart of the densimeter is a hair-pin shaped tube placed between the poles of a permanent magnet. An alternating electric current flows through the tube and induces an oscillating force on the tube. When the frequency of the current matches one of the natural bending frequencies of the tube, a resonance occurs. The square of the resonance frequency is inversely proportional to the total oscillating mass, which includes both the tube's mass and the mass of fluid within it. At each temperature, two measurements are required to calibrate the densimeter -- one determines the effective spring constant for the bending mode and the other determines the effective volume within the tube. For calibration, the resonance frequencies were measured with the tube evacuated and with the tube filled with water, a fluid with a well known density.

Ultimately, we expect that the high temperature limit of the present design will be 800 K, the maximum service temperature of the Alnico 5 magnet. However, under many conditions, oxidation of the vibrating tube, chemical instability of the sample, or a reaction of the sample with the tube will reduce the maximum temperature at which useful data can be acquired. At present, the effective high temperature limit is 600 K. This limit is determined by a persistent, slow upward drift of the resonance frequency. Typically at 700 K, the initial drift is equivalent to a density change of 20 mg/cm³ per day. As the densimeter undergoes several thermal cycles between 600 K and 700 K, the drift rate decreases but it does not vanish. We have observed drifts in every densimeter we have made, even though they have used very different materials and designs. Experts in the Metallurgy Division of NIST have been unable to explain our observations. As in commercially manufactured densimeters, these drifts are virtually imperceptible near ambient temperature.

In an effort to eliminate the frequency drift, we designed and fabricated six new prototypes during this reporting period. (Four others were made during the previous reporting period.) Distinguishing features of these designs were:

- #1: Vacuum feedthroughs were used as insulating supports. The vibrating tube was stainless steel, 0.062" diameter, and was silver soldered to the supports. The magnetic field was provided by a horseshoe magnet and a pair of pole pieces. The body was stainless steel.
- #2: A large vacuum break (1.5" diameter x 2.5" long) was used as the electrical insulator. The support frame was made massive (approximately 2"x 2"x 4").
- #3: Sapphire washers were used as electrical insulators.
- #4: Small vacuum breaks (0.5" diameter x 3" long) were used as insulated supports.
- #5: Thin mica sheets were used as electrical insulators. The main body of the densimeter was reduced to 2"x 2"x 3". The magnetic pole pieces were eliminated by replacing the horseshoe magnet with a c-shaped magnet.
- #6: Instead of silver soldering, the tube was clamped to its support. This model was used to test various metal tubes and wires.
- #7: The design was similar to #6; however, high temperature metals were used. (Inconel for the body and Hastelloy for the tube.)
- #8: Stainless steel construction but with 0.032" diameter tube.
- #9: The vibrating tube was bent into a circle rather than a hairpin.
- #10: The insulators were made from machinable ceramic (MACOR) instead of mica.

The best results were obtained with model #6 using a stainless-steel tube that had been annealed in vacuum prior to installation. This configuration was tested by measuring the density of toluene in the temperature range 298 K - 575 K and the pressure range 0.1 MPa - 14 MPa. The test measurements were compared with a published correlation [R.D. Goodwin, J. Phys. Chem. Ref. Data 18, 1565 (1989)]. The root-mean-square (rms) deviation of the measured densities from Goodwin's correlation was only 0.45 mg/cm³. This is comparable to the rms deviation of the calibration data from the NBS/NRC Steam Tables; thus, it is essentially the limit of performance of the present instrument.

DYNAMIC PHASE EQUILIBRIA APPARATUS

Cynthia D. Holcomb and William M. Haynes

The dynamic phase equilibrium apparatus will complement existing low- and high-temperature vapor-liquid equilibria apparatus and will incorporate equilibrium

and dynamic surface tension measurements. This will be the first apparatus of this type able to measure vapor-liquid equilibria, coexisting densities, equilibrium surface tension, and dynamic surface tension over a wide range of temperatures and pressures. It will extend the temperature and pressure range of our current capabilities by operating in the intermediate range from 223 to 423 K at pressures to 40 MPa. The experimental uncertainty of the temperature measurement will be better than 30 mK, while the experimental uncertainty of the pressure measurement will be better than 0.05%. The experimental uncertainty of the density measurements should be better than 0.2 kg/m³. By designating liquid only and vapor only densimeters, we will calibrate each densimeter over its expected density, pressure, and temperature range. This should reduce the manufacturer's stated experimental uncertainty by at least 50%. The experimental uncertainty of the surface tension measurements will be 0.1 mN/m.

