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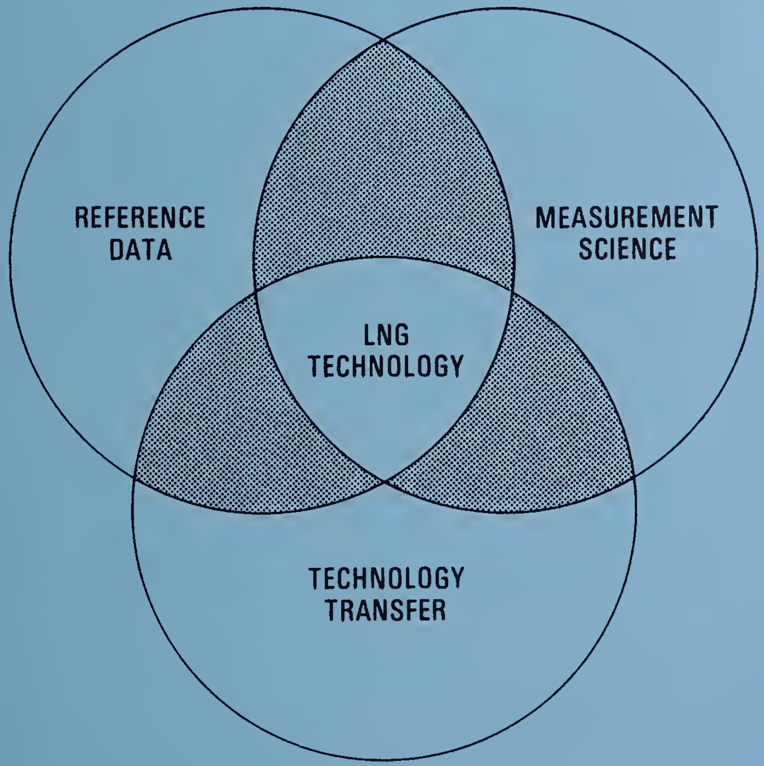
LIQUEFIED NATURAL GAS RESEARCH *at the* NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 January - 30 June, 1980



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

NBSIR 80-1636

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 January - 30 June, 1980

U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, Secretary
Luther H. Hodges, Jr., Deputy Secretary
Jordan J. Baruch, Assistant Secretary for Productivity, Technology and Innovation
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Prepared for:

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U. S. Department of Commerce
National Bureau of Standards
Office of Standard Reference Data
Washington, DC 20234

LNG Custody Transfer Measurements Supervisory Committee

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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 NBS-NEL Themophysical Properties Division, NBS-NEL Mechanical Processes Division and NBS-NML Fracture and Deformation 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 $646,000 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 Data or other information must be considered preliminary, subject to change and unpublished, and therefore not for citation in the open literature.

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

NOTICE

This LNG Semiannual Report has been compiled and distributed to over 150 sponsor designates every six months since 1972. Although the report still identifies the composite research at NBS on LNG and related subjects, some basic programs have been completed and others have broadened research activities into areas which are not strictly LNG related. We are, therefore, considering the following actions as to the continuation of this reporting procedure:

1. Discontinue this report as of 1 January 1981. One additional report would be issued in 1981 to cover this period progress.

2. Continue this report on LNG research but confine the contents to only LNG research activities.

3. Broaden the scope of this report to include research on gases in general, related material research and engineering measurements.

COMMENTS AS TO THE MOST DESIRABLE COURSE OF ACTION SHOULD BE DIRECTED TO: Douglas Mann, Thermophysical Properties Division, Continuous Process Technology Program, National Bureau of Standards, 325 Broadway, Boulder, CO 80303.

CONTENTS

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, B. A. Younglove, and H. J. M. Hanley

2. Cost Center Numbers. 7730574, 7732289

3. Sponsor Project Identification. Gas Research Institute Grant No. 5014-361-0131. 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 Normal and Isobutane, Thermophysical Properties -- R. D. Goodwin

Interagency reports have been printed, as follows:

NBSIR 79-1612, Isobutane: Provisional Thermodynamic Functions from 114 to 700 K at Pressures to 700 Bar, R. D. Goodwin, July, 1979.

NBSIR 79-1621, Normal Butane: Provisional Thermodynamic Functions from 135 to 700 K at Pressures to 700 Bar, R. D. Goodwin, September 1979.

For each substance, PVT data are lacking at temperatures roughly below the normal boiling point (NBP) but accurate densities for the saturated liquid are available down to the triple point.

Specific heats for ideal gas states and for the saturated liquid below the NBP were combined with the experimental heat of vaporization at the NBP, and a virial equation to derive new data from the triple to the NBP for saturated vapor densities, vapor pressures, and for heats of vaporization.

By use of these data with the highly-constrained, nonanalytic equation of state, a thermodynamic network was derived for all fluid states at temperatures above the triple point.

For propane and the two butanes new PVT data now are available (W. M. Haynes), including some other properties data such as vapor pressures for propane. Work therefore is in progress to replace the NBSIR reports on these fluids by revised work in NBS Technical Notes.

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

All measurements are now complete. This includes sound velocity, temperature, and pressure measurements on isotherms at 90, 100, 110, 120, 140, 160, 180, 200, 220, 240, 260, 280, and 300 K to a maximum pressure of about 5000 psia (34.7 MPa). The isotherms extrapolate well to the values measured at saturation which were mentioned in the previous report. The results are now complete.

7.3 Calculational Methods -- R. D. McCarty and H. J. M. Hanley

Methods to calculate LLE and VLE via the technique of corresponding states have been initiated.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980.

Staff-years expended	1.0
Equipment and/or Services Purchased	
Approximate expenditures, total	80.0K$

10. Future Plans.

Future plans are concerned with predicting and measuring phase equilibria (LLE and VLE) of the LNG systems.

1. Title. FLUID TRANSPORT PROPERTIES

Principal Investigator. Howard J. M. Hanley

2. Cost Center Number. 7732290, 7730125, 7732291

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) investigation of the properties and structure of fluids via computer similarities.

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 ,[1] CH_4,[2] C_2H_6,[3] C_3H_8.[4]

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. A correlation of the transport properties of ethylene is near the manuscript stage.[5] A computer program to predict the viscosity of mixtures suitable for a wide engineering audience is near completion.

8. Problem Areas. The lack of suitable experimental mixture transport properties data for comparison purposes remains a problem. Also equation of state (PVT) data for mixtures are needed. Recent measurements on the methane-nitrogen system will help alleviate the problem. (See 7.5 Thermophysical Properties Data for Pure Components and Mixtures of LNG Components.)

9. Level of Effort. January 1 - June 30, 1980.

Staff-years expended	0.5
Equipment and/or Services Purchased	21.4K$
Approximate expenditures, total	60.0K$

10. Future Plans. The theoretical transport program related to LNG is near completion. Future efforts will be directed towards mixtures of the heavier hydrocarbons.

References

1. H. J. M. Hanley, Prediction of the Viscosity and Thermal Conductivity Coefficients of Mixtures, Cryogenics, Vol 16, No. 11, 643-51 (Nov 1976); H. J. M. Hanley, Prediction of the Thermal Conductivity of Fluid Mixtures, Proceedings 7th ASME Conf. on Thermophysical Properties; H. J. M. Hanley in "Phase Equilibria and Fluid Properties in the Chemical Industry," ACS Symp. Series No. 60 (1977).

