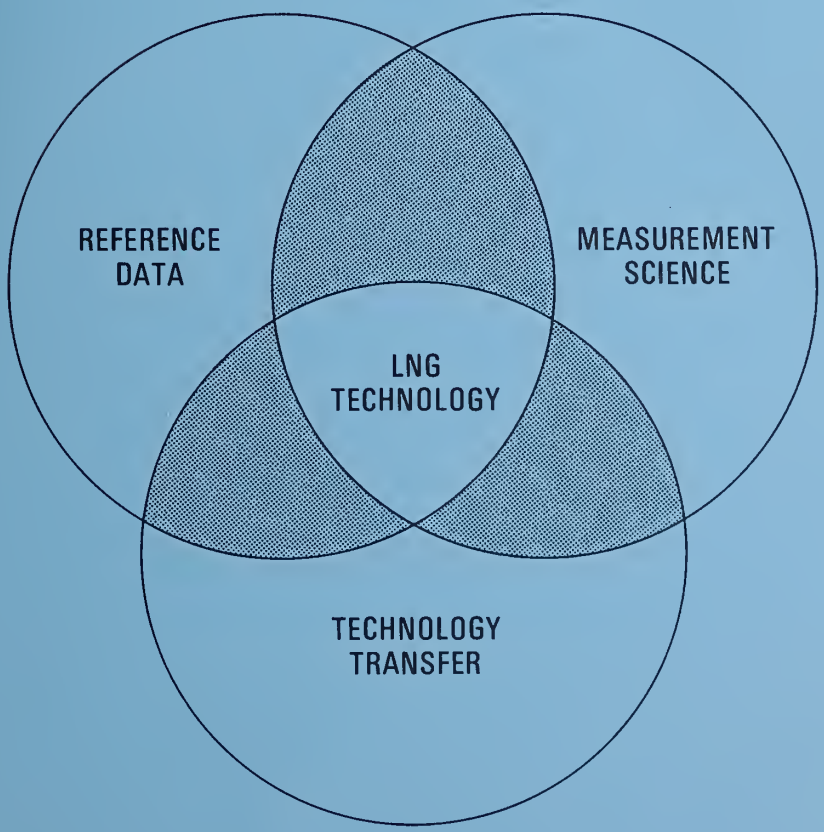
NBSIR 79-1603 (R)

LIQUEFIED NATURAL GAS RESEARCH

at the

NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 July - 31 December 1978



THERMOPHYSICAL PROPERTIES DIVISION, NATIONAL ENGINEERING LABORATORY,
NATIONAL BUREAU OF STANDARDS, BOULDER, COLORADO

NBSIR 79-1603

LIQUEFIED NATURAL GAS RESEARCH
at the
NATIONAL BUREAU OF STANDARDS

Thermophysical Properties Division
National Engineering Laboratory
National Bureau of Standards
Boulder, Colorado 80303

Progress Report for the Period
1 July - 31 December 1978

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(in cooperation with the American Gas Association, Inc.)

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LNG Custody Transfer Measurements Supervisory Committee

National Aeronautics and Space Administration
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ABSTRACT

The objective of this report is to:

1. provide all sponsoring agencies with a semiannual report on the activities of their individual programs;

2. inform all sponsoring agencies on related research being conducted at the Themophysical Properties Division;

3. provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paperwork at the cost center level.

The work is supported by NBS and seven other agencies and represents the collective expenditure of $400,000 during the 6-month reporting period. The contents of this report augment quarterly progress meetings for certain of our sponsors and provide a perspective which is missing when the parts are viewed individually. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished, and therefore not for citation in the open literature.

During this reporting period we have issued the first supplement to the "LNG Material and Fluids" Users Manual.

Key words: Cryogenics; liquefied natural gas; measurement; methane; properties; research.

CONTENTS

CONTENTS (continued)

1. Title. THERMOPHYSICAL PROPERTIES DATA FOR PURE COMPONENTS AND MIXTURES OF LNG COMPONENTS

Principal Investigators. R. D. Goodwin, H. M. Roder, G. C. Straty, W. M. Haynes, R. D. McCarty, D. E. Diller, and B. A. Younglove

2. Cost Center Numbers. 7360574, 7360548

3. Sponsor Project Identification. Gas Research Institute Grant No. 5010-362-0019 and American Gas Association, Inc., Project BR-50-10. National Aeronautics and Space Administration, Lewis Research Center, Purchase Order C-78014-C.

4. Introduction. Accurate phase equilibrium, equation of state (PVT), and thermodynamic properties data are needed to design and optimize gas separation and liquefaction processes and equipment, and for mass and heat transfer calculations. Accurate data for the pure components and selected mixtures of hydrocarbon systems will permit developing comprehensive accurate predictive calculation methods which take into account the dependence of the thermophysical properties of mixtures on the composition, temperature, and density.

This project will provide comprehensive accurate thermophysical properties data and predictive calculation methods for compressed and liquefied hydrocarbon gases and their mixtures to support the development of LNG technology at NBS and throughout the fuel gas industry. It will also serve as the base for a comprehensive mixtures prediction methodology.

5. Objectives or Goals. The objectives of our work are the determination of comprehensive accurate thermophysical properties data and predictive calculation methods for the major pure components (methane, ethane, propane, butanes, and nitrogen) and selected mixtures of liquefied natural gas and hydrocarbon mixtures at temperatures between 80 K and 320 K and at pressures up to 35 MPa (5000 psi). Our goal is to provide a range and quality of data that will be recognized as definitive or standard for all foreseeable low temperature engineering calculations.

6. Background. Liquefied natural gas is expected to supply an increasing percentage of the United States' future energy requirements. It is likely that massive quantities of liquefied natural gas will be imported during the years 1978 - 1990. Ships and importation terminals are being built for transporting, storing, and vaporizing liquefied natural gas for distribution. Accurate physical and thermodynamic properties data for compressed and liquefied natural gas and hydrocarbon mixtures are needed to support these projects. For example, accurate compressibility and thermodynamic properties data are needed to design and optimize liquefaction and transport processes; accurate data for the heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition, are needed to provide a basis for equitable custody transfer. Accurate mixture data prediction methods are needed for use in automated heat transfer calculations.

Accurate thermodynamic properties data for liquefied gas mixtures must be based on precise compressibility and calorimetric measurements; compressibility data give the dependence of thermodynamic properties on pressure and density (at fixed temperatures); calorimetric data give the dependence of thermodynamic properties on temperature (at fixed pressures and densities). It is impossible, however, to perform enough compressibility and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation of the data to arbitrary compositions, temperatures and pressures. Instead, thermodynamic properties data for multicomponent mixtures must usually be predicted

(extrapolated) from a limited number of measurements on the pure components and their binary mixtures. This project was initiated to provide the natural gas and aerospace industries with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, "Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar," by Robert D. Goodwin (April 1974), and National Bureau of Standards Technical Note 684, "Thermophysical Properties of Ethane, From 90 to 600 K at Pressures to 700 Bar," by Robert D. Goodwin, H. M. Roder, and G. C. Straty (August 1976). These reports contain the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane and ethane, and provide an accurate basis for calculating thermophysical properties data for LNG and other hydrocarbon mixtures.

7. Program and Results.

7.1 Propane, PVTx and Dielectric Constant Measurements -- W. M. Haynes

The experimental measurements of the densities of liquid mixtures of LNG components have been completed. The LNG density project used the same apparatus that is now being employed for PVT and dielectric constant measurements on propane. A summary of the LNG density project is given in the report for cost center 7361574.

After testing the dead weight gauge measurement system, PVT measurements have been carried out for liquid propane at pressures to 360 bars along three isotherms at 146, 160, and 178 K (approximately 14 data points per isotherm). These data have been compared with the calculated values from the equation of state for propane developed by R. D. Goodwin. The maximum difference between the calculated and experimental densities was 0.07% while the average deviation was 0.02%. No problems were encountered in using the apparatus at high pressures.

