NBSIR 75-802

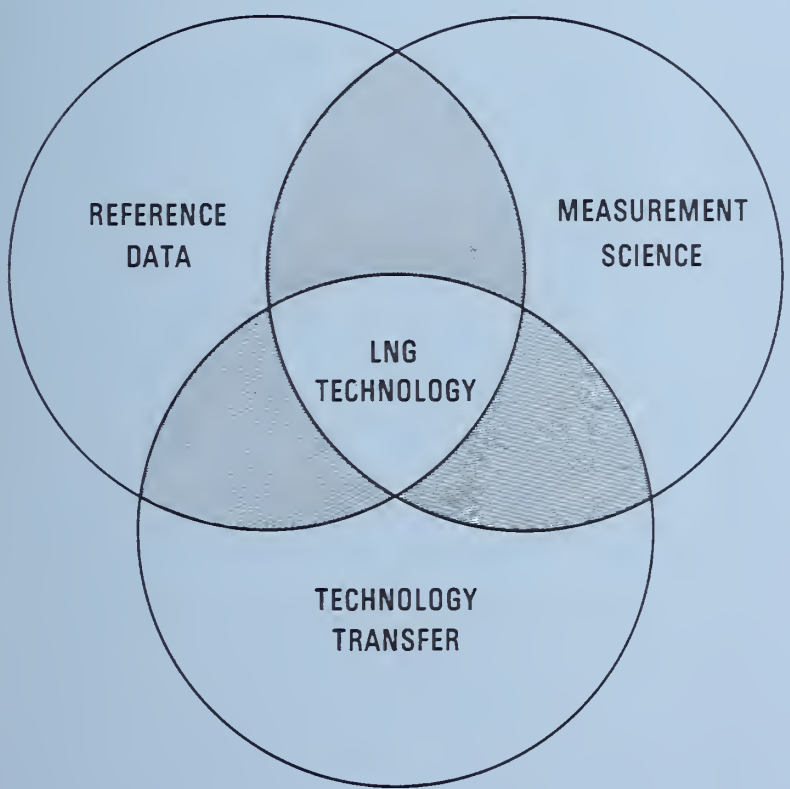
LIQUEFIED NATURAL GAS RESEARCH

at the

NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 JULY - 31 DECEMBER, 1974

D. B. Mann, Editor



RYOGENICS DIVISION • NBS–INSTITUTE FOR BASIC STANDARDS • BOULDER, COLORADO

NBSIR 75-802

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D. B. Mann, Editor

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

Progress Report for the Period
1 July - 31 December, 1974

U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS Richard W. Roberts, Director

Prepared for:

American Gas Association, Incorporated
1515 Wilson Boulevard
Arlington, Virginia 22209

LNG Density Project Steering Committee
(in cooperation with the American Gas Association)

Pipeline Research Committee
(American Gas Association)

Federal Power Commission
Bureau of Natural Gas
Washington, DC 20426

General Services Administration
Motor Equipment Research & Technology Division
Washington, DC 20406

U. S. Department of Commerce
Maritime Administration
Washington, DC 20235

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

Aerospace Safety Research and Data Institute
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

Eighteen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at an 18 man-year level with funding expenditures of over $485,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.

2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.

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 contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. 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: Cryogenic; liquefied natural gas; measurement; methane; properties; research.

CONTENTS

1. Title. Refractive Index of Fluid Methane

   Principal Investigator. James D. Olson

2. Cost Center Number. 2750122

3. Sponsor Project Identification. NBS-NRC Postdoctoral Research Associate Program.

4. Introduction. This experimental program will provide accurate measurements of the refractive index of liquid and gaseous methane. The data can be related to the fluid density by the Lorenz-Lorentz electromagnetic equation of state and, as such, offers the possibility of fluid density gauging by optical techniques. This pure fluid data is essential to the possible study of mixture refractive index properties.

5. Objectives or Goals. The refractive index of liquid and vapor methane will be measured along the two-phase saturation boundary. In addition, gaseous isotherms will be obtained at 220 K, 250 K, 280 K, and 300 K at pressures to 200 atm. Low pressure isotherms will be measured below the saturation boundary.

6. Background. The high precision interferometric technique used to measure the refractive index was developed in this laboratory by D. E. Diller (J. Chem. Phys. 49, 3096 (1968)). An improved optical data gathering method was the principal modification of this technique. Prior to this reporting period, a literature survey of Lorenz-Lorentz and Clausius-Mossotti virial equation data was conducted. A cryostat was constructed using the design of Diller. The saturation boundary data and high-pressure isotherms were measured in the last reporting period. (See NBSIR 74-373.)

7. Program and Results. The program was concluded with a series of low density isothermal measurements between 140 K and 300 K. These data can be used to analyze the virial equation of state PVT surface. A final analysis of the data was completed and a manuscript describing the work written. Some points of interest to the molecular theory of refraction were considered.

8. Problem Areas. No problems were encountered.

9. Funding.

Labor	.25 MY	5.0
Other Costs		1.5
Total		6.5

10. Future Plans. This report concludes the program. A publication of the results of this work has been submitted to the Journal of Chemical Physics (1975 - in review).

1. Title. Fluid Transport Properties

   Principal Investigator. Howard J.M. Hanley

2. Cost Center Number. 2750124

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

4. Introduction. Studies of the transport properties of mixtures have not received the attention or support that have been given to equivalent studies of pure fluids and, at this time, methods for predicting the transport properties of fluid mixtures are unreliable. Yet from the standpoint of the liquefied natural gas industry mixtures are more important than pure fluids. Properties cannot be measured for all possible mixtures, thus adequate prediction methods are needed in order 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 guidelines for future areas of experimental work.