2. B. J. Ackerson and H. J. M. Hanley, J. Chem. Phys. (In press, 1980).

3. H. J. M. Hanley, W. M. Haynes and R. D. McCarty, The Viscosity and Thermal Conductivity Coefficients for Dense Gaseous and Liquid Methane, J. Phys. Chem. Ref. Data, Vol 6, No. 2, 597-609 (1977).

4. H. J. M. Hanley, K. E. Gubbins and S. Murad, A Correlation of the Existing Viscosity and Thermal Conductivity Coefficients of Gaseous and Liquid Ethane, J. Phys. Chem. Ref. Data, Vol 6, No. 4, 1167 (1977).

5. H. J. M. Hanley, P. M. Holland, K. E. Gubbins and J. M. Haile, J. Phys. Chem. Ref. Data 8, 559 (1979).

1. Title. PROPERTIES OF CRYOGENIC FLUIDS

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

2. Cost Center Numbers. 7730122, 7730124, 7730125, 7730424

3. Sponsor Project Identification. NBS, Department of Energy

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.

7. Program and Results.

7.1 Transient Hot-Wire Apparatus - H. M. Roder. Measurements. Measurements of the thermal conductivity of oxygen on isotherms of 77, 99, 122, 145, 160, 180, 202, 218, 241, 264, 282, 296, and 308 K are complete.

Data Distribution.

Oxygen measurements	
cell alinement	162
reproducibility, accuracy, precision checks	151
points requiring additional analysis	90
"isotherms", points plotted in graph 1	1387
Helium measurements	
"isotherm," 307 K	78
Total	1868

Plot. A point plot of 1387 conductivity measurements is given in graph 1. Nominal isotherm temperatures ($\pm$ 2 K) are indicated on the graph. Surprisingly, the influence of the critical point is clearly evident, even though the apparatus supposedly is not capable of measuring in the near critical regime. A comparison with calculated thermal conductivities, NASA SP-3071, yields systematic differences between experimental measurements and the correlation. Deviations are 5 to 20% at the very lowest densities and 15 to 25% at the very highest densities, with most isotherms reaching a zero departure at some intermediate density.

Future. Additional analysis is still required on the points below the vapor pressure curve, on points on the 160 K isotherm for densities less than critical, and for all isotherms at densities below 1 mol/L for pressures less than about 4 bars where the influence of the outer wall on the experiment is likely. After that preparation of a final report will be undertaken.

7.2 Laser Light Scattering Measurements. This project is inactive at the present time.

7.3 High Temperature PVT Apparatus - G. C. Straty and B. A. Younglove. Funding for this program was obtained in December 1978. Nearly all of the required equipment for the new PVT apparatus has now been constructed or acquired and the apparatus is being assembled. Initial temperature run-up and apparatus check out have been made followed by some preliminary measurements, probably on methane. The completed apparatus will be a semi-automated PVT data acquisition system for measurements to pressures of 35 MPa at temperatures from room temperature to about 1000 K. This will complement existing PVT facilities used for measurement below room temperature.

7.4 Mixture Composition Determination Using Raman Spectroscopy - D. E. Diller. A joint project on in-situ mixture composition determination was carried out while Diller was on an exchange visit with NML, NBS, Gaithersburg during October 1978 - June 1979. The feasibility of using Raman spectrometry for determining the composition of mixtures of natural gas components was examined. Raman intensity measurements were carried out on eight, gravimetrically prepared, binary gas mixtures containing methane, nitrogen and isobutane at ambient temperature and at pressures to 0.8 MPa. The repeatability of the molar intensity ratio, $(I_2/y_2)/I_1/y_1)$, where y_1 is the concentration of component 1 in the mixture, and I_1 is the intensity of the related line in the mixture spectrum, was examined. The compositions of two gravimetrically prepared methane-nitrogen-isobutane gas mixtures were determined spectrometrically with an estimated precision of about 0.001 in the mole fraction. Typical differences from the gravimetric concentrations were less than 0.002 in the mole fraction. The Raman spectrum of a gravimetrically prepared, eight component, hydrocarbon gas mixture was obtained to show that the Raman spectrometric method has potential for being applicable to natural gas type mixtures.

A manuscript entitled "Composition of Mixtures of Natural Gas Components Determined by Raman Spectroscopy" by D. E. Diller and R. F. Chang has been accepted for publication by Applied Spectroscopy.

Equipment is being assembled to continue this work in Boulder. The method has potential for studying multiphase, multicomponent equilibria at extreme conditions and near the critical point of a mixture.

7.5 Methane, Viscosity Measurements - D. E. Diller. The dependence of the shear viscosity coefficient of compressed gaseous and liquid methane on temperature, pressure and density has been determined at nine temperatures between 100 K and 300 K and at pressures up to about 30 MPa with a torsionally oscillating quartz crystal viscometer. The estimated imprecision and inaccuracy of the measurements are about 0.5% and 2% respectively. The measurements have been compared with an equation previously proposed (J. Phys. Chem. Ref. Data 6, 597 (1977)) for calculating the viscosity of compressed gaseous and liquid methane. Most of the differences between the equation and the measurements are within our experimental error. Significant differences between the measurements and the equation are reported only at the lowest temperature and highest pressures (100 K, $\leq$ 30 MPa), and along a supercritical isotherm at 200 K ($T \approx 1.05\ \overline{T}_C$).

A manuscript entitled "Measurements of the Viscosity of Compressed Gaseous and Liquid Methane" has been submitted to Physica (Leiden) for publication.

7.6 Ethane, Viscosity Measurements -- D. E. Diller. Measurements of the shear viscosity coefficient of compressed gaseous and liquid ethane (95-320 K, 30 MPa) are in progress. Measurements along the saturated liquid curve (95-300 K) and along isotherms at 290, 250, 200, 150, 120 and 100 K have been completed. The measurements are being compared with an equation previously proposed (J. Phys. Chem. Ref. Data 6, 1167 (1977)) for calculating the viscosity of compressed gaseous and liquid ethane. The differences between measured and calculated viscosities are less than 6%.

Measurements along isotherms at additional temperatures are planned for completion during the next quarter.

7.7 Prediction of Thermophysical Properties of Mixtures - J. F. Ely. Efforts are underway to develop accurate methods of predicting thermophysical properties of mixtures containing polar and non-polar components. Currently, a general computer program for predicting phase equilibria is being developed and tested for simple equation of state models. When fully developed, this program will be used to explore a modified extended corresponding states model and the Leung-Griffiths model for phase equilibria and other thermophysical properties.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	2.5
Equipment and/or Services Purchased	21.0K$
Approximate expenditures, total	180.0K$

10. Future Plans.

Objectives and Schedule:	Quarter 3	Quarter 4
Complete experimental data on thermal conductivity of oxygen		
Design, construct and performance test high temperature-high pressure PVT apparatus.		
Measure, analyze and report viscosity data for ethane in compressed liquid and gas region.		
Complete computer program for predicting mixture phase equilibrium.		
Develop accurate model for thermophysical properties of polar-nonpolar mixtures.		