This apparatus utilizes a magnetic suspension densimeter, which is based on an application of Archimedes' principle. The uncertainty in the measured density depends directly upon the uncertainty in the determination of the volume of the magnetic float. The volume of the float changes with pressure. Thus measurements have been carried out by H. M. Ledbetter of our division to determine the bulk modulus of the float material (barium ferrite) as a function of temperature between 76 and 300 K. These measurements demonstrated that the change in the volume of the float is less than 0.03% for a pressure change of 360 bars. (The bulk modulus (or compressibility coefficient) of barium ferrite changes approximately 2% from 76 to 300 K. This corresponds to a volume change of less than 0.001% for a pressure of 500 bars. For all practical purposes it can be assumed that the bulk modulus of barium ferrite is independent of temperature over the temperature range of the propane measurements.)

One of the coaxial leads to the capacitor used in the dielectric constant measurements broke when an effort was being made to remove a short to ground from the capacitor cylinder to which this coaxial cable was connected. The apparatus must be disassembled and the coaxial cable replaced.

7.2 Calculational Methods -- R. D. McCarty

Work is continuing, at a partial staff-year level, on the extension and optimization of the corresponding states method to mixtures of methane with nitrogen and other fluids. The transformation of the methane surface to N_2, O_2, Ar, H_2 and C_2H_4 has been accomplished and the development work on the transformation function itself has begun.

We have determined that the transformation function previously used for liquid density near saturation is inadequate for a broader range of pressure and temperature. Initial efforts in finding a new function are encouraging.

7.3 Propane, Specific Heat Data -- R. D. Goodwin

This project is complete and the results published in "Specific Heats of Saturated and Compressed Liquid Propane," by R. D. Goodwin, J. Res. Nat. Bur. Stand. (U.S.) 83, 449-58 (Sep-Oct 1978).

7.4 Butane, Preliminary Thermophysical Properties Data -- R. D. Goodwin

The objective is to prepare provisional tables of thermodynamic properties of normal and isobutane, using available physical properties data. In this work we expect to discover those areas of properties data most in need of further experimental measurements.

In general, there is an abundance of quite inconsistent data from different laboratories, requiring tedious weightings, selections, and eliminations. There are few data for liquid butanes at LNG temperatures.

Satisfactory formulations have been developed for the virial equation, the saturated liquid densities, specific heats for the saturated liquid below the boiling point, and for the ideal gas thermodynamic functions for both fluids.

By thermal loops, in a procedure first developed by W. T. Ziegler, we have derived new "data" (where none existed) from the triple- to the boiling-point for vapor pressures, densities of the saturated vapor, and for heats of vaporization. The vapor-pressure equation has been adjusted to include these new data, and a provisional description has been developed for the heats of vaporization up to the critical point.

Manuscripts for reports on the equation of state and provisional tables of thermodynamic properties for both n-butane and i-butane are complete and in the final stages of the NBS review process. They will be published as NBS Interagency reports.

The work on isobutane was done sooner than planned because of a Department of Energy funded experimental project on that fluid which will be used as a geothermal working fluid. The latter work is being done at NBS-Gaithersburg and the two projects will be done on a collaborative basis so that the resulting 'final' tables will serve both projects. The need for measurements to be made on i-butane at Boulder will be, consequently, reduced greatly.

7.5 Pure Nitrogen and Nitrogen-Methane PVTx Property Measurements -- G. C. Straty and D. E. Diller

Gas expansion PVT measurements on pure compressed and liquefied nitrogen have been completed. About 300 measurements were made at 21 densities in the range 11.2 - 28.4 mol/L, 80 - 270 K, 1 - 350 bars. These measurements were made to provide more accurate pure component data for an accurate mathematical model of the PVT properties of nitrogen-methane mixtures.

Twelve isochoric gas-expansion PVT runs have been made on a gravimetrically prepared 50.115 mole % nitrogen-49.885 mole % methane mixture in the T, P, ρ range 82 - 320 K, 2 - 350 bar, 11 - 28.6 mol/L. The measurements are being compared with the extended corresponding states model (R. D. McCarty, NBSIR 77-867 (Oct 1977), which was previously

optimized to saturated liquid density measurements on this mixture at temperatures below 140 K. Differences between calculated and measured densities range from several tenths percent at low temperatures and high densities to several percent near the critical temperature (~ 161 K) and critical density (~ 10.5 mol/L). About eight more measurement runs are planned.

7.6 Sound Velocity of Propane -- B. A. Younglove

New measurements of the sound velocity of propane have been initiated. We will evaluate the performance of the sound velocity approach in liquid propane at 100 K to see if the previous geometry is satisfactory. Drawings were made for a new configuration of spacer length twice the old length in case the former arrangement does not work. Calculations for dispersion from correlations available in the literature indicate that this should not be a problem. This and other features of the proposed measurements were recently discussed during a visit by Bruce Gammon of DoE, Bartlesville, Oklahoma, an expert in the field of sound velocity measurements. We have installed and tested a new vacuum jacket for the sound velocity cryostat which allows much more convenient dismantling of the system. The computer programming necessary for experimental sound velocity measurement has commenced. We have a computer file for computation of propane density from measured values of temperature and pressure, and a file for computation of sound velocity from a measurement of frequency using the information obtained from the previously mentioned calculation. The latter file is not in complete form. We will next work on checking the system as mentioned above for general behavior in liquid propane. Also we will check the sample holder system for temperature gradients, temperature measurement accuracy and other features required for proper measurement of sound velocity.

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	1.1
Equipment and/or Services Purchased	11.2K$
Approximate expenditures, total	96.4K$

10. Future Plans.

Objectives and Schedule: Quarter	1	2
Evaluate and optimize promising calculation methods for the thermodynamic properties of methane-nitrogen mixtures.	——————→	
Measure, analyze and report PVT and dielectric constant data for propane.	————————	
Publish provisional tables of thermodynamic properties for the butanes and develop an accurate equation of state.	——→	
Measure, analyze and report sound velocity data for propane.	————————	

1. Title. FLUID TRANSPORT PROPERTIES

Principal Investigator. Howard J. M. Hanley

2. Cost Center Number. 7362290

3. Sponsor Project Identification. NBS-Office of Standard Reference Data

4. Introduction. Methods for predicting the transport properties of fluid mixtures are unreliable and data are scarce. Prediction methods are needed, however, to supply the necessary design data needed to increase efficiency and reduce costs.

5. Objectives or Goals. The long range or continuing goal of the program is to perform a systematic study of the theories and experimental measurements relating to transport properties, specifically the viscosity and thermal conductivity coefficients, of simple mixtures over a wide range of experimental conditions. The specific objectives of the program include: 1) the systematic correlation of the transport properties of simple binary mixtures and the development of prediction techniques, 2) development of a mixture theory for the dilute gas region and the dense gas and liquid regions, 3) extension of the theory and prediction techniques to multicomponent systems, and 4) suggested quidelines for future areas of experimental work.

6. Background. A continuing program has successfully expanded the state-of-the-art of transport phenomena for pure fluids. Information for pure fluids is required as a prerequisite for mixture studies. The theory of transport phenomena has been developed and applied to produce practical numerical tables of the viscosity, thermal conductivity and diffusion coefficients of simple fluids: Ar, Kr, Xe, N_2, O_2, F_2, He, H_2, CH_4,[3] C_2H_6,[4] C_3H_8.[5]

It has been shown that a successful mixture program can emerge from combining the results for pure fluids with mixture equation of state studies. The equation of state work is being carried out by other investigators in this laboratory.

7. Program and Results. We continue to develop the prediction procedure for the transport properties of mixtures reported previously.[1] We have recently studied the fundamentals via computer simulation[6] to assess the scientific justification of the corresponding states approach.

The critical point behavior remains of interest[2] and preliminary results are in process of publication.

The transport properties of pure ethylene are being correlated.

8. Problem Areas. The lack of suitable experimental mixture transport properties data for comparison purposes is the main problem. Also equation of state (PVT) data for mixtures are needed.