6. Background. A program was started in 1965 with the goal of producing tables of fluid transport properties through many approaches; e.g., data correlation and evaluation, statistical mechanics, kinetic theory, thermodynamics and statistics. The theoretical studies, along with data analysis, results in prediction techniques for the dilute gas region for monatomic and polyatomic fluids. These techniques were then successfully extended to the dense gas and liquid regions. To date tables of transport properties have been prepared for argon, krypton, xenon[1,3], oxygen[6], nitrogen[5], fluorine[4], hydrogen, helium[7], and methane[2]. In addition an analytical representation of the anomalous behavior of the thermal conductivity coefficient in the critical region has been developed.

7. Program and Results. Recent results include tables of dense gas and liquid transport properties of argon, krypton, xenon, oxygen and nitrogen[1], and molecular dynamic calculations on the equilibrium and transport properties of methane[2].

8. Problem Areas. There are no problem areas at this time.

9. Funding. July 1 - December 31, 1974

Allocation	57.5 K$	OSRD
Labor	0.5 MY	28.0 K$
Other Costs		1.8 K$
	Total	30.7 K$
	Remaining	26.8 K$

10. Future Plans. The transport properties of methane, ethane, and propane will be correlated and tabulated. Mixture studies are in progress but have to be coordinated with corresponding work on the equation of state. Preliminary studies along this line have been initiated.

References

1. H.J.M. Hanley, R.D. McCarty and W.M. Haynes, J. Phy. Chem. Ref. Data 3, (1974).

2. H.J.M. Hanley and R.O. Watts, Physics (In press, 1975); Mol. Physics (In press, 1975); Aust. J. Physics (In press, 1975).

3. H.J.M. Hanley, J. Phys. Chem. Ref. Data 2, 619-42 (1973).

4. H.J.M. Hanley and R. Prydz, J. Phys. Chem. Ref. Data 1, 1101-14 (1972).

5. R.T. Jacobsen, R.B. Stewart, R.D. McCarty, and H.J.M. Hanley, National Bureau of Standards Technical Note 648 (1973).

6. H.J.M. Hanley, R.D. McCarty, and J.V. Sengers, National Aeronautics and Space Administration Contractor Report 2440 (1974).

7. R.D. McCarty, National Bureau of Standards Technical Note 631 (1972).

1. Title. LNG Fuels Safety

Principal Investigators. Neil A. Olien and A. F. Schmidt

2. Cost Center Number. 2750427

3. Sponsor Project Identification. National Aeronautics and Space Administration, Cleveland, Ohio, Aerospace Safety Research and Data Institute. Order No. C-39327-C.

4. Introduction. The NASA-Aerospace Safety Research and Data Institute (ASRDI) was established to provide a focal point for information and research in aerospace safety. One of the areas of concern for ASRDI is Cryogenic Fluid Safety. In fact, this was the first area of effort for ASRDI. The thrust of the program is two-fold: first, to provide an automated information bank for retrieving references, and second, to publish series of state-of-the-art reviews. The information system is now operational and contains over 5000 references in cryogenic fluid safety. In addition, ASRDI has published approximately ten reviews.

Until this time, ASRDI has focused its attention and efforts on the two primary cryogenic propellants, hydrogen and oxygen. The oxygen work was started at NBS-Boulder in 1970 and the hydrogen work in 1972. With the coming possibility of methane or LNG fueled aircraft and the close affinity of LNG safety and cryogenic safety, ASRDI felt that it was timely to begin work in that area.

5. Objectives or Goals. The following objectives are to be achieved:

a) Review and modify an existing Cryogenic Fluids Safety Grid and thesaurus to include and adequately cover LNG safety.

b) Make a thorough search of over eleven information sources for LNG information. This will include published and unpublished material.

c) Catalog, index, abstract and put into machine readable form all available documents located in b) above. The indexing will be done by technical personnel with demonstrated competence in cryogenic safety and related fields.

6. Background. This program was started at NBS-Boulder by ASRDI in 1970. Since then considerable skill and experience has been gained in locating, processing and, most important, detailed subject indexing of safety-related information. In addition, NBS-Boulder has been

providing detailed coverage of the LNG field for the American Gas Association since early 1970. The present program, then, provides an opportunity for industry, government and the public to capitalize on the accumulated past efforts of two seemingly unrelated programs.

7. Program and Results. Under this and another ASRDI-funded program we have started a major review of the indexing and retrieval terminology which will be used in the Cryogenic fuels safety information system. This review will result in a thesaurus to be published by NASA. The review is complete and we are now in the process of editing and preparing the thesaurus in its final form. Most of the terminology unique to LNG safety is now incorporated into this thesaurus.

   During the period September 30, 1974 through December 31, 1974 we have indexed 78 papers, reports, etc. dealing directly with LNG safety. Of these, 63 were sent to ASRDI in machine-readable form on magnetic tape.

8. Problem Areas. None

9. Funding. September 30, 1974 - December 31, 1975

Allocation (9/30/74 - 10/1/75)	50 K$	NASA/ASRDI
Labor	0.2 MY	10.0 K$
Other costs		1.2 K$
	Total	11.2 K$
	Remaining	38.8 K$

10. Future Plans. The thesaurus mentioned above will be ready for editorial review in January and should be available in published form prior to July 1, 1975.

    We will continue to index safety-related papers and should complete approximately 200 of these in the next reporting period.

1. Title. Properties of Cryogenic Fluids.

Principal Investigators. G. C. Straty, D. E. Diller

2. Cost Center Number. 2750141

3. Sponsor. 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). 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.

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. 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. Sound velocity data are useful for testing the consistency of volumetric, calorimetric and thermodynamic properties data, and are potentially useful for density gauging applications. Thermal diffusivity data are required for performing thermodynamic and heat transfer calculations.