1. Title. PROPERTIES OF CRYOGENIC FLUID MIXTURES

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

2. Cost Center Numbers. 7730123, 7732290

3. Sponsor Project Identification. NBS, NBS (OSRD), Gas Research Institute grant No. 5014-361-0131

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. A summary of recent progress is as follows:

a) The paper discussing compilation, evaluation, and correlation of liquid-vapor equilibria data for methane + propane[1] is in press in the Journal of Physical and Chemical Reference Data.

b) A paper on experimental phase equilibria measurements principally exploring the liquid-liquid-vapor equilibrium region for nitrogen + ethene,[2] has been prepared for the journal Fluid Phase Equilibria. Included are some measurements on the nitrogen + ethane system. This paper is in editorial review.

c) The systematic effort to reexamine consistency tests for phase equilibria data, and criteria for evaluating PVTx in general, has been pursued at a low level of effort this past semester, but will be more active the latter part of this year. Testing of data over all PVTx space for nitrogen + methane is the goal.

d) The updated and expanded version of the bibliography[3] has been typed. We are now in the process of sorting, integrating, proofreading and revising the final product to prepare a copy for review, probably to start in the third quarter.

8. Problem Areas. None

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	0.8
Equipment and/or Services Purchased	15.0K$
Approximate expenditures, total	75.0K$

10. Future Plans.

Objectives and Schedule:	Quarter 3	Quarter 4
Complete proofreading and revisions of updated and expanded bibliography, initial review.	————	—
Prepare final draft of paper on liquid-liquid-vapor for nitrogen + ethene and nitrogen + ethane for submission to Fluid Phase Equilibria.	————	—
Continue systematic study of consistency tests. Begin analysis of available phase equilibria and PVTx data for nitrogen + methane.	————	————

References

1. R. C. Miller, A. J. Kidnay, and M. J. Hiza, A Review, Evaluation, and Correlation of the Phase Equilibria, Heat of Mixing, and Change in Volume on Mixing for Liquid Mixtures of Methane + Propane, J. Phys. Chem. Ref. Data (in press).

2. K. A. Massoud Gasem, M. J. Hiza, and A. J. Kidnay, Phase Behavior in the Nitrogen + Ethylene System from 120 to 200 K, prepared for Fluid Phase Equilibria (in review for BERB).

3. M. J. Hiza, A. J. Kidnay, and R. C. Miller, Equilibrium Properties of Fluid Mixtures - A Bibliography of Data on Fluids of Cryogenic Interest, NSRDS Bibliographic Series, IFI/Plenum, New York, 1975.

1. Title. MATERIALS FOR LNG APPLICATIONS

Principal Investigators. L. L. Sparks, and J. M. Arvidson

2. Cost Center Number. 7733574, 5621570

3. Sponsor Project Identification. Gas Research Institute Grant Number 5014-361-0131.

4. Introduction. Safe, economical storage and transportation of LNG depend to a large extend on the materials used in the construction of capital equipment, i.e., ships, storage facilities, transfer terminals, liquefiers, and pipelines. Thermal insulations constitute a critical link in the materials for use in LNG oriented energy efforts because of the cryogenic nature of the liquid.

Expanded plastics (foams) are being used or are being considered for use in facilities such as these. Low-temperature properties data, standardized low temperature test methods, and standard reference materials are not presently adequate to meet the needs of complicated insulation systems. These materials are anisotropic for most properties so that properties data must be accompanied by specimen characterization in order to be of general use. Standard reference materials, for use in checking experimental systems are completely lacking. With the exception of thermal conductivity, standardized test methods for low-temperature testing of foams are also completely lacking.

5. Objectives or Goals. The broad objectives of this project are twofold: first, provide the users of thermally insulating foams with basic knowledge about the behavior of expanded plastics at cryogenic temperatures and methodology to allow safe, economical use of specific materials; second, serve as a center of insulation material information for GRI and associated users of cryogenic fuels. The first objective will be achieved by determining the low-temperature thermal and mechanical properties of selected, well characterized foams. The methodology of testing at low temperatures and characterizing the test materials will be stressed. The second objective will result as a consequence of this research effort.

6. Background. The Thermophysical Properties Division has been involved in the development and application of thermal insulations since being established in 1951.

The Properties of Solids group at Boulder has successfully examined the thermal and mechanical properties of a wide variety of materials: metals, polymers, insulations, and composites. The group, as a whole, has the equipment and expertise to establish and perform low temperature tests to determine the mechanical and thermal properties of foams. Close working relationships with private companies, universities, and professional associations provide guidance in the areas of material selection, quality control, and standardization of materials and methods.

The groundwork for the current foams research was done while working on the Insulation Section of the LNG Materials Handbook (funded by Maritime Administration).

7. Program and Results. The program designed to meet the need for data and standards for expanded plastics includes the following items: assessment of materials, assessment of methods, specimen acquisition, specimen characterization, and testing. A continuing survey of the literature and contacts with many foam related companies are being used to assess materials and methods.

The cooperation of users, producers, standardization societies, and other government labs, is extremely important to the success of the program. It is being stressed, particularly with the producers, that this program is not intended to do their research for them; our results will be related to identifiable characteristics such as general type of foam, cell size, membrane thickness, manufacturing process, etc. Property dependence on these parameters can be related to new as well as existing products. Cooperation with users of foam insulations benefits the program by increasing our knowledge of practical, field-type problems.

All program areas mentioned above (assessment of materials and methods, specimen acquisition, specimen characterization, and testing) have shown progress during this reporting period:

Assessment of materials and specimen acquisition. The material to be tested in the initial tests was selected and acquired in the previous reporting period. Additional specific information on this material is being sought from the producer, in addition to the NBS characterization discussed below. Material (polyurethane foam) from a commercial LNG ship tanker has also been obtained and is being characterized. The cooperation of several commercial foam producers has been assured and will allow us to obtain materials on request. Since many of the properties in question are somewhat time dependent, specimens will not be stockpiled, but rather obtained as near to the time of use as practical.

Test Methods. All procedures for mechanical and thermal testing have been outlined. These procedures are continuously evaluated and refined as our experience with new experimental systems accumulates. Thermal contraction of large inhomogeneous specimens will be accomplished utilizing a recently completed system designed for this purpose. This system includes an environmentally controllable test space. The mechanical properties will be determined in a recently completed system which utilizes capacitance gauge techniques. This system also allows a controlled test environment. Initial tests on both the thermal contraction and mechanical properties systems indicate that extremely precise and accurate measurements will be possible.

Specimen Characterization. This area has again been emphasized during this period. Optical methods of characterization have continued: Statistical methods are being used to evaluate reproducibility and observer influence. Preparations are being made to add scanning electron microscopy to the list of optical methods of evaluation. Differential thermal analysis (DTA) techniques were used to study several foams including the LNG ship foam and the initial material chosen for testing here. These tests were performed at NASA-Marshall Space Flight Center (MSFC) in Hunstville, Alabama. Although the data analysis is not yet complete, the preliminary results indicate that this test may be extremely useful in comparing the chemical makeup of foams.

Testing. Testing during this reporting period is of a preliminary nature and was done to evaluate various apparatus functions.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	0.57
Equipment and/or Services Purchased	$ 6,020
Approximate expenditures, total	$31,180

10. Future Plans. During the next reporting period we will complete the thermal and mechanical testing programs for the material now being considered. We will continue to refine our cellular study techniques and our analysis capability. A crucial phase of the program, relating observed cryogenic properties to foam structure, chemistry, and processes, will begin. Our cooperation with other government agencies and industrial users of foams will continue and expand as relevant opportunities come to our attention. In particular, differential scanning calorimetry will be fruther evaluated as a possible tool; this work will be done at NASA-MSFC by NBS personnel.