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	0.4
Equipment and/or Services Purchased	2.5K$
Approximate expenditures, total	36.7K$

10. Future Plans. The corresponding states predictive procedure for mixtures will be more fully developed and expanded in line with the concurrent equation of state studies. We intend to investigate, in particular, the behavior of the transport properties at gas/liquid and liquid/liquid equilibria. Computer simulation studies will be expanded. Mixtures in which the components are very different (shape, size, mass, etc.) will be emphasized.

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6. D. J. Evans and H. J. M. Hanley, Phys. Rev. (submitted).

1. Title. PROPERTIES OF CRYOGENIC FLUIDS

Principal Investigators. G. C. Straty, N. A. Olien, B. A. Younglove, H. M. Roder, L. A. Weber, B. J. Ackerson, and D. E. Diller

2. Cost Center Numbers. 7360122, 7360124, 7360125

3. Sponsor Project Identification. NBS

4. Introduction. Accurate thermophysical properties data and predictive calculation methods for cryogenic fluids are needed to support advanced cryogenic technology projects. For example, liquefied natural gas is expected to supply an increasing percentage of the United States' energy requirements through 1990. Liquefaction plants, ships and receiving terminals are being constructed to transport and store natural gas in the liquid state (LNG). Accurate thermophysical properties data for LNG are needed to design low temperature processes and equipment. Accurate data will benefit the energy industries and the consumer by providing for safe and efficient operations and reduced costs. We are now examining the data needs of a number of higher temperature industries such as the synthetic natural gas (SNG) industry. This area of technology as well as the liquefied petroleum gas (LPG) industry are logical extensions of the current LNG work. SNG mixtures can be characterized as much more complex than natural gas, containing unlike (including highly polar) molecules. Interactions between unlike molecules are not well understood and the accurate data necessary to quantitatively understand the interactions are lacking. The needs for accurate predictive methods for SNG are essentially the same as LNG, i.e., to reduce capital and operating costs and improve energy efficiency.

5. Objectives or Goals. The objectives of this project are to provide comprehensive accurate thermodynamic, electromagnetic and transport properties data and calculation methods for technically important compressed and liquefied gases (helium, hydrogen, oxygen, nitrogen, methane, ethane, etc.) at low temperatures. In addition we intend to develop the capability to perform accurate PVT measurements on gaseous mixtures and pure components at high pressures and above room temperature. Precise compressibility, calorimetric and other physical property measurements will be performed to fill gaps and reconcile inconsistencies. Definitive interpolation functions, computer programs and tables will be prepared for engineering calculations. The immediate goals of this work are to obtain accurate sound velocity and thermal diffusivity data for compressed and liquefied gases by using laser light scattering spectroscopy techniques; design, construct and performance test a precision PVT apparatus for the region 250 - 900 K with pressures to 35 MPa; and design, construct and performance test a transient hot-wire thermal conductivity apparatus for the region 70 - 350 K with pressures to 80 MPa.

6. Background. The application of laser light scattering techniques to obtaining thermophysical properties data was initiated to complement and check other measurement methods and to solve measurement problems inherent in more conventional methods. For example, laser light scattering techniques permit measurements of sound velocities for fluids under conditions for which sound absorption is too large to perform ultrasonic measurements; laser light scattering techniques permit measurements of thermal diffusivities under conditions for which convection interferes with measurements of thermal conduction. The feasibility of light scattering experiments to obtain data on binary diffusion coefficients has also been demonstrated.

Light scattering allows thermal diffusivity measurements in the region where density fluctuations are relatively large, but accuracy drops significantly as you pass outside the extended critical region. To complement the scattering method, thermal conductivity measurements can be made with more conventional techniques such as a hot-wire technique. In the latter method a very small platinum wire is surrounded by the fluid and a voltage pulse is applied to the wire. The temperature of the wire is momentarily raised and the resistance increases. A series of very closely spaced resistance measurements would describe the return of the wire to equilibrium. These resistance vs. time measurements can be related to the rate of heat dissipation in the surrounding fluid and thus the thermal conductivity (provided convection heat transfer is prevented).

The development of accurate mathematical models (equation of state) for fluid mixtures requires accurate PVT data for the pure constituents and binary mixtures of key molecular pairs. Experience with LNG has identified the type and accuracy of the data required. In addition to that, work on SNG at high temperatures is a logical follow-on to the low temperature work on LNG. Typical constituents of raw SNG from coal via the Lurgi process are: water - 50.2%; hydrogen - 20.1%; carbon dioxide - 14.7%; carbon monoxide - 9.2%; methane - 4.7%; ethane - 0.5%; hydrogen sulfide and others - 0.6%.

An apparatus has been assembled for laser light scattering spectroscopy measurements on compressed and liquefied gases (76 - 300 K, 35 MPa). The apparatus consists of a high pressure optical cell, a cryostat refrigerated by means of liquid nitrogen, an argon ion laser and low-level light detection equipment.

The light scattered from fluctuations in the fluid can be analyzed with either digital autocorrelation techniques for the examination of the very narrow lines associated with scattering from temperature fluctuations (Rayleigh scattering) or with a scanned Fabry Perot interferometer for the measurement of the Doppler frequency shifts associated with the scattering from propagating density (pressure) fluctuations (Brillouin scattering).

Apparatus for photon-counting and digital autocorrelation has been assembled, interfaced with computer facilities and programmed to enable on-line data accumulation and analysis. Initial problems associated with signal modulations from excessive building vibrations have been solved by levitating the apparatus on an air suspension system. A small, highly stable capacitor has also been designed, constructed and installed inside the scattering cell to permit the dielectric constant of the scattering fluid to be determined, which should allow more accurate fluid densities to be obtained for use in the data analysis. Apparatus tests on well characterized, strongly scattering, test fluids have been made to verify data analysis programs.

Extensive thermal diffusivity data have been obtained for methane. Measurements have been made along the coexistence curve, the critical isochore, and critical isotherm. The measurements extend outside the critical region as well as deep into the critical region. In the deep critical region the effect of temperature gradients and impurities have been investigated. Outside the critical region, these effects do not affect measurements beyond experimental accuracy. The range of the measurements extends from 150 K to 230 K and 3 mol/L to 22 mol/L. The inaccuracy of the measurements is about 5% in the critical region, increasing to 10% or greater further away. A detailed analysis of the data and experimental error has been made and a paper[1] reporting the results has been submitted to the Journal of Chemical Physics.

Some preliminary results on a mixture of 70% methane and 30% ethane were obtained very near the vapor-liquid critical point (plait point). The results are interesting in that the thermal conductivity of the mixture does not exhibit a critical anomaly whereas pure methane does exhibit an anomaly in the thermal conductivity as the critical point is approached. The anomalous behavior of pure fluids and nonanomalous behavior of mixtures is qualitatively and quantitatively in agreement with theoretical predictions (see preceding title 'Fluid Transport Properties'). We hope to be able to perform more definitive measurements on hydrocarbon mixtures in the near future.

7. Program and Results.

7.1 Transient Hot-Wire Apparatus. The assembly of the apparatus is complete and some preliminary measurements on air at low pressure and near room temperature have been made. Some difficulties have arisen due to the limited precision of the Nova minicomputer. The machine carries only 16 binary digits precision and must be run in double precision. Operation in this mode, however, increases execution time by a factor of three. The data acquisition on this type of apparatus dictates that a number of measurements be acquired in a little over two seconds. The number of data points read in double precision is only marginally adequate. Software means of circumventing this problem are now being explored.

7.2 Laser Light Scattering Measurements. During the past reporting period some additional measurements were made on a 70% methane-30% ethane binary mixture near the mixture critical point (plait point). These results are not definitive enough to establish for certain the existence or non-existence of an anomaly in the thermal conductivity. What is needed is a systematic study of the behavior of a series of well-characterized mixtures, especially as the concentration of one component goes to zero.