6. Background. When light is incident on a perfectly homogeneous fluid, the reradiated (scattered) light field sums to zero in all but the exact forward direction. For a "real" fluid however, fluctuations, arising through various mechanisms, destroy the perfect homogeneity and results in the scattering of light in other directions as well. For example, thermally activated density fluctuations (phonons), propagating with the characteristic velocity of sound, give rise to scattered light which is doppler shifted in frequency from the incident light frequency and whose spectrum contains

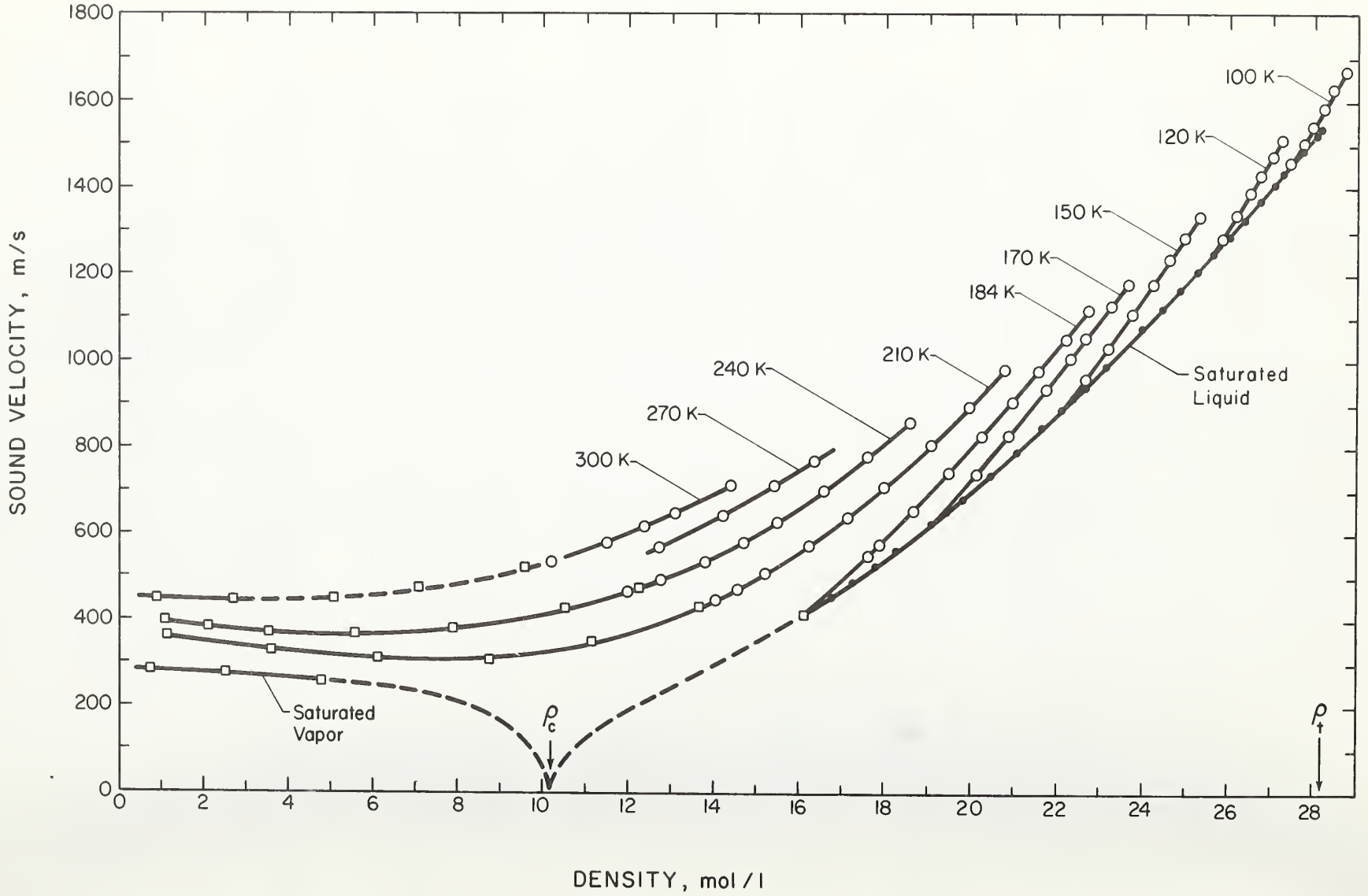
information on the sound velocity and attenuation. Local non-propagating temperature fluctuations, which decay diffusively, give rise to scattered light in a narrow frequency band about the incident light frequency and whose spectrum contains information on the lifetime of the fluctuations (thermal diffusivity). Since the frequency shifts are generally very small, it was not until the advent of the lasers with their extremely well defined frequency, that practical experiments using these phenomena were possible.

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 and 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 recently been demonstrated.

We have assembled and performance tested apparatus for laser light scattering spectroscopy measurements on compressed and liquefied gases (76 - 300 K, 350 bars). The apparatus consists of a copper optical cell with fused quartz windows, cryostat for refrigeration with liquid nitrogen, an argon ion laser, pressure scanned Fabry-Perot interferometer, and photon counting equipment.

7. Program and Results. Preliminary data on the hypersound velocities in pure methane have been obtained at low densities (< 14 mol/ℓ) where the large sound absorption in methane prohibits ultrasonic measurements. Data have been obtained along several isotherms from 210 K to 300 K at densities down to 1 mol/ℓ. Agreement with previously measured ultrasonic velocities in the regions of overlapping data is good. (See the attached Figure. The □ indicate the light scattering measurements, the O indicate the ultrasonic measurements. See the report on Cost Center 2750364 for further discussion of the ultrasonic measurements.) Agreement with values calculated directly from PVT data is also satisfactory.