Most of the major pieces of equipment have been selected and acquired. The dewar, densimeters, multimeter, computer, heater power supply, refrigerator, pressure transducers, and a platinum resistance thermometer have been obtained. Some other minor pieces of equipment also have been obtained. The temperature control and data acquisition computer software is almost complete.

More detailed designs for the new vapor-liquid equilibria apparatus have been completed. These designs address the optimal layout of the equipment both inside and outside of the dewar. The new designs will make it possible to house and calibrate the pressure transducers in a temperature controlled box at 150°C. This will eliminate head effects and zero drift which would reduce the accuracy of the pressure measurement. The valves need to be at nearly the same temperature as the system but not immersed in the silicon bath. Therefore, the valves will be located just above the liquid. There will be 10 cm of vapor space inside the dewar above the liquid level to create a vapor zone near the temperature of the system. Designs for the liquid level control of the bath and the temperature control of the system have been completed. Two issues related to sampling the liquid and vapor at high pressures have been addressed. The high-pressure gas chromatograph valves are adequate for temperatures between 223-423 K and pressures up to 15 MPa. An alternative design for trapped sampling has been investigated and will be used for systems operating outside of the design range of the gas chromatograph valves. The alternative sampling

system also may be used if the gas chromatograph valves have difficulty sealing at the coldest temperatures. Potential problems with sealing the densimeters and valves against the silicon oil bath have been investigated. Designs for secondary sealing containers for the densimeters to prevent oil contamination of the electronics are in progress.

Final designs for the equilibrium cell, the vapor pump, the liquid pump, and the support structure will be completed during the coming year. Construction of the apparatus will be completed within the next year and evaluation of the performance of the apparatus should be initiated.

APPARATUS FOR DILUTE SOLUTIONS

Lloyd A. Weber and Graham Morrison

The objectives of this task are to develop apparatus for making accurate vapor pressure measurements of pure fluids and for measuring infinite dilution activity coefficients of binary mixtures. The data will be used to calculate the vapor-liquid equilibrium behavior of solutions.

During the current reporting period, we evaluated our new comparative glass ebulliometer for mixtures based on measurements on the system acetone + methyl acetate at ambient pressure. Our results agreed well with literature values. From this we gained valuable experience in making the measurements, calculations, and necessary apparatus corrections.

Based on the experience with the comparative glass ebulliometer, we have designed and constructed a new, semi-automated all-metal system for measurements on refrigerant mixtures over a wide range of temperatures at elevated pressures. To our knowledge, this is the first ebulliometer to cover such a range of conditions. In addition, while we were in the process of designing and constructing peripheral equipment for this system, we used the basic apparatus to make pure-fluid vapor-pressure measurements in the range from ambient pressure to 1000 kPa, complementing the results from our glass apparatus. We also used it to make preliminary phase equilibrium measurements on the system R125 + R115. This system forms an azeotrope, which makes it difficult to obtain very pure samples of R125. In addition, we studied the effect of water contamination in

R123 samples. During the coming year, we will use this apparatus to determine the phase equilibrium behavior of several binary refrigerant mixtures.

We have also developed a new all-stainless-steel ebulliometer for measuring vapor pressures of pure fluids at elevated pressures. It is of the same general size and design as a prototype sapphire device described previously. Preliminary testing with R141b, R123, and R236ea showed that it agrees with our earlier measurements to within 0.05% in pressure. During the coming year we will incorporate computer automation, investigate the optimum temperature and pressure range of the apparatus, and attempt to improve the accuracy to 0.02 %. We will also make measurements on new refrigerants such as R143a.

THERMOELECTRIC TOTAL-ENTHALPY FLOW CALORIMETER

Joseph W. Magee

The constant-pressure flow calorimeter will operate between 200 and 700 K at pressures to 20 MPa. It will be well-suited for measurements of total enthalpy of fluids of interest to the energy industry, including reactive, corrosive, and thermally-labile substances. It will produce benchmark-quality data with uncertainties of approximately 0.2% at temperatures to 500 K. The system will use a thermoelectric cooling element to remove energy from the calorimeter at a precisely controlled rate. Energy will be supplied to the calorimeter either by an electrical heater or by the sample fluid flowing through the apparatus. The enthalpy of the fluid will be measured by observing changes in the power delivered by the electrical heater required to maintain the calorimeter at constant temperature.