7.3 High Temperature PVT Apparatus. Adequate funding for this program was obtained in December 1978; as a result design, procurement and construction will proceed at a level of effort of approximately 1.5 staff-years/year. An automatic self-balancing thermometry bridge has been obtained and checked out. Two precision quartz pressure transducers (to 35 MPa) have been received and are installed in the NBS Pressure Calibration System for calibration and long term stability testing. Preliminary design of the experimental method and cell are in progress as well as an examination of available high temperature baths. A desktop calculator for data acquisition and experimental control is on order.

8. Problem Areas. Light scattering has proven to be a valuable tool for obtaining thermal diffusivity data on fluids. This is particularly true in a broad temperature and density range around the critical point, where more conventional experimental methods fail or are severely limited. The intensity of the scattered light however decreases drastically as one moves away from the critical region. Data accuracy in this region becomes limited by the statistical nature of the scattering process and the ability to maintain stability and precise experimental parameters over the extended periods of time necessary for data accumulation.

The difficulties outlined in 7.1 regarding the processing capabilities of the present minicomputer persist in delaying the start of experimental measurements at low temperature and high pressure.

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	0.8
Equipment and/or Services Purchased	6.3K$
Approximate expenditures, total	61.0K$

10. Future Plans.

Objectives and Schedule: Quarter	1	2
Complete performance test transient hot-wire thermal conductivity apparatus.	——→	
Design, construct and performance test high temperature-high pressure PVT apparatus.	————————	
Laser light scattering measurements on well-characterized binary systems.		———

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1. Title. PROPERTIES OF CRYOGENIC FLUID MIXTURES

Principal Investigators. M. J. Hiza, A. J. Kidnay (part-time), and R. C. Miller (part-time)

2. Cost Center Numbers. 7360123, 7362289, 7368574

3. Sponsor Project Identification. NBS, NBS (OSRD), GRI

4. Introduction. Accurate thermodynamic properties data and prediction methods for mixtures of cryogenic fluids are needed to design and optimize low temperature processes and equipment. This project provides new experimental measurements on equilibrium properties and compilations of evaluated equilibrium properties data which are suitable for direct technological use or for the evaluation of prediction methods.

5. Objectives or Goals. The overall objectives of this project are to provide critically evaluated data on the phase equilibria and thermodynamic properties of cryogenic fluid mixtures. The program has been divided into the following elements:

   a) Preparation of a comprehensive bibliography on experimental measurements of equilibrium properties for mixtures of selected molecular species of principal interest in cryogenic technology.

   b) Selection and/or development of methods for correlation, evaluation and prediction of equilibrium properties data.

   c) Retrieval and evaluation of experimental data for specific mixture systems selected on the basis of theoretical and/or technological importance.

   d) Preparation of guidelines for future research based on the deficiencies noted in (a), (b), and (c).

   e) Performing experimental research to alleviate deficiencies and provide a basis for improvement of prediction methods.

6. Background. A physical equilibria of mixtures research project was established in the Thermophysical Properties Division in 1959. The initial effort, based on a bibliographic search and other considerations, was directed toward the acquisition of new experimental data on the solid-vapor and liquid-vapor equilibria and physical adsorption properties for a limited number of binary and ternary mixtures of components with widely separated critical temperatures. Most of the systems studied included one of the light hydrocarbon species -- methane, ethane, or ethylene (ethene) -- with one of the quantum gases -- helium, hydrogen, or neon. The data for these systems led to significant improvements in the predictions of physical adsorption equilibrium and a correlation for the prediction of deviations from the geometric mean rule for combining characteristic energy parameters. In addition, significant new information was obtained for interaction third virial coefficients which was used in a correlation by one of our consultants, J. M. Prausnitz. The approach taken in this work has been as fundamental as possible with the intention of having an impact on a broad range of mixture problems.

   Recent efforts have been directed toward problems associated with systems containing components with overlapping liquid temperature ranges, such as nitrogen + methane, methane + ethane, etc.

7. Program and Results. The recent progress is summarized as follows:

   a) Thermodynamic consistency tests and comparison of G^E values derived from liquid-vapor equilibria data for methane + ethane using different equations of state to correct for the non-ideality of the vapor phase have been completed. The paper[1] discussing compilation, evaluation, and correlation of liquid-vapor equilibria data for the methane + ethane system has been revised accordingly. It has now been accepted for publication in the Journal of Physical and Chemical Reference Data and should be in print in late 1979.

   b) A compilation, evaluation, and correlation of the liquid-vapor equilibria for the methane + propane system, similar to that for the methane + ethane system, has been completed. A first draft of a paper reporting this work is nearing completion.

   c) Graphs of K-values and equilibrium compositions for methane + propane based on selected data from b) are being prepared for the LNG materials and fluids handbook.

8. Problem Areas. None

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	0.7
Equipment and/or Services Purchased	2.7K$
Approximate expenditures, total	63.0K$

10. Future Plans.

Objectives and Schedule: Quarter	1	2
Complete draft of paper reporting compilation, evaluation, and correlation of liquid-vapor equilibria data for methane + propane. Initiate editorial review.	——→	
Complete and report graphs of K-values and equilibria compositions for methane + propane.	——→	
Update bibliography on equilibrium properties of fluid mixtures, beginning with section on liquid-vapor.	——	

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2. M. J. Hiza, An Empirical Excess Volume Model for Estimating Liquefied Natural Gas Densities, Fluid Phase Equilibria 2, No. 1, 27-38 (1978).

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1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

Principal Investigators. W. M. Haynes, R. D. McCarty and M. J. Hiza

2. Cost Center Number. 7361574

3. Sponsor Project Identification. LNG Density Project Steering Committee; American Gas Association, Inc., Project BR-50-11.

4. Introduction. Accurate density measurements and calculational methods for liquefied natural gas mixtures are needed to provide a basis for custody transfer agreements and for mass, density, and heating value gauging throughout the fuel gas industry.

The basis for the custody transfer of natural gas is its heating value. It is difficult to determine and agree on the heating value of extremely large volumes of natural gas in the liquid state. For example, methods for calculating the heating value of a liquefied natural gas mixture require knowing its density, which in turn depends on its composition, temperature, and pressure. As the compositions of LNG mixtures vary considerably, depending on the sources of the gas and the processing conditions, accurate methods are needed for calculating liquid densities at arbitrary compositions, temperatures and pressures. The accuracy is important because of the extremely large volumes of liquid involved.

5. Objectives or Goals. The objectives of this work are to perform accurate (0.1%) and precise (0.02%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures mainly in the temperature range 105 - 140 K, and to test and optimize mathematical models for calculating the densities of LNG mixtures at arbitrary compositions and temperatures.

6. Background. This project is being carried out at NBS because of the realization that equitable custody transfer agreements could be reached more readily if the density measurements and the evaluation and development of calculational methods were performed by independent professionals.

An apparatus incorporating a magnetic suspension technique has been developed for absolute density measurements on liquids and liquid mixtures, particularly at saturation, for temperatures between 90 and 300 K. The estimated imprecision of measurement is less than 0.02% and the estimated inaccuracy is less than 0.15%.

7. Program and Results.

7.1 Measurements. All measurements for this project have been completed. The last series of measurements included the following: (a) two methane-rich binary mixtures of CH_4 and iC_4H_{10}, (b) four methane-rich binary mixtures of CH_4 and nC_4H_{10}, and (c) seventeen methane-rich multicomponent mixtures of LNG components, including five 7- and 8-component mixtures containing up to 0.44% pentanes. The data have been analyzed and comparisons of the experimental densities with calculated values from mathematical models developed for predicting LNG densities have been made.

Papers describing the apparatus, experimental procedures, the data and its analysis, and comparisons of the data with other experimental data and calculated densities are being prepared.

7.2 Calculational Methods. Final optimization and modifications have been made to the extended corresponding states model and to the hard sphere model. Final optimization of the cell model will be made by Mel Albright at Phillips Petroleum and some testing is still being made with the Klosek and McKinley model.

Changes which were made to the extended corresponding states model and the hard sphere model as a result of the new data were minimal and have made very little difference in the calculated LNG densities.