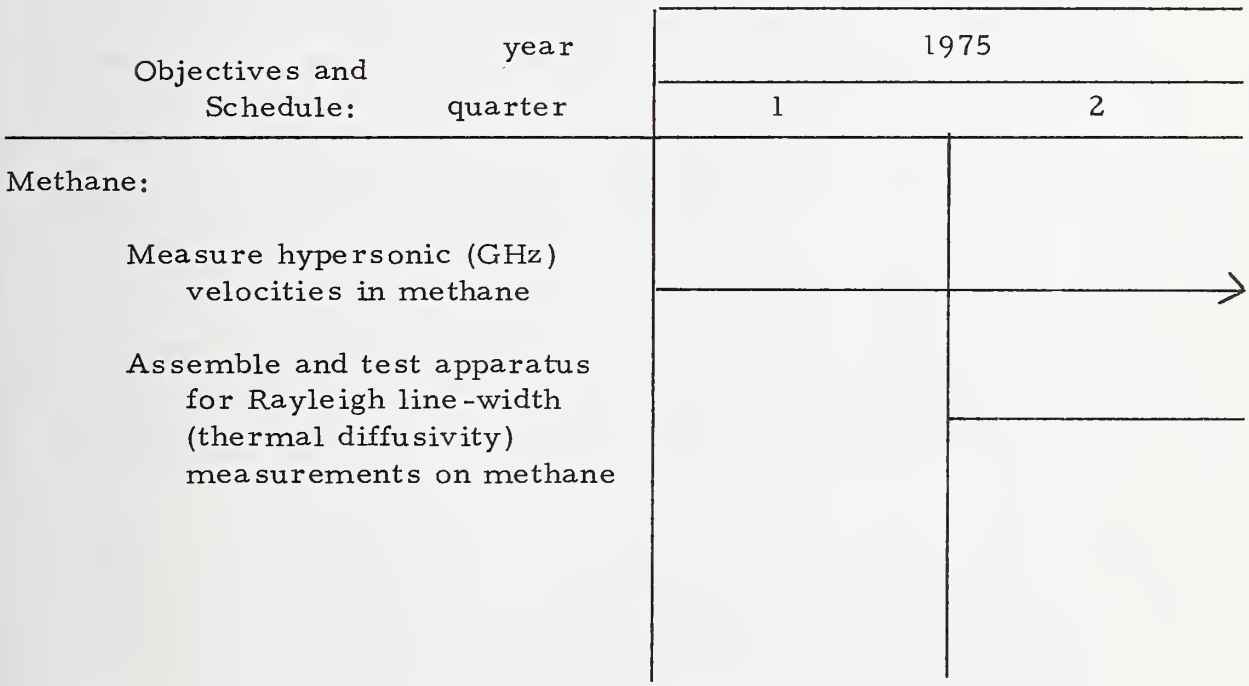
8. Problem Areas. Progress on the light scattering experiment has been primarily limited by our assignment of priorities to other LNG related efforts. Data already obtained has been sufficient to enable completion of related work on methane. Additional measurements of the hypersonic sound velocity are considered desirable for the sake of completeness, and completion of this project has been rescheduled accordingly.


SOUND VELOCITY, m/s
DENSITY, mol/l
100 K
120 K
150 K
170 K
184 K
210 K
240 K
270 K
300 K
Saturated Liquid
Saturated Vapor
ρ_c
ρ_t

9. Funding.

Man-years expended (July-Dec. 1974)	0.25
Equipment and/or Services Purchased	1.8 K$
Total Reporting Period Cost	15.0 K$
Balance Remaining (Dec. 31, 1974)	20.0 K$

10. Future Plans.



1. Title. Properties of Cryogenic Fluid Mixtures.

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

2. Cost Center Numbers. 2750142; 2750145

3. Sponsors. NBS; NBS(OSRD)

4. Introduction. Accurate thermodynamic properties data and predictive calculation methods 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 predictive calculation methods. This project supports the development of LNG technology in the areas of separation, purification, liquefaction and custody transfer by defining relationships between the composition, temperature, pressure, and equilibrium state properties for mixtures related to LNG.

5. Objectives or Goals. The overall objectives of this project are to provide critically evaluated data, original and from other sources, 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 Cryogenics 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 the nitrogen + methane system.

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

a) The comprehensive bibliography of fluid mixtures data, completed earlier, was accepted for publication by Plenum Press as the first of a series of books for the Office of Standard Reference Data. The published volume will be entitled: EQUILIBRIUM PROPERTIES OF FLUID MIXTURES: A BIBLIOGRAPHY OF CRYOGENIC DATA. To assure that the product is current and saleable, Plenum has asked that the work be updated through 1974, and that a camera-ready copy be transmitted to them on April 1, 1975 for publication in June. The updating process will be a major part of the effort for the next quarter.

b) Work is currently in progress on the compilation and derivation of the excess Gibbs functions, critical loci, and Henry's law constants for the systems argon + methane, nitrogen + methane, methane + ethane, methane + propane, methane + n-butane, and methane + isobutane. Currently, a numerical method, referred to as orthogonal collocation, is being evaluated which allows critical evaluation of liquid-vapor equilibria data when one of the components is supercritical.