During the first year, the overall design was finalized. During the second year, manufacturers of the key elements of this design were selected. This year, construction began on the calorimeter vessels. They were machined from aluminum alloy materials exhibiting excellent thermal conductivity and machinability properties. The thermoelectric cooler and a thermometer were installed on the inner calorimeter vessel. Performance tests verified that these components work properly.

In the coming year, the high-pressure tubing coil, heater, and thermoelectric

cooler will be assembled within a metallic disk sandwich which is placed inside the inner calorimeter vessel. This assembly will be equipped with fine-wire thermocouples which will allow observations of any temperature gradients on the surfaces. Also, a pre-heater section will be constructed which is capable of heating or cooling a fluid sample to a temperature between 200 and 700 K. In addition, a high-precision, automated syringe pump will be obtained and tested. This pump will be used to create a constant volumetric flow of gas or liquid through the calorimeter. The flow tubing will be connected from the pump to the pre-heater and calorimeter sections. Tests of the thermoelectric cooler and its matching heater will be conducted to ascertain their optimal setpoints.

DIELECTRIC CONSTANT APPARATUS

Anthony R.H. Goodwin, and M.R. Moldover

The objective of the project is to extend the range of conditions under which accurate dielectric constant measurements can be made.

During previous reporting periods, we developed parallel-plate and concentric cylinder capacitors. During the current reporting period, we decided to develop a measurement capability at high frequencies because the measurements can be made with low-impedance components. (High electrical impedances are difficult to maintain at high temperatures, and high impedance circuits cannot be used for fluids that are even slightly conducting.) Thus, we have designed, fabricated, and tested a reentrant radio-frequency (rf) cavity that can be operated as a resonator near 375 MHz to measure changes in the dielectric constant of fluids within it. A paper entitled "Dielectric studies of fluids with reentrant resonators", was prepared by A.R.H. Goodwin and M.R. Moldover and presented at the 11th Symposium on Energy Engineering Sciences at Argonne, IL, May 3-5, 1993. A copy of that paper is attached as Appendix B of this report.

The utility of the reentrant cavity was demonstrated first by determining the temperature-dependent dipole moment of 1,1,1,2,3,3-hexafluoropropane, a candidate replacement refrigerant (denoted R236ea). For this application, the temperature and density dependence of the dielectric constant had to be measured in the gaseous phase. The rf resonator was first calibrated with helium and then, as a test, used to redetermine the molar polarizability of argon. The argon results

were in excellent agreement with published values. As a second application, the reentrant resonator was used to determine the phase boundaries in mixtures of CO_2 + C_2H_6 and mixtures of CH_4 + C_3H_8 . In these instances, the fluids used are at high pressures and liquid-like densities. The quality of the results for CO_2 + C_2H_6 is comparable to the best published work. The data for CH_4 + C_3H_8 demonstrate the utility of this instrument in automated detection of phase boundaries in systems of interest in petroleum engineering. A high-temperature version of the reentrant resonator has been fabricated from Inconel 625 and is about to undergo shake-down tests at temperatures up to 400°C.

BENCHMARK MEASUREMENTS

Using the glass ebulliometer, metal ebulliometer, and Burnett PVT apparatus (supported by an earlier contract), we have made new and highly accurate vapor pressure measurements and gas-phase PVT measurements on alternative refrigerants R124 and R125, fluids for which relatively little data exist.

We also have used the Burnett apparatus to make selected measurements of the virial coefficients for the binary systems R32 + R134a, R32 + R125, R125 + R134a, and R134a + R152a. From these results, we have extracted binary interaction parameters which are necessary for modeling these mixtures. To our knowledge, these are the first such measurements on these systems, and possibly the first high-accuracy measurements of third virial coefficients for polar/polar systems.

We have configured one of the Division's vibrating tube densimeters to operate in a fully automated mode in the temperature range from -30 to 100 K and the pressure range from 0 to 6 MPa. We used this instrument during the current reporting period to measure the densities of propane (R290), butane, and the refrigerants R22 and R218 (cyclopropane), and a mixture of R11 + R123. The measurements with propane, butane, and R22 were made to better understand the limitations of the instrument. The data show that the instrument is accurate to $\pm 0.02\%$, or better. (The uncertainty is determined by the uncertainty in the reference data.) The data for R218 and the mixture R11 + R123 were taken in anticipation of the industry's need to better characterize these materials as alternative refrigerants.