The corresponding states model predicts all of the multicomponent densities to within 0.1% with the exception of one point which shows a deviation of 0.11% which satisfies the original goal of the modeling efforts.

8. Problem Areas. None

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	0.3
Equipment and/or Services Purchased	7.5K$
Approximate expenditures, total	7.5K$

10. Future Plans. This program is complete apart from the publication of the final results. There are three experimental papers in preparation, an apparatus paper, a paper detailing the performance of the predictive models and a final report encompassing all results of this six year project.

1. Title. PROGRAM FOR REDUCING THE COST OF LNG SHIP HULL CONSTRUCTION -- PHASE II SHIP STEEL IMPROVEMENT PROGRAM

Principal Investigators. H. I. McHenry, M. B. Kasen and R. P. Reed

2. Cost Center Numbers. 7363430, 7361430, 7362430

3. Sponsor Project Identification. Maritime Administration Misc. P.O. 400-58073

4. Introduction. Construction of LNG tankers requires the use of fine grain normalized steels for the part of the hull structure that is cooled by the cargo to temperatures in the range of 255 K (0°F) to 228 K (-50°F). Several ABS steels have satisfactory base plate properties but extreme care must be exercised during welding to avoid degradation of the steel adjacent to weld (the heat affected zone) to a level of toughness below U. S. Coast Guard requirements. Significant cost problems are being encountered by U. S. Shipyards due to the resulting inefficient low-heat-input welding procedures that must be employed to meet the fracture requirements in the heat affected zone.

The feasibility of reducing the cost of LNG ship hull construction was investigated in Phase I of this project, leading to the Phase II program described below.

5. Objective. The objectives of the Phase II program are 1) to have the four major plate producers supply three LNG shipyards with production heats of ABS steels modified to possess improved transverse fracture properties at low temperatures, 2) to have the LNG shipyards evaluate these plates by qualifying optimum welding procedures in accordance with the USCG requirements and 3) to provide a metallurgical evaluation of factors that influence heat affected zone toughness in the improved steels.

6. Background. Early in 1974, the Welding Panel of MarAd's Ship Production Committee recommended that a program be conducted to reduce the cost of ship hull construction. NBS was requested by MarAd to propose such a program to the LNG subcommittee of the Welding Panel at a meeting in Boulder in August. In mid-October, MarAd approved the intial phase of NBS's recommended program, i.e., to survey the problem and the technology available for its solution. On the basis of this survey and as the result of a meeting of the Welding Panel in March, 1975, a coordinated program involving the LNG shipyards, the steel suppliers and NBS was recommended to MarAd and to the Welding Panel. This program was approved and work started in May 1975. Cost-sharing contracts for the evaluation of the improved steels were awarded in 1975 to the three participating shipyards: Avondale Shipyards, Inc., Newport News Shipbuilding and Drydock Co. and General Dynamics-Quincy Shipbuilding Division. A similar contract was signed with Lukens Steel Co. to evaluate Cb-treated V-051 steel with and without sulfide shape control. The three participating shipyards and Lukens Steel Co. completed the shipyard evaluation phase of the program in 1977. The ABS steels with sulfide shape control had excellent toughness and the HAZ toughness was improved, particularly for shielded metal arc (SMA) and gas metal arc (GMA) welds. The most promising results for high-heat-input welds were obtained with the Cb-treated V-051 steel with sulfide shape control.

Follow-on contracts were awarded to the three participating shipyards to further evaluate the most promising ship steels: ABS grades V-051

(Cb, SSC), V-062 (SSC) and (Cb, SSC). The work on these contracts has been completed. The results indicate that each of the steels retains satisfactory HAZ toughness at -51°C (at higher heat inputs than conventionally used) providing the weld metal toughness exceeds the 27J (20 ft lb) minimum.

7. Program and Results. During this reporting period, work on the final report was started. No additional research was conducted.

8. Problem Areas. None

9. Level of Effort. July 1, 1978 to December 31, 1978

Staff-years expended	0.1
Approximate expenditures, total	4.0K$

10. Future Plans. An evaluation by Avondale Shipyards Incorporated of submerged arc weldments with Linde M1-88 wire will be completed. Upon completion, the final report on the program will be finished.

1. Title. CUSTODY TRANSFER - LNG SHIPS

Principal Investigators. W. C. Haight, R. J. Hocken, B. R. Borchardt, R. G. Hartsock, R. C. Veale, J. D. Siegwarth, J. F. LaBrecque, and C. L. Carroll

2. Cost Center Numbers. 7360460, 7361575, 7362575, 7363575, 7311573, 7311577

3. Sponsor Project Identification. LNG Custody Transfer Measurements Supervisory Committee and Maritime Administration Misc. P.O. #400-79005.

4. Introduction. In response to the requests from the U.S. shipbuilding industry, NBS is independently examining the accuracies of LNG tank cargo capacity tables and developing alternative survey techniques.

5. Objectives. The objectives of the program are to develop new techniques for LNG transport tank calibration and to test the accuracy of present calibration techniques as part of an overall study of custody transfer methods aimed at increasing the accuracy of custody transfer measurements.

6. Background. Initial funding by the Maritime Administration (7360460) supported some preliminary tests of calibration of spherical LNG ship tanks. As a result of these measurements, the LNG Custody Transfer Supervisory Committee and the Maritime Administration have funded extension of the work to the membrane tanks and the free standing prismatic tanks now under construction in U.S. shipyards.

7. Program. Techniques for accurately dimensioning prismatic tanks of the membrane type have been developed by the Macrometrology Group at NBS. The technique requires establishing a model of a solid of the same shape as the tank just inside the tank walls using laser planes. Distances from the laser planes to the wall are measured at a larger number of points. The size and shape of the solid defined by the laser planes is measured by a multiple redundant method so the accuracy of the measurement of the dimensions of the solid can also be determined. Measurements using this technique have been completed on the tanks of two ships and three tanks of the third ship. Any disagreements between these results and the results of the primary tank survey are smaller than the allowed calibration uncertainty of $\pm$ 0.2% of total volume.

Two of the free standing prismatic tanks have been tested for distortions resulting from lifting and loading them onto the ships. The distortion detected was not significant relative to the accuracy required of the photogrammetric survey.

An external laser plane survey method has been developed for a free standing prismatic tank and the hardware is under construction.

The accuracy and precision of the photogrammetric tank survey method is being tested with length standards. Invar tapes are being employed to give accurate target separations for test lengths near the maximum dimensions of the tank. Of the three tanks thus far completed, the accuracy and precision of the photogrammetric measurements of the test target separations indicate this survey technique meets volume accuracy requirements. Measurements to check the photogrammetric survey have been completed on ten tanks.

8. Problem Areas. None

9. Level of Effort. July 1 - Dec. 31, 1978

Staff-years expended	1.4
Equipment and/or Services Purchased	$1,500
Approximate Expenditures, Total	$72,500

10. Future Plans. The checks of the surveys of the remaining three membrane tanks will be completed. The laser plane dimensioning technique will be applied to check the capacity of one of the free standing prismatic tanks and to examine hydrostatic distortion effects. The test tape measurements will continue on subsequent tanks to look for possible survey distortions and to examine horizontal and vertical calibration factors.

1. Title. HEATING VALUE OF FLOWING LNG

Principal Investigators. J. A. Brennan

2. Cost Center Number. 7362570

3. Sponsor Project Identification. Pipeline Research Committee (American Gas Association) PR-50-48.

4. Introduction. This project will test instrumentation for making heat value measurements on flowing LNG in actual applications. Information from projects currently underway by Siegwarth (cost center 7367574) on densimeters, by Haynes and Hiza (cost center 7361574) on mixture densities and by Richards (cost center 7363570) on LNG sampling will be utilized where appropriate to provide state of the art information.

5. Objectives. The objective of this project is to measure total heating value of LNG flowing in a pipeline by the integration of individual measurements of flow, density and specific heating value. Flow measurement requires determination of flowmeter performance in line sizes larger than presently available calibration facilities. Therefore, a secondary objective is to establish appropriate flowmeter scaling laws.