1. Title. LNG MATERIALS RESEARCH, CONCRETES

Principal Investigators. L. L. Sparks and J. M. Arvidson

2. Cost Center Number. 7730403, 5621511

3. Sponsor Project Identification. Maritime Administration, Miscellaneous Purchasing Order No. 400-89019.

4. Introduction. Concretes are attractive materials for construction of large LNG installations because of lower material cost and economies of fabrications compared to alternative construction methods. They exhibit favorable mechanical and thermal properties for use in LNG applications. Although these materials are presently used to some extent in LNG construction, lack of confidence in their cryogenic behavior has restricted their use to noncritical components or has resulted in overly conservative and expensive designs. This reflects the lack of dependable cryogenic thermal and mechanical properties data and a poor understanding of the effect of field fabrication variables on cryogenic performance.

   Applications of special concretes such as lightweight, cellular, fiber reinforced, and polymer will depend on their cryogenic properties, which are unknown at this time. The experimental program to determine these properties will be executed in cooperation with the USCG, Portland Cement Association (PCA), and several private corporations.

5. Objectives or Goals. The program objectives are to determine the properties ($76 K \leq T \leq 300 K$) of concretes which are presently being used in LNG applications and those which may provide design alternatives in the future. The properties which may be determined include: thermal conductivity, Young's modulus, thermal expansion, compressive strength, fatigue strength, splitting strength, permeability to water and LNG, and thermal shock. The dependence of these properties on parameters such as moisture content, air content, water-to-cement ratio, additives, aggregate type and grade, and aging will be determined. The parameter dependencies will be studied in order to understand the fundamental basis for the cause/effect relationships which are observed. Specimen characterization and parameter control are extremely important to this phase of the program. Knowledge gained from the parameter dependencies will be used to assess variabilities found in field-erected structures. This information is needed to establish the quality control necessary to assure fitness-for-service in cryogenic applications. The testing procedures which are used must produce reproducible and accurate data. With the exception of thermal conductivity tests, there are no standardized procedures for testing concretes at low temperatures. The large variations found in the literature are due, in part, to this deficiency. Whenever possible, ASTM, and ACI procedures, modified to accommodate the extreme environment, will be used throughout this program.

6. Background. The initial involvement of the Thermophysical Properties Division in the use of concretes as low temperature structural materials was in 1973. Safety aspects of concrete, in low-temperature installations were stressed. Data from the literature were collected and used in these safety evaluations; it became very clear that reliable low-temperature data, basic cause/effect relationships, and standardized low-temperature experimental procedures were inadequate. The situation has not changed significantly.

7. Program and Results. The long-range objective for the program is to establish an understanding of the behavior of concrete in the temperature range above 76 K. This understanding or model will be based on and tested by state of the art measurements on two "ordinary" concrete mixes (portand cement, sand and gravel aggregates). The effects of parameters such as moisture and air content, water to cement ratio, additives, aggregate type and size, and age will be determined. Properties to be used in this study include thermal conductivity and contraction, and the strengths and moduli. Field poured concrete and alternative types of concrete will be studied using the procedures and basic knowledge gained from the ordinary concrete tests and analysis.

The initial compressive tests exhibited an unexpected degree of scatter in both the strength and moduli, particularly at 76 K. The primary effort for this reporting period (funding was not available until 28 April 1980) has been to reevaluate testing procedures and specimen composition in an effort to reduce the observed scatter. We are developing the capability to make specimens at NBS (the initial set of specimens was purchased from a non-NBS laboratory). This will allow tighter control on specimen composition and aging. The facility for aging (specified in ASTM C192) has been completed. Portland cement, type I, has been acquired along with a detailed chemical analysis of the cement (as specified in ASTM C150). Petrographic analysis of the locally acquired aggregate is in progress as is the chemical analysis of admixtures to be used in the concrete specimens.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	0.1
Equipment and/or Services Purchased	$ 4,547
Approximate expenditures, total	$11,263

10. Future Plans. Thermal and mechanical properties of the well characterized concrete mix, tested in compression in the 1979 program, will be completed in the temperature range $76 \leq T \leq 300$ K. The specific properties which remain to be determined are thermal conductivity, thermal contraction ($\Delta L/L$), flexural strength, and splitting strength. These properties plus compressive strength will also be determined for a second, different concrete mix. This testing program involves a large number of individual tests, since multiple (a minimum of three) specimens are required at each temperature for each test. Knowledge of specimen variability obtained from these multiple tests is an essential part of the basic property data for concrete specimens.

The apparatus to be used in determining $\Delta L/L$ for large, inhomogeneous specimens such as concrete has been completed, and is now being calibrated. Preliminary testing and evaluation will be completed in the next reporting period along with data on concrete. In view of the lack of reliable data for this important design property, these measurements will be stressed; it is tentatively planned to study this property for other concretes in addition to the two mixes discussed above.

Characterization of specimens, which includes obtaining detailed information of moisture content, aggregate type and distribution, air content, porosity, and chemical composition of the cement, are required for each type of specimen. We will continue to develop and refine our capability to make, characterize, and test concrete specimens in the temperature range $T \gtrsim 76$.

In addition to producing much needed low-temperature data for concrete, the 1980-81 program will provide the groundwork for the very important parameter variability study anticipated in 1981-82. Established test method and characterization procedures are prerequisites for determining effects of parameters such as aggregate variability, moisture content, air content, void density, and cement composition on the thermal and mechanical properties. The results of the 1980-81 effort will be published in the open literature, reported to the sponsor in technical reports, and presented at appropriate technical meetings.

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, C. L. Carroll, C. P. Reeve, and F. E. Scire

2. Cost Center Numbers. 7730460, 7731575, 7732575, 7733575, 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 meansurements.

6. Background. Initial funding by the Maritime Administration (7730460) supported some preliminary tests of calibrations 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. The calibration reports have been completed and issued for all three of the membrane ships. The NBS determined volume height relationships for these tanks agree with those determined by the primary surveyor to better than $\pm$ 0.2%.

Interim reports of analyses of the three photogrammetric surveys are completed for the ships employing the free standing prismatic tank design. The volume determined by the primary survey agrees with the independent determination by NBS to better than $\pm$ 0.2%.

8. Problem Areas. Completion of this work has been delayed because of problems with the tank insulation system.

9. Level of Effort. January 1 - June 30, 1980

Staff years expended	.1
Approximate expenditures, total	8K$

10. Future Plans. The results of other measurements related to tank calibration accuracy will be reported. These various reports will be combined into a final report estimating the calibration accuracy of the cargo tanks of these three ships.

1. Title. LNG CUSTODY TRANSFER - LIQUID LEVEL

Principle Investigators. J. D. Siegwarth

2. Cost Center Number. 7730460

3. Sponsor Project Identification. Maritime Administration

4. Introduction. Except for liquid level, the National Bureau of Standards has examined the accuracy of all the measurements required to establish cargo value in the LNG trade. Density, composition, and volume determination techniques as well as models relating density to composition and temperature have been examined and the measurement accuracy estimated.

5. Objective. By examining the level gauge design, calibration and performance under operating conditions as well as intercomparing gauges on the same tanks when possible, we will estimate gauge accuracies.

6. Program. We are collecting manufacturer's information and papers from the open literature on the various gauging systems and methods.

7. Problem Areas. Possible delays due to shutdown in the major import operation to United States.

8. Level of Effort. January 1 - June 30, 1980

Staff years expended	0.1
Approximate expenditures	4K$

9. Future Plans. We will complete our collection of published information. We will make the necessary arrangements to visit manufacturing facilities to observe gauge calibrations and visit those firms. From these visits we should obtain some knowledge of repeatability and accuracy under laboratory conditions. Coincidentally, we will arrange to visit sites where the level gauges are in use and observe gauging operations under actual field conditions. From such observations, we should be able to obtain qualitative estimates of the repeatability and resolution under actual service conditions.