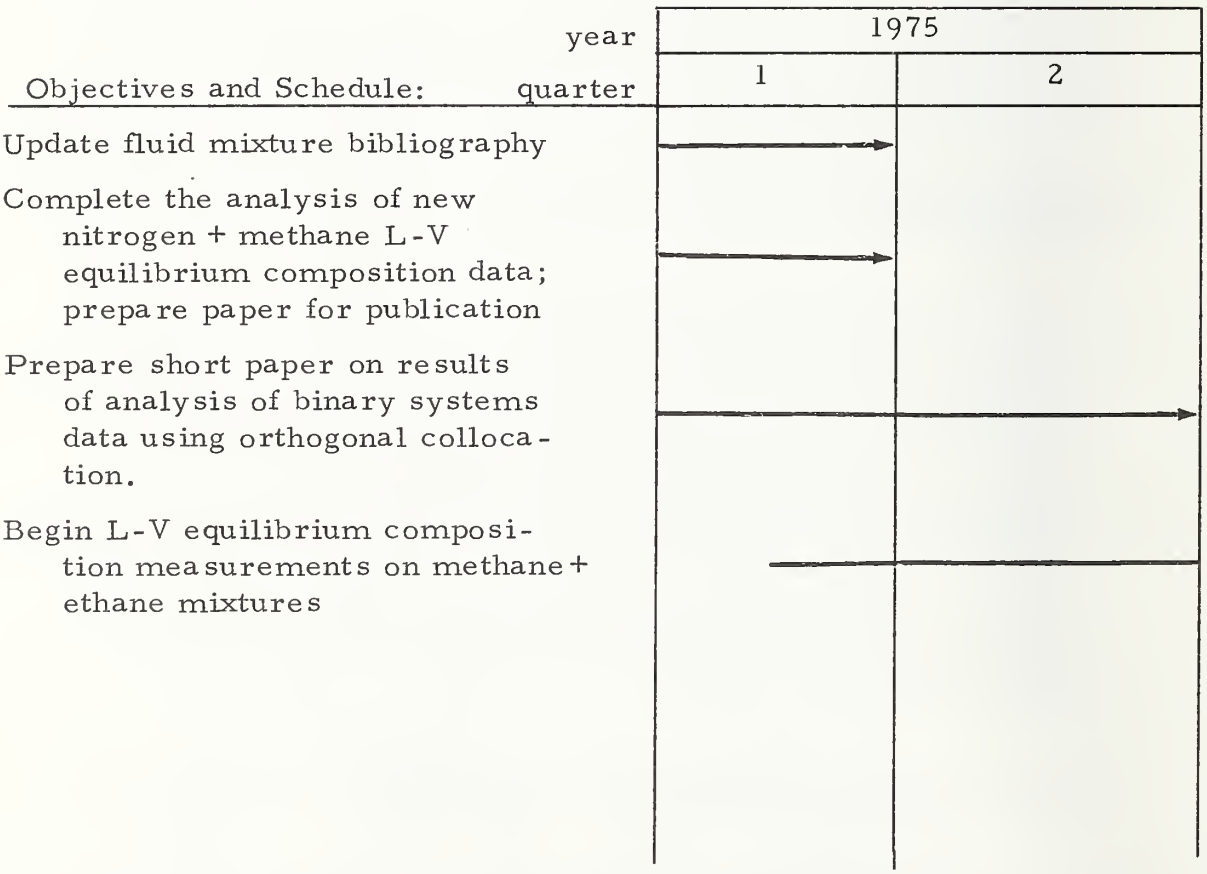
c) Measurements have been completed on the nitrogen + methane system at temperatures between 130 and 180 K, to complete the data set for the system from our laboratory at temperatures between the triple point (90.7 K) and critical point (190.5 K) of methane.

8. Problem Areas. None.

9. Funding.

Man-years expended (July-December 1974)	0.7
Equipment and/or Services Purchased	5.0 K$
Total Reporting Period Cost	43.0 K$
Balance Remaining (December 31, 1974)	52.0 K$

10. Future Plans.



1. Title. Survey of Current Literature on LNG and Methane.

   Principal Investigator. Neil A. Olien

2. Cost Center Number. 2750362

3. Sponsor Project Identification. American Gas Association 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 continuing awareness of the current publication scene will be 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 three bibliographies involved: methane properties, methane mixtures properties, and processes and equipment involving methane and LNG. These three will be updated each October.

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 300 primary publications and nearly 30 secondary publications. Of these approximately one-third are directly related to LNG. In addition, within the past year we have increased our coverage of the energy field to include hydrogen as a future fuel. 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 and the Liquefied Natural Gas Survey has been published quarterly since 1970.

7. Program and Results. Two issues of the LNG Quarterly were prepared and distributed. There are now 118 subscriptions going to AGA Member Companies and 191 to other subscribers.

The three comprehensive bibliographies mentioned in section 5 have been reviewed and shorter, more selective bibliographies have resulted. These were prepared in October 1973 and will be updated.

B-1055 THERMOPHYSICAL PROPERTIES OF METHANE - A SELECTED BIBLIOGRAPHY, 61 pp., indexed by property, phase and author (Sept. 1973) $8.00.

B-1056 PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY, 95 pp., indexed by property, system and author (Sept. 1973) $10.00.

B-1075 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPH 52 pp., indexed by subject and author (Oct 1973) $5.00

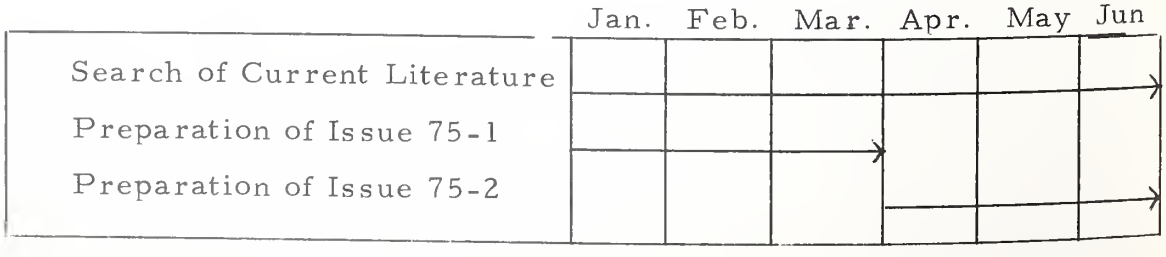
During the period July through December 1974 we have distributed 19 copies of these and the comprehensive bibliographies.

8. Problem Areas. We have no problem areas at this time.

9. Funding. July 1 - December 31, 1974.

Labor	9.7 K$
Other Costs	1.8 K$
Total	11.5 K$
Remaining	6.5 K$

10. Future Plans. Issue 74-4 of the LNG Quarterly will be mailed to the National Technical Information Service for printing and distribution on January 10, 1975. Issue 75-1 will be published in April. The three comprehensive bibliographies discussed in Item 7 above are in the process of being updated and will be available for distribution the latter part of January 1975.