6. Background. The LNG flow facility at NBS was used to evaluate the response and integration of the individual elements of the heating value measurement. Different compositions of LNG were tested to provide a range of densities and temperatures sufficient to determine any dependencies. Sampling work was combined with the sampling project (cost center 7363570) to better define the important criteria of this phase of the measurement problem.

   Flowmeter scalling work utilizes the cryogenic and water flow facilities at NBS as well as private LNG peak shaving and import facilities.

7. Program and Results. All test instrumentation for the Southern Energy Import Terminal has been installed and the recording equipment connected. Preliminary tests of pressure, temperature, and flow were completed during the last quarter. Some problem areas were identified and corrected. These instruments and the recording instrumentation have all been checked out at the site.

   The densimeter was not checked out during the preliminary tests because the sensing head was not inserted into the LNG line. It was decided to leave the densimeter retracted until after the facility had been in operation for a period of time to prevent possible damage to the densimeter during the start up procedures. The densimeter has now been inserted and will be included during the next test.

8. Problem Areas. All known problem areas have been corrected.

9. Level of Effort. July 1 - December 31, 1978

Staff years expended	0.2 MY
Equipment and/or services purchases	None
Approximate Expenditures, Total	$7,200

10. Future Plans. LNG flow tests will be run at Southern during the first quarter of 1979.

1. Title. LNG DENSITY REFERENCE SYSTEM

Principal Investigators. J. D. Siegwarth and J. F. LaBrecque

2. Cost Center Number. 7367574

3. Sponsor Project Identification. American Gas Association, Inc., Project BR-50-10; Gas Research Institute.

4. Introduction. A density reference system has been developed to evaluate the ability of commercially available instruments to measure densities of LNG directly. Density is an essential measurement in determining the total energy content of natural gas reservoirs.

5. Objectives. The object of this research is to develop and supply adequate calibration methods and calibration standards to densimeter manufacturers and users for providing traceability of accuracy to field density measurement systems.

6. Background. The density reference system project was initiated in 1973. Since that time the reference system has been designed, constructed, and is now in operation, evaluating commercial density metering systems. Reports describing the density reference system and the results of the tests of four commercial densimeters have been published. These reports are:

Siegwarth, J. D., Younglove, B. A., and LaBrecque, J. F., Cryogenic fluids density reference system: provisional accuracy statement, National Bureau of Standards (U.S.) Technical Note 698, 24 pages (1977), and

Siegwarth, J. D., Younglove, B. A., and LaBrecque, J. F., An evaluation of commercial densimeters for use in LNG, National Bureau of Standards. (U.S.) Technical Note 697, 43 pages (1977).

The work has also been presented in the following papers:

Siegwarth, J. D., Younglove, B. A., and LaBrecque, J. F., Test of densimeters for use in custody transfer of LNG, Proc 53rd International School of Hydrocarbon Measurement, Normon, Oklahoma (1978).

Parrish, W. R., Brennan, J. A., and Siegwarth, J. D., LNG custody transfer research at National Bureau of Standards, American Gas Association Operating Section Proc. T243 (1978).

7. Program and Results. The tests on the seven Archimedes densimeters were completed. The results of the tests suggested some modifications to the instruments to improve both the repeatability and calibration of the instrument.

The Archimedes densimeter calibrated for a transfer was recalibrated. A 0.1% shift in calibration was encountered.

The redesign of the DRS has been completed. The parts have been built and assembly of the new system is in progress.

An enlarged version of this redesign system is under construction by an LNG importer to serve as a calibration system for ship board densimeters.

8. Problem Areas. The recent densimeter tests have shown that LN_2 is not the best choice of a calibration fluid for densimeters to be used in LNG. Better calibration techniques for commercial instruments are needed.

9. Level of Effort. July 1 - Dec. 31, 1978

Staff-years expended	0.8
Equipment and/or Services Purchased	$ 4,000
Approximate Expenditures, Total	$48,000

10. Future Plans. The rebuilding is expected to be completed about mid February and a vibrating cylinder densimeter of a new type will be tested at the same time the new DRS is checked out. A transfer standard will be sent to Gaz de France, Paris, when the calibration problems with the Archimedes densimeter are solved. The DRS will be used to check the calibration of the densimeter in the industrial calibration system presently under construction.

1. Title. LNG SAMPLING MEASUREMENT STUDY

Principal Investigators. R. J. Richards, J. F. LaBrecque, and J. A. Brennan

2. Cost Center Numbers. 7363570

3. Sponsor Project Identification. Pipeline Research Committee (American Gas Association) PR-50-94.

4. Introduction. Composition is used to determine both the heating value and the quantity (through density) of LNG shipments. Thus, any error in composition doubles when calculating the total heating value and dollar value of a LNG tanker cargo. Compositions are determined by sampling LNG, on either a batch or continuous basis, and analyzing the vaporized mixture. Although several sampling techniques exist, none have received a widespread acceptance in the LNG industry. Also, a standard technique has not been established for analyzing the vaporized sample.

5. Objectives. The objectives of this work are the same as the last reporting period with emphasis on vaporizer and accumulator design.

6. Background. This work was performed because there is a need to determine the best means for obtaining the composition of LNG shipments. Current LNG buying contracts include specifications on when and how many liquid samples are to be taken but omit the sampling technique to be used. The evaluation of sampling techniques by NBS is expected to lead to the acceptance of the most accurate composition determination method by all parties involved in LNG custody transfer.

7. Program. Based on previous work, the two factors preventing development of a general design are sampling rate and vaporizer-accumulator design. Test results showed that the precision of the system diminishes below a certain sampling rate. Attempts to correlate sampling rate with the limited range tested for the other variables failed. However, by process of elimination, the most likely factors causing the effect of sampling rate on precision are probe size, line size between the probe and vaporizer and heat leak. All of these variables are being evaluated in a laboratory apparatus, where the operating variables are controlled closely and mixtures of known composition are used.

Previous tests demonstrated that using a simple tube-vaporizer required the use of an accumulator to average out composition fluctuations. It was surmised that a non-equilibrium vaporization process was causing the fluctuations. New experiments have shown that non-steady flow into the vaporizer was also an important contributor to the problem. Using vaporizers of different designs and insuring single phase flow into the vaporizer, it has been possible to operate the sampling system without an accumulator with much less variation in composition.

Although improvement in sampling system performance has been significant, the use of an accumulator still gives the most consistent results. It may be possible to reduce the accumulator size by better flow control to the vaporizer and more controlled vaporization. Reducing the accumulator size would decrease the systems time constant thus making it more responsive to actual changes in composition. These parameters will be investigated during the final phase of the program.

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1978

Staff years expended	0.8
Experiments and/or services purchased	None
Approximate Expenditures, Total	$34,000

10. Future Plans. Complete work on alternate vaporizer and accumulator designs and write a final report.

1. Title. SURVEY OF CURRENT LITERATURE ON LNG AND METHANE

   Principal Investigator. Neil A. Olien

2. Cost Center Number. 7369574

3. Sponsor Project Identification. Gas Research Institute Grant No. 5010-362-0019 and American Gas Association, Inc., Project BR-50-10.

4. Introduction. It is important that all NBS personnel working in LNG, as well as the AGA and others, keep up with what is going on throughout the world in the LNG field. This project is designed to provide the Current Awareness and other information services to allow workers to keep abreast of new research and other developments.

5. Objectives or Goals. We will publish and distribute each April, July, October, and January a listing of all significant papers, reports, and patents relating to methane and LNG properties and technology. The references will be listed under convenient subject headings. The Quarterly will be distributed to all interested AGA member companies and be made available to the general public on a subscription basis. In addition, LNG-related information will be entered into the Cryogenic Data Center's Information System for quick retrieval. A systematic review of the current publication scene is maintained for any new periodicals to be reviewed cover-to-cover. Finally we will update and make available comprehensive bibliographies on the properties and technology of LNG. There are four bibliographies involved: methane properties, methane mixtures properties, processes and equipment involving methane and LNG, and patents relating to methane and LNG technology. These four will be updated annually.