1. Title. LARGE SCALE LNG MEASUREMENTS

Principal Investigators. J. A. Brennan

2. Cost Center Number. 7730570

3. Sponsor Project Identification. Pipeline Research Committee (American Gas Association) PR-50-104.

4. Introduction. This project will investigate the scaling of a vortex shedding flowmeter from 12 inch (30 cm) to 32 inch (81 cm) diameter. The method used for testing the scale-up will be comparisons to storage tank volumes. Liquid level measurement in and volume determination of large storage tanks will be an important element in this investigation. Also included within this project will be work on LNG densimetry in pipeline applications and LNG flow measurement using ultrasonic flowmeters.

5. Objectives and Goals. The major objectives of this project are to extend flowmeter scaling to larger pipe diameters, to evaluate LNG densimetry under actual end use conditions and begin liquid level evaluation in large land based tanks. The work will be completed at a new LNG import terminal now under construction.

6. Background. Previous work on LNG flow element investigations was limited to a maximum line size of 12 inch (30 cm). The work was completed utilizing industrial LNG peakshaving and import facilities and was related back to the NBS cryogenic flow facilities in Boulder, Colorado, and the NBS water flow facilities in Gaithersburg, Maryland. Extensive densimeter evaluations have also been completed at NBS-Boulder with some additional testing at an LNG import terminal. This project will extend the previous work to larger line sizes and also start work on liquid level measurements in large storage tanks.

7. Program and Results. The new recording instrumentation referred to in the last report has been received. Some initial checkout and familiarization tests have been completed. The complete checkout at Southern Energy Company's import terminal cannot be performed until LNG imports are resumed.

   LNG storage tank volumes at the Trunkline import terminal are being measured by a commercial firm under a separate contract using photogrammetric techniques. Some redundant scale tapes will be provided by NBS to provide an independent check on the volume vs. height determinations. These tank measurements are critical to the flowmeter tests since they will provide the reference values for the flowmeter comparisons.

8. Problem Areas. The selection of an ultrasonic flowmeter has been delayed because of the requirement to have retractable transmitters. Of the flowmeters available with demonstrated cryogenic performance none has been found with the retraction capability. The necessary mounting flanges are being included on the pipeline so that the flowmeter can be installed when the problem is solved.

9. Level of Effort. January 1 - June 30, 1980

Staff years expended	.2
Equipment and/or Services Purchased	31K$
Approximate expenditures, total	40K$

10. <u>Future Plans</u>. NBS will provide scale tapes for the photogrammetric survey of the first LNG storage tank. This survey is scheduled for mid-July. Check procedures on future tanks will depend on the results obtained on the first tank.

Instrumentation checkout tests will be scheduled when LNG becomes available again.

1. Title. LNG DENSITY REFERENCE SYSTEM

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

2. Cost Center Number. 7737574

3. Sponsor Project Identification. Gas Research Institute, Grant No. 5014-361-0131.

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. The Portable Density Standard (PDS) has been completed and compared to the DRS densimeter in the DRS. The densities measured by the two instruments are indistinguishable since the difference is well under 0.01%.

An updated accuracy statement for the DRS is nearing completion. A report of the results of the comparison between the DRS and PRD is in preparation.

The third vibrating element densimeter for a calibration transfer standard was tested in two fillings and returned for repair since a leak was causing an instability in the resonant frequency.

The work on a second report of measurements on commercial densimeters has started but is not planned for completion until the third vibrating element densimeter has been returned for testing.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	1/3
Equipment and/or Services Purchased	$ 5,000
Approximate expenditures, total	$28,000

10. Future Plans. The DRS update and the Portable Density Standard reports will be completed next period. The report of the further studies of commercial densimeters should be nearly complete. The third vibrating element densimeter calibrations should be completed by then and included in that report. The comparisons of the DRS and the Gaz de France densimeter calibration facilities via the portable reference densimeter is still in the planning stage.

1. Title. BASIC NATURAL GAS METERING

Principal Investigators. Douglas Mann, James A. Brennan, Charles E. Sindt, and Clarence Kneebone

2. Cost Center Number. 7730571, 7732571, 7731571

3. Sponsor Project Identification. Gas Research Institute Research Grant No. 5014-361-0131 and American Gas Association, Inc.

4. Introduction. The National Bureau of Standards has under development a gas flow reference system capable of directly relating gas meter peformance to standards of mass and time. The facility coupled with existing liquid flow capabilities will provide a basis for significant improvements in gas quality and quantity measurements.

The new system will provide a factor of five to ten improvement in the total uncertainty of gas flow measurement which may be applied immediately to gas industry developed standards and codes. This could reduce the bias within field meters of the same generic type and size or meters of different types. The benefits are two fold; possible reduction in unaccounted for gas and increased credibility of measurement.

Reporting progress of this project under the NBS LNG Research program is justified by the general interst of the natural gas industry in both liquid and gas measurement research and a direct relationship of natural gas flow measurements to LNG flow measurements. Specifically, the project HEATING VALUE OF FLOWING LNG (see table of contents) relies heavily on the measurements of vaporized LNG (natural gas) to establish accuracy and precision of the LNG flow metering.

5. Objectives and Goals. The objectives of the program are to apply the capabilities of the new gas flow reference system to an existing well characterized gas industry measurement problem to assess the value of the new system in significantly improving gas flow measurements. If successful, the program will be directed to improving gas flow measurement through upgraded existing codes and the development of necessary data for defining new model codes and standards for gas flow measurement.

6. Background. Natural gas is collected, transported and distributed to industries, residences and utilities through one million miles of pipelines and mains. Ownership changes many times as the gas is delivered from the producer to the consumer and at each change of ownership, the value is established by some type of measurement. The establishment of value of natural gas in commerce as to both quantity and quality is usually made under dynamic flow conditions.

Measurement of value is accomplished using many different types of instruments such as positive displacement meters for small residential users to large head type or turbine type meters in transmission lines. Establishment and maintenance of the measurement system is a vital element of interest to both the gas industry and the National Bureau of Standards.

Calibration or proving of meters can be quite simple or complex depending on the gas flow rate, temperature, pressure, and mixture. Low pressure, low flow rate meters may be calibrated using water displacement which is economical and can be quite accurate and precise. Instruments for measurement of flow at several thousand cubic meters per minute at pressures of .27 to 1.37 MPa can not be directly calibrated in a routine manner, and therefore, infered methods must be used. These methods currently involve construction of the meter to empirically established specifications, water calibration to confirm basic meter factors, and then modification of the meter factor to account for compressibility and other non-ideal properties of the fluid to be measured. Other methods of proving of high flow rate capacity meters such as series operation with nozzles or multiple parallel meters are expensive and rely heavily on calculated performance rather than direct experimental evidence.

A Steering Committee was formed to aid in the planning and review of the Basic Natural Gas Metering Program. The committee is composed of eight natural gas industry members and the NBS staff. The committee met at NBS Boulder in October to review progress and has been instrumental in planning tests to establish the value of this new research tool. Future meetings are planned on a two to three a year basis.

7. Program and Results. The demonstration of feasibility of the reference system was completed in July, 1979. At that time, a standard four inch orifice meter run was installed at the inlet to the gas test section and subsequent testing involved a comparison of the performance of the meter run to the reference system. This was only one of several procedures used to establish the credibility of measurement. Performance of the four inch orifice meter run followed the procedures of AGA Measurements Committee Report No. 3.