BRIEF WORK STATEMENT FOR THE PERIOD
DECEMBER 1, 1993 - NOVEMBER 30, 1994

Extend the lower temperature range of the tantalum hot-wire thermal conductivity apparatus to 80 K and complete performance tests with toluene and water. Finalize design and continue development of the vibrating wire viscometer. Fabricate and install final sinkers in the dual-sinker densimeter and initiate and complete performance tests. Continue to explore the drift in the high-temperature vibrating tube densimeter and integrate it into an automated measurement system so that it can be calibrated under computer control. Complete final design details and construction of the dynamic phase equilibria apparatus and initiate evaluation of its performance. Complete additional measurements on mixtures using the all-metal ebulliometer and automate and improve the accuracy of the stainless-steel system for measuring the vapor pressures of pure fluids at high pressures. Continue the development and performance testing of key components of the total-enthalpy flow calorimeter. Complete shake-down tests of the new high-temperature re-entrant resonator for measuring dielectric constants and detecting phase transitions automatically and non-visually. Continue to perform benchmark measurements on CFC and HCFC alternatives.

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PUBLICATIONS RELATED TO DE-A105-88ER13823

FOR THE APPROXIMATE PERIOD DECEMBER 1, 1990 - JULY 31, 1993

The following publications describe applications of the apparatus developed under this contract as well as the development of the apparatus themselves. Asterisks indicate publications added since the last report.

- * Boyes, S.J. and Weber, L.A., Vapor Pressures and Gas-Phase PVT Data for 1-Chloro-1,2,2,2-Tetrafluoroethane (R124), Int. J. Thermophysics (submitted).
- * Bruno, T.J. and Outcalt, S.L., Fugacity Coefficients of Hydrogen in (Hydrogen + n-Butane), J. Chem. Thermodynamics (in press).
- * Bruno, T.J. and Haynes, W.M., Thermophysical Properties of Fluids for the Gas Industry, NIST Internal Report 5003 (in press).
- * Bruno, T.J. and Outcalt, S.L., Fugacity Coefficients of Hydrogen in (Hydrogen + n-Butane), J. Chem. Thermophys. (submitted).

Defibaugh, D.R. and Morrison, G., Compressed Liquid Densities and Saturation Densities of Chlorodifluoromethane (R22), J. Chem. & Eng. Data 37, 107 (1992).

Defibaugh, D.R. and Morrison, G., Compressed Liquid Densities and Saturation Densities of Pentafluoroethane (R125), Fluid Phase Equilibria (in press).

Defibaugh, D.R., Gillis, K.A., Moldover, M.R., Morrison, G., and Schmidt, J.W., Thermodynamic Properties of $\text{CHF}_2\text{-O-CHF}_2$, Bis(difluoromethyl) Ether, Fluid Phase Equilibria (in press).

Defibaugh, D.R., Goodwin, A.R.H., Morrison, G., and Weber, L.A., Thermodynamic Properties of 1,1-Dichloro-1-Fluoroethane (R141b), Fluid Phase Equilibria (submitted).

Defibaugh, D.R. and Morrison, G., Compressed Liquid Densities, Saturated Liquid Densities and Saturation Pressures of Mixtures Difluoromethane + 1,1,1,2-Tetrafluoroethane (R32 + R134a) and Difluoromethane + 1,1-Difluoroethane (R32 + R152a), Proceedings of the International Refrigeration Conference on Energy Efficiency and New Refrigerants, West Lafayette, IN, p. 473 (1992).

- * Defibaugh, D.R., Morrison, G., and Weber, L.A., Thermodynamic Properties of Difluoromethane (R32), J. Chem. & Eng. Data (submitted).

Diller, D.E., Aragon, A.S., and Laesecke, A., Measurements of the Viscosities of Saturated and Compressed Liquid Chlorodifluoromethane (R22), Int. J. Refrig. (in press).

Diller, D.E., Torsional Crystal Viscometer, IUPAC Volume on Transport Properties (1991).

- * Diller, D.E., Aragon, A.S., and Laesecke, A., Measurements of the Viscosities of Compressed Liquid Air at Temperatures between 70 and 130 K, Cryogenics 31, 1070 (1991).

- * Diller, D.E. and Peterson, S.M., Measurements of the Viscosities of Saturated and Compressed Fluid 1-Chloro-1,2,2,2-Tetrafluoroethane (R124) and Pentafluoroethane (R125) at Temperatures Between 120 and 420 K, *Int. J. Thermophysics*, 14, 55 (1993).

- Gillis, K.A. and Moldover, M.R., Apparatus for Acoustic Measurements of Gases with Applications for High Temperatures, *Proceedings of the Ninth Symposium on Energy Engineering Science*, Dept. of Energy CONF-9105116, p. 310 (1991).

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