6. Background. In 1969 we made a thorough review of the world's publications to determine which periodicals and abstracting services should be scanned cover-to-cover to adequately encompass the LNG field. The result is that we now scan over 330 primary publications and nearly 25 secondary publications. Of these, approximately one-third are directly related to LNG. In addition, we have increased our coverage of the energy field to include SNG (coal gas, hydrogen, etc.). Much of this information is also pertinent to LNG and as such is listed in our LNG-related publications. Our Current Awareness Service has been published weekly since 1964 (beginning in 1975 the publication became biweekly) and the Liquefied Natural Gas Survey has been published quarterly since 1970.

7. Program and Results. Four issues of the LNG Quarterly are prepared each year and distributed. There are now 121 subscriptions going to AGA Member Companies and 155 to other subscribers.

   The four comprehensive bibliographies mentioned in section 5 have been reviewed and shortened, and more selective bibliographies have resulted. The latest versions were completed as of January 21, 1977.

   B-1525 THE THERMOPHYSICAL PROPERTIES OF METHANE AND DEUTERO-METHANE IN THE SOLID, LIQUID AND GASEOUS PHASES - A SELECTED BIBLIOGRAPHY. Indexed by property, phase and author, 100 pages (Jan 1977). ($10.00).

   B-1526 THE THERMOPHYSICAL PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY. Indexed by property, system and author, 166 pages (Jan 1977). ($15.00).

B-1524 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPHY. Indexed by subject and author, 285 pages (Jan 1977). ($25.00).

B-1527 PATENTS RELATING TO METHANE AND LNG TECHNOLOGY - A SELECTED BIBLIOGRAPHY. Indexed by author, 150 pages (Jan 1977). ($15.00).

Over the past seven years we have distributed over 500 copies of these and the comprehensive bibliographies.

The size of these has grown to the extent that their usefulness is limited, therefore it was decided that they would not be updated and a series of more specialized bibliographies would be made available. The following list gives those currently available. Additional topics will be added as necessary. To date 70 copies of the following have been distributed.

B-1528 LIQUEFIED NATURAL GAS STORAGE INCLUDING INSULATION SYSTEMS. 1181 references, indexed by author and subject, 210 pages ($20.00).

B-1529 LIQUEFIED NATURAL GAS PEAKSHAVING AND SATELLITE OPERATIONS. 221 references, indexed by author, 36 pages ($10.00).

B-1530 LIQUEFIED NATURAL GAS STRATIFICATION AND ROLLOVER. 38 references, indexed by author and subject, 10 pages ($5.00).

B-1531 LIQUEFIED NATURAL GAS SAFETY INCLUDING SPILLS. 368 references, indexed by author and subject, 72 pages ($10.00).

B-1532 LIQUEFIED NATURAL GAS PIPELINES AND TRANSFER LINES. 226 references, indexed by author, 44 pages ($10.00).

B-1533 LIQUEFIED NATURAL GAS SHIPS, BARGES AND OVERWATER TRANSPORTATION. 805 references, indexed by author, 138 pages ($15.00).

B-1534 LIQUEFIED NATURAL GAS VAPORIZORS INCLUDING COLD UTILIZATION. 330 references, indexed by author and subject, 58 pages ($10.00).

B-1535 LIQUEFIED NATURAL GAS HEAT TRANSFER. 155 references, indexed by author, 34 pages ($10.00).

B-1536 LIQUEFIED NATURAL GAS LIQUEFACTION AND REFRIGERATION. 551 references, indexed by author, 94 pages ($15.00).

B-1537 LIQUEFIED NATURAL GAS ECONOMIC FACTORS. 470 references, indexed by author, 84 pages ($15.00).

B-1538 LIQUEFIED NATURAL GAS OVERLAND TRANSPORTATION. 76 references, indexed by author, 15 pages ($5.00).

B-1539 LIQUEFIED NATURAL GAS PATENTS. 747 references, indexed by author and subject, 119 pages ($15.00).

B-1540 LIQUEFIED NATURAL GAS INSTRUMENTATION. 85 references, indexed by author and subject, 23 pages ($5.00).

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	0.25
Equipment and/or Services Purchased	2.2K$
Approximate expenditures, total	7.5K$

10. Future Plans. Issue 78-4 was delivered to the printer the second week of January and should be distributed before the end of January.

1. Title. LIQUEFIED NATURAL GAS TECHNOLOGY TRANSFER

Principal Investigators. D. E. Diller, H. M. Ledbetter, and N. A. Olien

2. Cost Center Numbers. 7360403, 7361403, 7364574, 7368574, 7362287, 7360461, 7360594

3. Sponsor Project Identification. Maritime Administration, Miscellaneous Purchase Order No. 400-79005; American Gas Association, Inc. Project BR-50-10; Gas Research Institute; NBS Office of Standard Reference Data.

4. Introduction. The liquefied natural gas program at the Thermophysical Properties Division of NBS Boulder represents an investment by industry and government agencies of over $5 million over the past six years. This investment was designed to develop reference quality properties data for both fluids and materials and instrumentation and measurement technology for the use of the LNG and related industries. Information developed under this program must be transmitted to the ultimate user in a timely and useful format. The classical publication methods of NBS most certainly provide the scientist and research engineer information in a form most useful to the academic or near academic community. However, as a result of extensive assessments of user requirements, it was found that an additional effective mode for technology transfer would be an LNG Materials and Fluids User's Manual. A complete outline and planned table of contents have appeared in previous semiannual reports. The Maritime Administration of the Department of Commerce and the American Bureau of Shipping have agreed to sponsor the first year's efforts on the materials section, and the American Gas Association, Inc. and the NBS Office of Standard Reference Data have agreed to sponsor the section on fluids and fluid mixtures. The project was begun on April 1, 1976.

5. Objectives or Goals. The Liquefied Natural Gas Materials and Fluids User's Manual will provide a method of quick dissemination of property data and related information for the effective generation, utilization and transportation of LNG. The object is to improve technology transfer from the current NBS Thermophysical Properties Division LNG physical measurements program to the users, including federal agencies, the states and industry. For the purpose of this data book, liquefied natural gas is defined as a cryogenic mixture (at less than approximately 150 K) of hydrocarbons, predominantly methane, with less than a total of 20% of the minor components ethane, propane, iso and normal butane, and nitrogen as an inert contaminant. LNG materials will be those associated with the liquefaction, transport and storage of liquefied natural gas.

6. Background. The User's Manual is only one of a number of information dissemination methods used to provide workers in the liquefied natural gas (LNG) industry with properties data of known quality in a format consistent with the requirements of the intended user. In the case of the LNG User's Manual the intended audience is the field engineer, plant manager, ship designer or process engineer interested in a ready reference of assessed quality for data to be used in conceptual design, process monitoring, process analysis, and intercomparisons where precision and accuracy are secondary to specific problem solutions. The hierarchy of accuracy and precision will be defined and traceable through references to scientific and engineering literature.

Data are classified into three groups by the NBS Thermophysical Properties Division.

Group 1. Data which have been generated experimentally by NBS, or have been assessed, evaluated or experimentally verified by NBS.

Group 2. Data which have been assessed and evaluated by NBS.

Group 3. Data available in the scientific engineering literature through the NBS Cryogenic Data Center or elsewhere. No NBS evaluation or assessment has been made at this date.

In general, most data included in the LNG User's Manual will be from groups 1 and 2. Few new assessments or correlations are anticipated or required for this work.

Data will be presented primarily in graphical form. Tables and analytical expressions will be used only where absolutely necessary. Graphs and charts will be in loose-leaf form for ease of updating and additions. This form will also allow immediate implementation for data already available under the NBS LNG program and will provide a convenient format for the output of data from existing projects. The User's Manual will not be a substitute for traditional publications in the scientific literature where measurement science, technique, precision and accuracy are paramount, but will provide the data and references for the necessary assessment by the user.