The intercomparison of the orifice run and the reference system for several orifice sizes showed a reproducible and distinct flow dependence relative to the NBS reference system. In an effort to define the cause of this problem, a four inch gas turbine type flow meter was placed downstream in series with the orifice run. The gas turbine had been previously calibrated on a gas industry facility using natural gas as the process fluid and choked nozzles as the flow reference. Testing of this combination only confirmed the flow dependence results by showing a good agreement between the gas turbine meter and the NBS reference system.

In addition to the orifice meter flow dependence, large flow dependent pressure fluctuations were observed in the measurement of orifice differential pressure. A number of tests were conducted to locate the source of these fluctuations and to relate, if possible, the magnitude of the fluctuations to the flow measurement dependence. All tests were unproductive.

A separate four inch orifice run was tested on the gas industry test facility and confirmed the performance of this meter type to that predicted by the AGA Measurements Committee Report No. 3. Therefore, the problem then centered on the NBS reference system and the location of the orifice run in this system.

The relative position of the orifice meter and gas turbine meter were reversed and it was shown that both the flow dependence and the pressure fluctuations were markedly reduced if not eliminated. The reasons for this improvement are still under investigation and the current work continues to stress measurement credibility of the NBS reference system and performance of the orifice meter in pipe sizes 2, 3, 4 and 6 inches.

8. Problem Areas. The above investigations have delayed the progress of the program and the establishment of a statement of total reference system flow measurement uncertainty. At the present time no technical barriers are foreseen in the accomplishment of the program objectives.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	1.5
Equipment and/or Services Purchased	$ 26,000
Approximate expenditures, total	$121,000

10. Future Plans. A test plan will be developed to provide data on orifice run pipe sizes 2, 3, 4, and 6 inch diameter with seven different orifice plate diameters per line size. It is anticipated that data on the four inch line size can be completed. A major effort will be made to develop and publish a statement of total uncertainty of the gas flow reference system.

Preprint
AGA Transmission Conference
Salt Lake City, Utah May 5-7, 1980
Session 17

GAS MASS FLOW REFERENCE SYSTEM
A PROGRESS REPORT

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ABSTRACT

A new type of gas flow reference system under development at the National Bureau of Standards is described. The closed loop system allows continuous flow of nitrogen gas at line pressures of 4.1 MPa (600 psia) and at ambient temperatures. The gas flow is then cooled to liquid nitrogen temperature, and weighed at low pressures and at a density of up to 17 times the density in the gas phase. This results in direct, accurate and precise mass flow rate measurements.

This new flow reference tool is currently undergoing extensive testing and evaluation to establish total system uncertainty relative to national standards of mass. The program sponsored by the Gas Research Institute and the American Gas Association, Inc., will be directed to improving accuracy and precision of natural gas flow measurements, such as new gas flow data on orifice meter discharge and expansion coefficients.

A description of the NBS process is provided as well as preliminary performance information. Present mass flow rates are from 3000 kg/h (6600 lb/h) to 10000 kg/h (22000 lb/h) and plans for increasing this range are presented.

Key Words: Gas, Mass Flow, Fluid Flow, Instrumentation, Measurement, Metering, Thermodynamics

This work was conducted at the National Bureau of Standards under sponsorship of the American Gas Association, Inc. and the Gas Research Institute.

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INTRODUCTION

The new gas flow reference system developed as a logical extension of a cryogenic flow metering reference system in operation at the National Bureau of Standards Laboratories located at Boulder, Colorado. This liquid nitrogen system was part of a joint government-industry program designed to develop a National Model Code for Cryogenic Flow Metering which was successfully completed in 1976. Descriptions of the program appear in the literature [1 to 9].

The concept of extending the cryogenic flow reference system to gaseous flow operation was proposed by Mann and Brennan [10] in 1977. Funding to modify the existing facility to demonstrate feasibility was made available from NBS and the gas flow operation was demonstrated in July of 1979. Industry funding was made available in late 1979 for a program which would continue the cryogenic capability and at the same time provide a gas flow reference system of high accuracy and precision to study a range of current gas metering problem areas. This NBS-gas industry effort is directed through a joint steering committee which plans program objectives, reviews current progress and aids NBS in the selection of experiments directed at current gas metering problems.

PROCESS DESCRIPTION

The process is shown schematically in figure 1. Basically, the process is a closed loop thermodynamic cycle. The process fluid, nitrogen, is circulated between temperature limits of 85 K (153 R) and 300 K (540 R) at pressures of 0.5 MPa (75 psia) to 4.1 MPa (600 psia) depending on the point of the cycle under consideration. Work is done on the system by centrifugal pumps operating at 85 K (153 R) which increase the liquid nitrogen pressure to 4.1 MPa (600 psia) from 0.5 MPa (75 psia). Heat energy enters the system through a steam heat exchanger which controls the gas temperature at the test section. Heat energy is extracted from the system by refrigeration provided by boiling liquid nitrogen in the subcooler, auxiliary liquid nitrogen introduced at the main heat exchanger and cooling at the water heat exchanger following the gas test section.

The low pressure cryogenic portion of a cycle is maintained at a pressure of 0.5 MPa (75 psia) by means of helium gas introduced at the catch and weigh tank. This inert pressurant provides necessary over-pressure to inhibit boiling of the liquid nitrogen, allows liquid phase-gas phase separation for weighing of the liquid nitrogen and provides a controlled environment for the stable operation of the load cell and calibration weights. The interaction of the helium with the liquid nitrogen is negligible as the solubility of helium in liquid nitrogen is less than 0.1 percent. Pumping of the process fluid is accomplished in two steps. The boost pump increases the pressure about 0.2 MPa (25 psi) to the suction of the pressure pump. The pressure pump in turn raises the process fluid pressure to 4.1 MPa (600 psia). Both pumps are centrifugal types. The boost pump speed is variable while the pressure pump speed is fixed at about 8400 revolutions per minute. Mass flow rates are varied by operation of the expansion valve.

Selection of the high side pressure of 4.1 MPa (600 psia) was deliberate. The critical pressure of nitrogen is 3.4 MPa (493 psia) and operation above this pressure avoids two phase liquid-vapor boiling and condensing in the main heat exchanger, a possible source of flow noise.

The main heat exchanger is a five pass, plate-fin type constructed of aluminum. Cross section is 63.5 cm (25 inches) by 33 cm (13 inches) and is 4.92 meters (194 inches) in overall length including manifolds. The thermal load on the heat exchanger varies from 300,000 J/s to 1 million J/s (one million to 3.2 million Btu/h) depending on flow rate. Operation of the exchanger near the critical pressure requires additional heat transfer surface because of severe internal temperature pinch at the low temperature end. Figure 2 shows the internal temperature differences between the two counter-flow process streams for a set of typical operating conditions. As a result of this condition and the requirement for additional heat transfer surface, nearly 80 percent of the heat exchanger length is at a temperature of less than 150 K (270 R). To protect the exchanger from environmental heat leaks, polyurethane foam insulation was applied to a thickness of 30 cm (12 inches).