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

Principal Investigators. R. D. Goodwin, G. C. Straty

2. Cost Center Number. 2750364

3. Sponsor. American Gas Association, Inc., Project BR50-10

4. Introduction. Accurate phase equilibrium, compressibility (PVT), and thermodynamic properties data are needed to design and optimize gas separation and liquefaction processes and equipment. Accurate data for the pure components of LNG mixtures will permit developing comprehensive accurate predictive calculation methods which take into account the dependence of the thermophysical properties of mixtures on the composition.

This project will provide comprehensive accurate thermophysical properties data and predictive calculation methods for compressed and liquefied hydrocarbon gases to support the development of LNG technology at NBS and throughout the fuel gas industry.

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) of liquefied natural gas mixtures at temperatures between 90 K and 300 K and at pressures up to 350 bar (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 1976 - 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 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 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 usually must 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 industry 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). This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating thermophysical properties data for LNG mixtures.

7. Program and Results.

7.1 Ethane, Thermophysical Properties Data--R. D. Goodwin. Our major, new contribution on the thermophysical properties of the constituents of liquefied natural gas mixtures is the publication "Provisional Values for the Thermodynamic Functions of Ethane," NBS IR 74-398 (June 1, 1974). This report has been printed at NBS in Boulder, Colorado. This work on ethane provides background on available physical properties data, and may serve engineering needs for thermodynamic properties until such time as new physical data permit a revision of the tables. This report provides the first known tabulation of the thermodynamic properties of saturated and compressed liquid ethane at temperatures below its normal boiling point (184.5 K). See attached Appendix.

In additional to all of the new analytical formulations of physical properties data, developed for the above report on ethane, we have carried out further work on the equation of state for methane and for ethane to obtain the simplest possible form, amenable to corresponding states computations on mixtures. This work, "Equation of State for Thermodynamic Properties of Fluids," will appear in the NBS Journal

of Research, Vol. 79A(1), Jan. - Feb. (1975).

Appendix

"Provisional Values for the Thermodynamic Functions of Ethane"
NBS IR 74-398 (June 1, 1974)

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7.2 Ethane, Compressibility (PVT) Data--G. C. Straty

In the gas expansion technique used in this laboratory for accurate, absolute, compressibility (PVT) determinations, the molar volume V of a cryogenic fluid contained in a cell at temperature T and pressure P is determined by expanding the fluid from the calibrated cell into large calibrated volumes maintained near room temperature ($\sim$ 295 K). Using the near-ideal-gas-like behavior of the room temperature gas, the number of moles of gas residing in the total system can be computed accurately. One of the factors limiting the accuracy of this method is the ability to assign correctly the appropriate proportions of the fluid to the cell and to the various noxious volumes elsewhere in the system.

PVT measurements on ethane present an additional problem not encountered with most cryogenic fluids such as methane, oxygen, etc., because the critical temperature of ethane (305.33 K) is well above room temperature. The consequence is that during many of the density measurements on ethane, relatively high density fluid would reside in external parts of the system which could not be accurately accounted for in the present apparatus without some modifications.

During the previous period, appropriate portions of the apparatus were enclosed in ovens and/or provided with heaters to maintain their temperatures well above the critical temperature of ethane. Thermometric sensors were calibrated and installed to these various portions of the apparatus to enable the temperatures to be measured and accurate PVT data obtained. Volume calibrations of several new system components were made. Preliminary testing of the apparatus was performed with satisfactory results.

During this reporting period, data were obtained along several isochores of both methane and ethane. Measurements on methane were made using the apparatus as modified for the ethane experiments in order to check the accuracy and consistency of the data. Excellent agreement with the methane data of Goodwin and Prydz was obtained.

Preliminary measurements on ethane revealed that some additional modification of the apparatus and data reduction techniques would be worthwhile in order to further increase the accuracy of vapor pressure and density determinations. An additional heater has been installed on the PVT cell filling capillary to be used during vapor pressure determinations. Vapor pressures obtained with this modification are in agreement with available published data.

Data obtained along several isochores of ethane appear to be in good agreement with available data on the compressed liquid and with the saturated liquid densities obtained independently in this laboratory by Haynes.

Data analysis programs are being refined as additional data on ethane is accumulated.

7.3 Methane, Sound Velocity Data--G. C. Straty

The ultrasonic velocities of sound in pure saturated and compressed fluid methane have been measured at MHz frequencies. Data have been obtained along the saturation boundary from near the triple point to 186 K and along several isotherms from 100 K to 300 K at pressures up to about 345 bar. The sound velocity data have been combined with the previously measured PVT data to calculate the isentropic and isothermal compressibilities and the specific heat ratio C_p/C_v. Measurements along the compressed fluid isotherms at temperatures of 210 K and above were limited to a minimum density ranging from about 14 mol/ℓ at 210 K to about 10 mol/ℓ at 300 K due to the large sound attenuation in methane. A manuscript reporting the results of the ultrasonic sound velocity measurements on methane has been published in Cryogenics, 14, 367 (1974).

A light scattering spectroscopy apparatus has been employed to obtain hypersonic (GHz) velocity data at the lower densities where measurement by ultrasonic techniques were impossible. Data have been obtained to densities as low as 1 mol/ℓ along several isotherms. (See the figure attached to the report on Cost Center 2750141. The O indicate the ultrasonic measurements; the □ indicate the light scattering measurements.) Measurements in the regions of overlap with the ultrasonic data indicate excellent agreement, and overall agreement with calculated sound velocity data is satisfactory. Additional, more accurate measurements are planned.