The publication of both graphical and tabular data will be in a dual system of physical units. These units will be the traditional LNG industry British System of BTU, pound, degree Fahrenheit and the SI system of joule, kilogram and kelvin. It is the intent to give equal weight to each system of units.

7. Program and Results. The first edition of the User's Manual became available for distribution in September 1977. A complete description and ordering information are included as part of this report. About 550 copies have now been distributed to sponsors and purchasers. New orders are currently coming in at the rate of about ten per week. The first supplement to the User's Manual is printed out 210 copies have been distribution thus far. The first supplement contains 31 graphs of revised, updated and new material on the properties of structural metals and alloys (aluminums, nickel steels and stainless steels); 40 graphs on thermal insulations (polystyrene foams, polyurethane foams, polyvinyl chloride foams, balsa, perlite, cellular glass and glass fiber); 15 graphs and 3 wall charts on pure LNG components (ethane); and 9 sheets on binary and multicomponent mixtures of LNG components. The first supplement also contains 46 pages of materials specification tables and 38 pages of additional narrative and other descriptive materials.

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1978.

Staff-years expended	1.2
Equipment and/or Services Purchased	16.8K$
Approximate expenditures, total	91.8K$

10. Future Plans. Work on the second supplement is in progress. Propane graphs and thermodynamic property charts have been prepared. Additional graphs on mixtures of LNG components are nearly complete. Graphs on the properties of structural composites and aggregates (with emphasis on concretes) are underway. The second supplement is expected to be ready for distribution by September 1979. No additional supplements are planned at this time.

1. Title. OIML JOINT SECRETARIAT ON LNG MEASUREMENTS

Principal Investigators. Douglas B. Mann and James A. Brennan, NBS and T. L. Hillburn, Phillips Petroleum Company.

2. Cost Center Number. 7360290

3. Sponsor Project Identification. American Gas Association, Inc., NBS-Office of International Standards; and NBS.

4. Introduction. The liquefied natural gas program of the National Bureau of Standards Cryogenics Division has, over the past five years, provided the gas industry and interested Government agencies with properties data on materials and fluids, instrumentation, and measurement assistance in supplementary fossil energy supply. Support of this program by the American Gas Association, Inc., and Federal Government agencies such as the Maritime Administration (MarAd), NASA, GSA, Federal Power Commission and the NBS-Office of Standard Reference Data has provided a basis for the national acceptance of the results of the NBS LNG program. Through the U.S. membership in the International Organization of Legal Metrology there exists, at the present time, an opportunity to extend, internationally, the utility of data and measurement practice developed under our joint Government/industry program. We have been requested (by OIML membership) to establish a LNG Measurement Secretariat within OIML which, if implemented, would provide a significant international forum for the results of our joint work. It is believed that a joint Secretariat with the LNG industry would provide the most effective means of accomplishing these objectives.

5. Objectives or Goals. Our objective is to accomplish the following goals within the next three years.

a) To establish U.S. (NBS) thermophysical properties data for LNG as the standard data in international usage.

b) To establish U.S. (NBS) materials property data used in fabrication and construction of LNG facilities (liquefiers, storage, transport) as the standard data in international usage.

c) To establish U.S. (NBS) approved measurement technology and instrumentation as related to LNG (pressure, temperature, density, liquid level, flow) as the standard in international LNG trade. The precedent has been established with the successful completion of the joint NBS-CGA cryogenic flow measurement program which has resulted in the adoption of a cryogenic flow measurement code by the National Conference on Weights and Measures. We wish to extend this code on an international basis.

d) To establish and maintain the leadership of U.S. science, engineering, and industry in the research, technology, manufacture and marketing of instruments and measurement systems for liquefied natural gas.

6. Background. OIML was founded in 1955 to promote intergovernmental cooperation in the field of legal metrology which relates to the compatibility of standards of measurement and the legislation and government regulations which may affect such standards of measurement. OIML recommends uniform international requirements for scientific and measurement instruments used in industry and commerce and works out model laws and regulations for consideration by member nations; and, in

addition, serves as a center of documentation and information exchange in legal metrology. At present, 43 nations are members of this intergovernmental organization.

The United States joined OIML in 1972 (the Senate by resolution of August 11, 1972, gave its advice and consent to the accession of the U.S. to the convention establishing OIML). The responsibility for managing U.S. participation in OIML was assigned to the Department of Commerce and has since been delegated by the Department to the National Bureau of Standards (NBS). Under the general guidance of the Department of State and the Secretary of Commerce, NBS is directly responsible for formulating and implementing U.S. policy towards OIML. U.S. participation in the organization is deemed important for two reasons: First, to protect and enhance some $1 billion worth of scientific and measurement instruments exported each year by U.S. firms and to ensure equity in the trade of commodities measured by these instruments; and second, to maintain the U.S. as the world leader in the field of metrology.

In the spring of 1975 at a meeting in Paris of the International Committee of Legal Metrology, the French and U.S. representatives discussed the possibility of creating a new Reporting Secretariat No. 15 on "Liquefied Natural Gas (LNG) Measurement." The U.S. representative, W. E. Andrus, Jr. of NBS, agreed to explore the possibility with U.S. industry and interested government agencies. These discussions resulted in a decision to propose a joint Secretariat with the American Gas Association and NBS-Cryogenics Division in order to best accomplish the tasks. These conclusions were reached during several meetings extending through the latter part of 1975 and early 1976. During the summer of 1977, representatives of NBS met with PTB (West Germany) and SIM (France) to discuss the proposed scope and to explore expansion of the effort to include cryogenic fluids in general. Results of those discussions indicate some resistance to including different physical measurements (flow, density, etc.) under a single recommendation for a specific group of fluids.

The proposed plan and scope were presented at the meeting of The Advisory Committee for International Legal Metrology held at NBS-Boulder in September. The committee encouraged NBS to proceed with the present scope and to continue to explore the possible inclusion of other cryogenic fluids.

7. Program and Results. A revised work plan for cryogenic fluids was generated by the technical associates Douglas B. Mann of NBS and T. L. Hillburn of the Phillips Petroleum Co. representing A.G.A. and API. The scope of the work plan included instrumentation and procedures for the custody transfer measurements of pressure, temperature, density, liquid level, flow and calorific value of liquefied atmospheric and natural (hydrocarbon) gases having pure fluid or mixture normal boiling points of less than 150 K. Recommendations will be limited to establishing total mass and, where applicable, total heating value. Fluids and fluid mixtures considered will be limited to commercially important liquefied atmospheric gases, oxygen, nitrogen and argon and the primary components of liquefied natural gas, methane, ethane, propane, iso- and normal butane and pentane.

Flow measurements of pure cyrogenic fluids will be the first of the recommendations generated under the proposed work plan. This will be accomplished by combining the existing U.S. and European codes for flow measurements. A working group has been formed of interested parties and the first draft of this recommendation should be ready for review by

January of 1980. These plans are subject to funding during the present fiscal year.

8. Problem Areas. None

9. Level of Effort.

Staff-years expended	0.25
Equipment and/or Services purchased	0.00
Approximate Expenditures	$15,000

10. Future Plans. A first draft recommendation will be prepared by NBS as a simple combination of the two existing codes. This draft will be distributed to the four members of the working group for review. The revised first draft will then be submitted to the NBS-OIML representatives for OIML distribution.

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See page ii

13. Type of Report & Period Covered: 1 July 1978-31 Dec 1978

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The objective of this report is to:

1. provide all sponsoring agencies with a semiannual report on the activities of their individual programs;
2. inform all sponsoring agencies on related research being conducted at the Themophysical Properties Division;
3. provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paperwork at the cost center level.

The work is supported by NBS and seven other agencies and represents the collective expenditure of $400,000 during the 6-month reporting period. The contents of this report augment quarterly progress meetings for certain of our sponsors and provide a perspective which is missing when the parts are viewed individually. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished, and therefore not for citation in the open literature.

During this reporting period we have issued the first supplement to the "LNG Material and Fluids" Users Manual.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Cryogenics; liquefied natural gas; measurement; methane; properties; research.

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