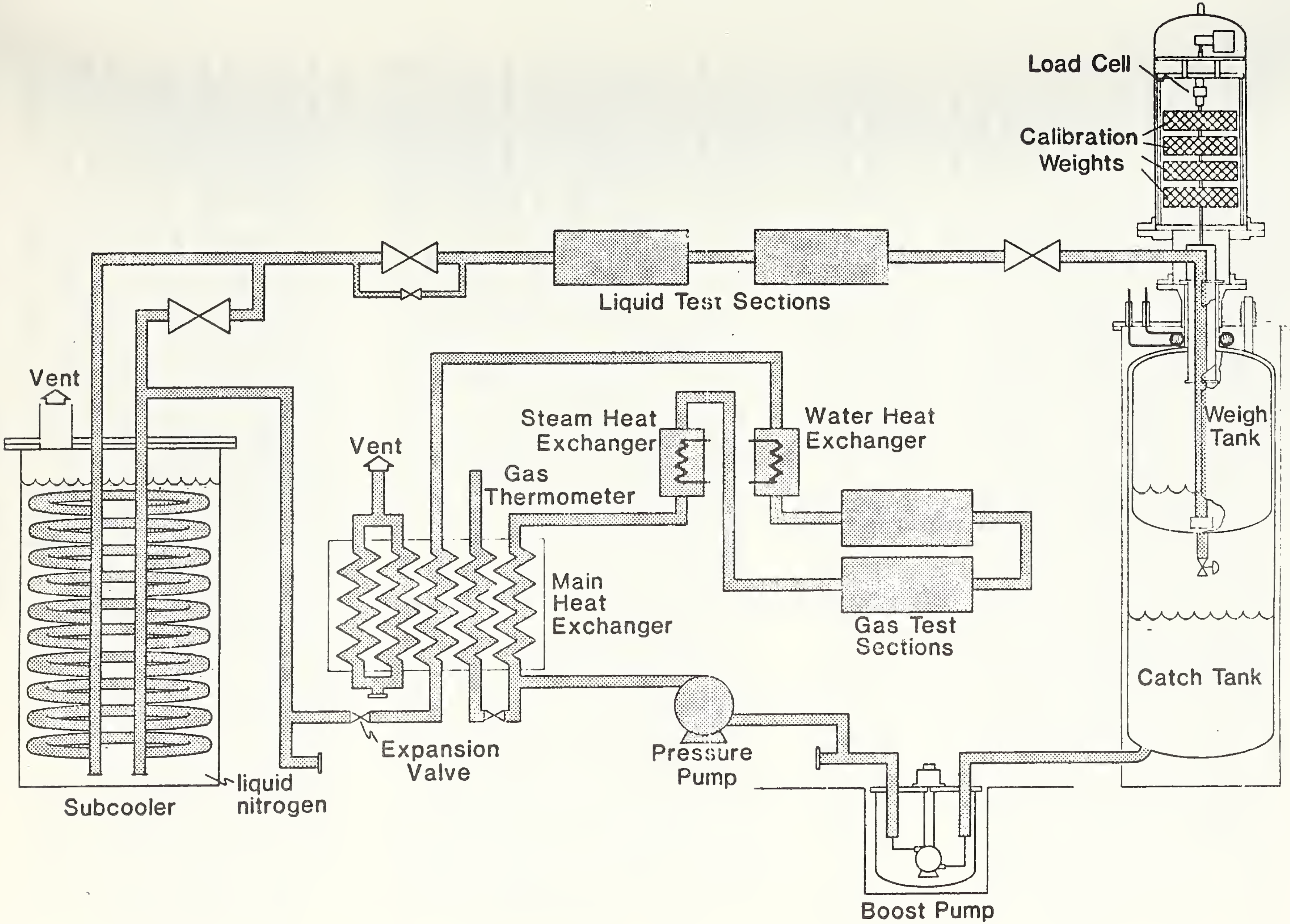

Figure 1. Flow Schematic of Gas Mass Flow Reference System

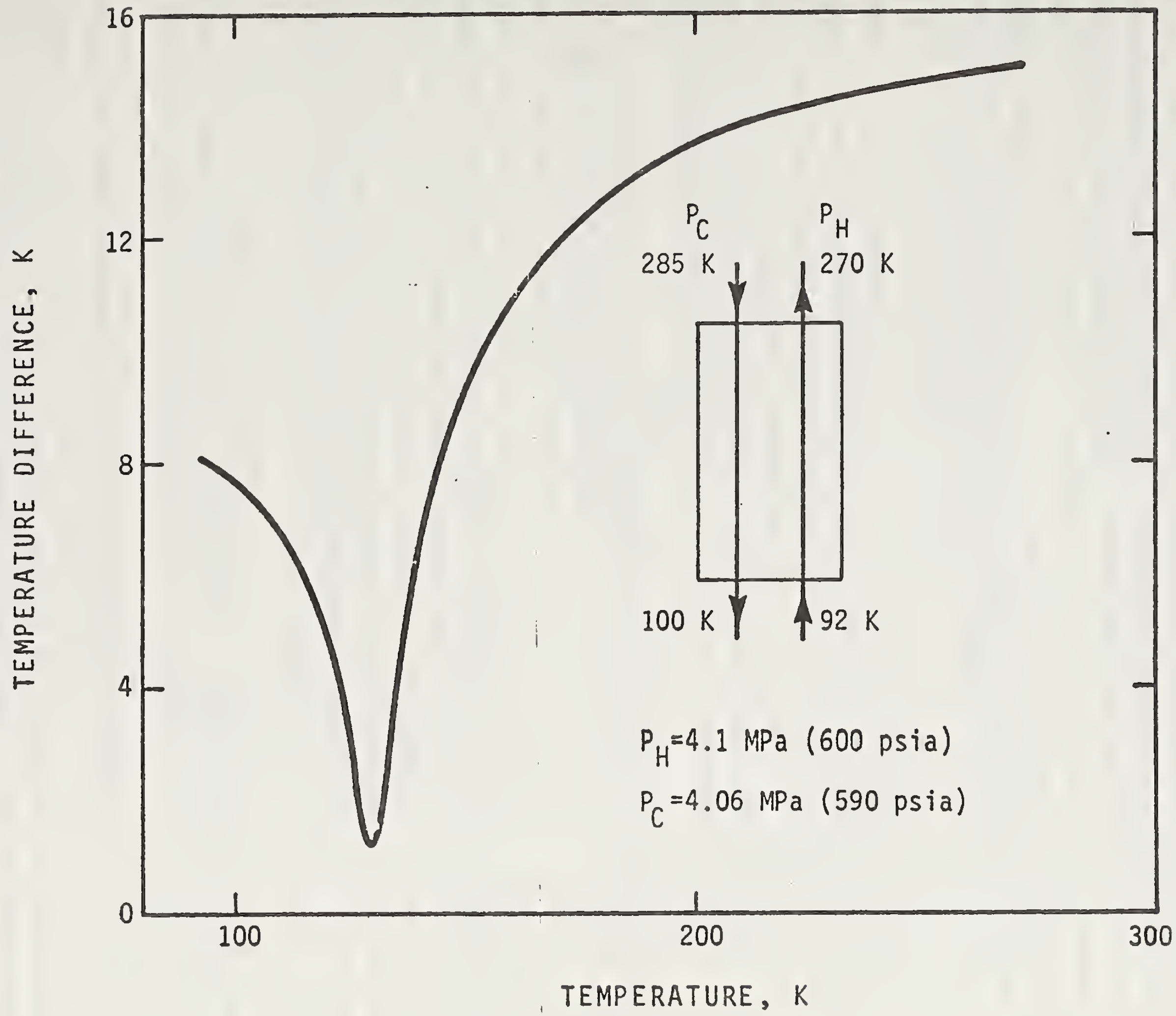

Figure 2. Cooling Curve of Main Heat Exchanger.