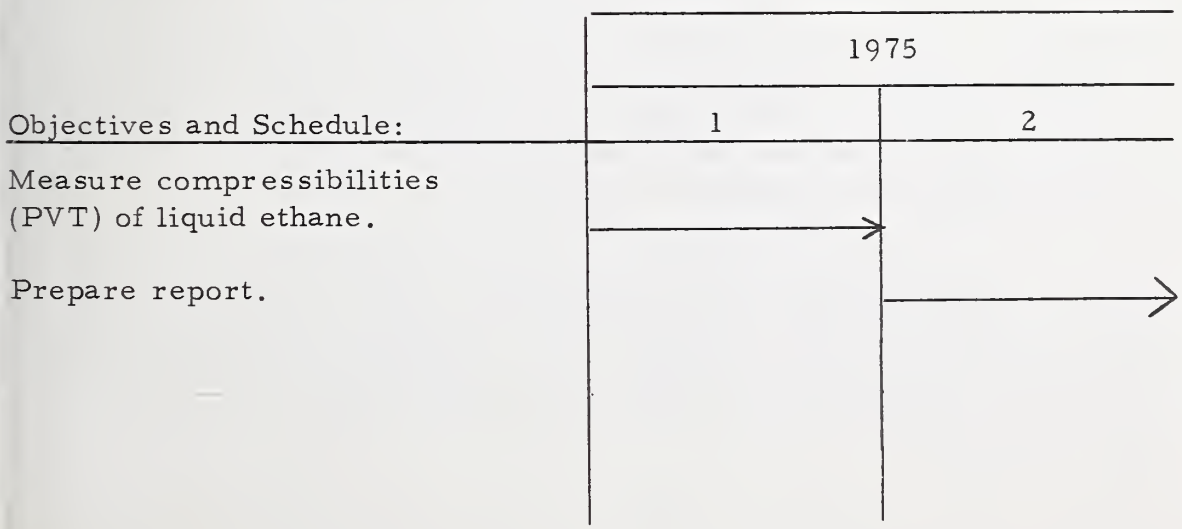
8. Problem Areas. For ethane, the computation of an accurate thermodynamic network in liquid states is more difficult than for methane. Vapor pressure measurements of high accuracy are needed at low temperatures, where these pressures are so small that no accurate experimental technique so far has been developed. Heats of vaporization are so large at low temperatures (17,000 J/mol) that the experimental error of greater than 1% in these data gives about 200 J/mol error in computations across the vapor liquid "dome." Densities of saturated liquid ethane in the mid-range of temperatures (160 to 250 K) apparently never have been measured. The melting line is known only with very low accuracy and initial attempts to measure it using the compressibility apparatus have been unsuccessful. Comparison of our calculated speeds of sound for saturated liquid ethane with experimental data suggests that derivatives of the $P(\rho, T)$ surface (via the equation of state) are not as accurate at low temperatures as desired. All of these deficiencies suggest the need for new highly accurate compressibility (P-ρ-T) measurements, sound velocity measurements in the homogeneous, single-phase domain, and possibly additional specific heat measurements, e.g. $C_v(\rho, T)$.

As mentioned above, we have been unable to make melting line measurements using the compressibility apparatus. It is hoped that these measurements can be made using other existing apparatus.

9. Funding.

Man-years expended (July-Dec. 1974)	0.8
Equipment and/or Services Purchased	4.4 K$
Total Reporting Period Cost	63.1 K$
Balance Remaining (Dec. 31, 1974)	56.9 K$

10. Plans for Future Work.



1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

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

2. Cost Center Numbers. 2751574, 2752574 (2751364, 2752364)

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

4. Introduction. Accurate density measurements and calculation 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 in the temperature range 105-140 K, and to test and optimize methods 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 calculation methods were performed by independent professionals of established reputation.

Prior to this reporting period 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 repeatability and estimated precision of measurement are better than 0.02% while the accuracy is better than 0.1%.

7. Program and Results. Saturated liquid density measurements have been completed for the pure components of liquefied natural mixtures in the temperature ranges as follows: (a) methane (105-160 K), (b) ethane (100-220 K), (c) propane (105-150 K), (d) normal butane (135-170 K), (e) isobutane (115-150 K), and (f) nitrogen (95-120 K). The saturated liquid densities of approximately equimolar mixtures of methane + ethane and ethane + propane have been determined in the temperature range from 105 to 140 K.

The task of producing and testing a mathematical model which will accurately predict the densities of LNG mixtures as a function of composition, temperature and pressure has continued during this reporting period. Extensive effort has been directed toward applications of the one fluid theory of corresponding states. New computer programs have been written to optimize the so-called "shape factors"using the recent pure fluid data from this laboratory. Significant improvements in the shape factors have been obtained. The testing and optimization of the predictive models [1-3] will continue during the next reporting period as new experimental data become available.

References:

[1] Albright, M. A., Technical Publication No. 3, A Report to the Gas Processors Assoc., 1812 First Place, Tulsa, Okla. 74103 (1973).

[2] Rodosevich, J. B. and Miller, R. C., Advances in Cryogenic Engineering, 19, 339 (1974).

[3] Mollerup, J. and Rowlinson, J. S., Chemical Engineering Science, 29, 1373 (1974).

8. Problem Areas. None.

9. Funding.

2751574 (measurements)

Man years expended, July-December 1974	0.8
Equipment and/or services purchased	$ 3.3 K
Total reporting period cost	$ 41.7 K
Balance remaining, December 31, 1974	$ 62.3 K

2752574 (calculation methods)

Man years expended, July-December 1974	0.4
Equipment and/or services purchased	$ 1.8 K
Total reporting period cost	$ 21.7 K
Balance remaining, December 31, 1974	$ 42.5 K

10. Plans for Future Work.

Objectives and Schedule:	year: 1975, quarter: 1	year: 1975, quarter: 2
Measure densities of binary mixtures containing methane, ethane, propane, butanes and nitrogen.		
Test and optimize available calculation methods.		

1. Title. Low Temperature Material Behavior

   Principal Investigators. R. P. Reed, R. L. Tobler, R. P. Mikesell, and R. L. Durcholz.

2. Cost Center Number. 2750430

3. Sponsor Project Identification. Maritime Administration Project 55-300-15-011.

4. Introduction. Data on thermal and mechanical properties of structural and insulation materials are essential to facilitate material selection on the basis of cost and safety. Proper material choice and reliable definition of material behavior using fracture mechanics is of major economic importance for cryogenic containers in the sea transport of LNG.