It is necessary to stabilize the process fluid inventory within the main heat exchanger to assure steady state mass flow through the gas test section. A control system suggested by Vander Arend [11] was made part of the main heat exchanger design by the addition of three flow passes during fabrication. The first of these additional passes is dead-ended at the cold end of the main exchanger allowing a quantity of nitrogen to be trapped for the full length of the exchanger. During startup, nitrogen is allowed to fill this pass at pump discharge pressure of up to 4.1 MPa (600 psia). When the operating pressure has been achieved the pass is valved off and the pressure within the pass is monitored. In effect, the pass becomes a gas thermometer and is sensitive to bulk temperature of the entire heat exchanger. The pressure within the pass reflects the average density of the exchanger. The final two additional passes allow control refrigeration or heating to stabilize the exchanger inventory. If the pressure in the gas thermometer pass increases, this indicates a bulk heating of the exchanger and a loss of inventory. Refrigeration in the form of supplemental liquid nitrogen is forced through one of the two additional passes. This additional refrigeration tends to reduce the bulk temperature of the exchanger to the original set point. Preliminary design provided for warm nitrogen gas to be forced through the final pass if the bulk exchanger temperature fell below the set point, but in practice, this condition did not occur and the two additional passes were piped in parallel to provide added refrigeration and control.

Process fluid, nitrogen gas, leaves the main heat exchanger at a pressure of 4.1 MPa (600 psia) and near 0°C. The temperature is raised to gas flow standards 15.6°C (60 F) by means of a shell and tube steam heat exchanger located just downstream of the main exchanger. Steam is supplied at 0.06 MPa (10 psia) at a flow rate of up to 114 kg/h (252 lb/h). The process fluid then enters the gas test section for experimental measurements and returns to the main exchanger. A shell and tube water heat exchanger removes a portion of the heat energy added at the steam exchanger and provides additional temperature stabilization of the process. Process fluid is cooled in the main heat exchanger to below 100 K and then is expanded in pressure from 4.1 MPa (600 psia) to 0.5 MPa (75 psia) at the expansion valve. Refrigeration is supplied at the subcooler reducing the fluid temperature to about 85 K. The process fluid can then be metered in the cryogenic fluid test section or piped directly to the catch and weigh system.

The operation, accuracy and precision of the cryogenic catch and weigh system is explained in detail by Dean, Brennan, Mann and Kneebone [5]. In summary, the dump valve at the outlet of the weigh tank is held in the open position until thermodynamic and porcess equilibrium has been established at a chosen flow rate. This procedure allows liquid nitrogen under helium gas pressure to circulate through the catch tank to the pump suction. When a test draft is to be run, the weigh tank valve is closed and sealed and liquid nitrogen accumulates e in the weight tank. The force resulting from the liquid accumulating in the weigh tank is measured by the load cell which in turn has been calibrated in reference to standard weights.

SYSTEM OPERATION

The system was run for the first time during July, 1979. During August, some preliminary data were obtained on a four inch orifice flowmeter that was obtained from the joint AGA-API Orifice Flowmeter project. This flowmeter was supplied with a set of six plates which gave a beta ratio range of 0.2 to 0.75. For the preliminary tests a flowmeter with a beta ratio of 0.496 was installed. This test was used to identify any serious problems associated with the system and to get a first look at the comparison between the flow facility and flow calculations based on AGA-3(12). Various system problems were identified that caused fluctuations in the gas temperature at the orifice and a rather noisy pressure signal at the orifice.

The problem with the gas temperature fluctuations was solved by changing the flow control on a steam heat exchanger. This stabilized the heat exchanger temperature and consequently the gas temperature.

Noise on the orifice pressure measurements has been more difficult to isolate and eliminate. The measurements are made using pressure transducers which are then scanned and the data sent to a mini-computer for data reduction. Single readings of the undamped signal are taken without any averaging, so the full range of any flow noise is observed. The average of a square root of the individual readings are used for calculating the flow rate. Since this procedure is not the normal recording method used by the gas industry, a parallel measurement system was also installed. This parallel system used instruments commonly used for natural gas orifice pressure measurements. This could be done because the orifice flanges have double tappings.

The parallel instruments used were a differential pressure transmitter and a mercury recording manometer. A dry type flow recorder will also be tested later in the program. In general the pressure transmitter, when operated in the undamped mode, gave the same information as the original pressure transducer. By increasing the damping with the built in electronic adjustment the pressure variations could be reduced by about 50%. The averages calculated using the damped and undamped signal were the same, so the overall results did not change.

The recording mercury monometer was only used in the undamped mode. Even in this mode the recorder was not able to duplicate the level of noise measured with the pressure transducer or the transmitter. In general the recorded signal exhibited a trace equivalent to about 498Pa (2 in. H_2O). Again the average agreed with the calculated average from the pressure transducer.

Introduction of additional pressure drop at various locations in the system was investigated as a possible way of reducing the noise level. This effort was not successful. Additional tests are planned to better define the noise source and affect so that corrective measures can be taken if deemed necessary and feasible.

FUTURE PLANS

The immediate objective of the current program is to refine the data and procedures so that a total uncertainty of measurement may be documented. This requires on the part of NBS a complete analysis of the system performance and documentation of all calibration and measurement procedures. With this portion of the program completed, the joint NBS-gas industry steering committee will devise a plan to systematically investigate the orifice discharge and expansion coefficients, flow conditioning and the general area of orifice plate fabrication.

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1. Title. LIQUEFIED NATURAL GAS TECHNOLOGY TRANSFER

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

2. Cost Center Numbers. 7730403, 7734574, 7738574, 7730594, 5621510

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 $7 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 agreeded 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 agreeded 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 is from groups 1 and 2. Few new assessments or correlations are anticipated or required for this work.

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

The publication of both graphical and tabular data is in a dual system of physical units. These units are 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. Over 850 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 and 500 copies have been distributed

On January 24, 1979 the LNG Materials and Fluids User's Manual received the Award of Distinction (first place) of the Society for Technical Communications. This award was in the category "Industrial Handbooks and Manuals" and we believe recognized the efforts and contributions of the sponsors and individual contributors.

Due to an initial uncertainty about the demand for the User's Manual only 750 of the cover and dividers were ordered, however 1000 copies of all graphs and text were printed. Our original stock of 750 was exhausted in April, therefore 250 additional covers and divider sets were ordered and are now in use for filling orders.

The second supplement has been completed. The second supplement contains 28 graphs on composites, 6 on concrete, 27 updated graphs on structural materials, 15 graphs and 3 wall charts on propane properties and three graphs on mixture properties. 686 copies of the second supplement have been distributed since it became available for distribution in January.

8. Problem Areas. None.

9. Level of Effort. January 1 - June 30, 1980

Staff-years expended	0.1
Equipment and/or Services Purchased	14.3K$
Approximate expenditures, total	7.5K$

10. Future Plans. This work is now essentially complete, except to continue distribution of the second supplement as well as the few remaining copies of the previous versions of the User's Manual.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 80-1636	2. Gov't. Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Liquefied Natural Gas Research at the National Bureau of Standards

5. Publication Date

August 1980

6. Performing Organization Code

7. AUTHOR(S)

Douglas B. Mann

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, DC 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

See page ii

13. Type of Report & Period Covered

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 NBS-NEL Thermophysical Properties Division, NBS-NEL Mechanical Processes Division and NBS-NML Fracture and Deformation 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 $646,000 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.

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.

18. AVAILABILITY ☐ Unlimited

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

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UNCLASSIFIED	
20. SECURITY CLASS (THIS PAGE)	**22. Price**
UNCLASSIFIED	