5. Objectives. The objective of this program is to obtain fracture toughness and fatigue crack growth rate data in the temperature range 76-300 K. These measurements are being conducted on a series of Fe-Ni alloys and Al alloys.

6. Background. To construct tanks for sea transport of LNG requires between 500,000 and 7,000,000 pounds of expensive alloys, depending on the type of tanker chosen. This large-scale consumption of costly alloys demands very careful material selection to insure economical but safe, storage tanks. Therefore, since MarAd's goal is to reduce ship costs, it is in their interest to insure the availability of relevant thermal and mechanical property data to enable the best possible material selection and dependable, efficient design.

7. Program and Results. The materials effort in this program has concentrated on two areas, a general materials properties assessment and the initiation of an experimental low temperature tensile, fatigue, and fracture study of candidate materials. The materials properties assessment has included a compilation of all fatigue and fracture data on Fe-Ni steels and their weldments, a collection of ship design data and an analysis of materials in use, an assessment of the current production and/or research efforts of the materials suppliers, an assessment of the current materials requirements for LNG containers by the American Bureau of Shipping, U. S. Coast Guard, and the ASME pressure vessel code, and the bibliography of literature containing data on aluminum alloys, non-metallics, and insulation materials. For the experimental program the materials were procured; specimens were made for tensile, fatigue and fracture tests for selected materials; a variable temperature cryostat was built; and the experimental procedures proofed, and fracture data obtained on selected Fe-Ni alloys and alluminum alloys.

   Materials Properties Assessment

   The literature data from some 60 references on the fatigue and fracture properties of the ferritic Fe-Ni steels (Ni 18%) has been extracted,

critically valuated, and compiled. The fracture data in the compilation are the impact energy; nil ductility transition, crack opening displacement, fracture toughness, and dynamic tear tests and their dependencies on temperature, composition, and heat treating or cold working. Fatigue data include fatigue lifetime and fatigue crack growth rates at LNG temperatures. Also included are tensile properties, hardness, impact energies, explosion bulge tests, and other fracture data. The entire compilation will be sent as an interagency report and included in a review article on LNG materials in the open literature.

The production and research capabilities of the major suppliers of LNG structural alloys were also assessed. Direct contact was made with the research personnel of all the major suppliers to assess what work on these materials has been done or was in progress. These in-house efforts indicated are generally low level. We have attended the LNG Materials Conference at the British Welding Institute and visited Technigaz, Det Norske Veritas, and the Welding Institute to provide information about the foreign efforts in LNG materials research. We also have a member of our staff on the Cryogenic Materials for LNG Tank Applications Committee of the Metals Properties Council.

Experimental Program

Test materials of 1-1/2 inch thick plate have been obtained for the 3-1/2, 5, 6 and 9% Ni steels and Al 5083. Fe-9Ni steel has been obtained from two sources.

A cryostat for variable temperature control near LNG temperatures was designed and built. The experimental procedures, especially J integral test techniques, were evaluated and proven satisfactory. New methods were devised to monitor the crack growth and crack opening.

Fracture toughness and fatigue crack growth rate tests at 300, 195, 111, 76, and 4 K have been completed. These alloys include Fe-6Ni and Fe-5Ni in the QLT or austenitized, temperized, and reversion annealed condition, two Fe-9Ni alloys from different suppliers in the quenched and tempered condition, and 5083 aluminum in the annealed condition.

Linear elastic fracture mechanics parameters (K_Q, K_{IC}) and J-integral (J_{IC}) test data have been measured for identical 1.25 inch thick compact tensile specimens. For the first time valid K_{IC} critical stress intensity data have been obtained for these alloys. Also, for the first time a decided temperature dependence of the fatigue crack growth rate in Fe-Ni body centered cubic alloys has been measured; the rate of crack propagation is higher at 67 K compared to room temperature for all alloys. For 5083 aluminum, however, the fatigue crack growth rate decreases at lower temperatures.

Program Publications and Talks

One paper has been included in the Special Technical Publication of the ASTM conference, "Low Temperature Fracture Behavior of Ferritic Fe-Ni Alloy Steels," by R. L. Tobler, et al.

8. Problem Areas. Testing has proceeded on schedule. There are no delays.

9. Funding. During this reporting period, about $40,000 has been spent. This completes research for the program described.

10. Future Plans. During the next six months the fatigue and fracture toughness properties of welded Fe-5Ni steel will be measured at 300, 195, 111, and 76 K.

1. Title. Program for Reducing the Cost of LNG Ship Hull Construction

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

2. Cost Center Number. 2751430

3. Sponsor Project Identification. Maritime Administration Project 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 0 to -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.

5. Objective. The objective of the current program is to survey the feasability of developing, evaluating and qualifying a ship steel that permits more efficient welding practices and retains satisfactory low-temperature fracture behavior.

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 initial phase of NBS's recommended program, i. e. to survey the problem and the technology available for it's solution. On the basis of this survey a coordinated program involving the LNG shipyards, the steel suppliers and NBS will be planned and recommended to MarAd and to the Welding Panel in the first quarter of 1975.

7. Program and Results. The survey of the feasability of reducing the cost of LNG ship hull construction consisted of four distinct tasks:

    1. Visit the shipyards to properly define the problem.
    2. Visit the regulatory agencies to define the limits that we must work within.

3. Visit the steel companies to assess the technology available to solve the problem.
4. Survey the technical literature.

Significant progress has been made on each of these tasks during the reporting period.

The four U. S. shipyards with contracts to build LNG tankers were visited:

Avondale Shipyards, Inc., New Orleans, LA.
General Dynamics, Quincy Shipbuilding Div., Quincy, MA.
Newport News Shipbuilding and Dry Dock Co., Newport News, VA.
Sun Shipbuilding and Dry Dock Co., Chester, PA.

At each shipyard, the design and fabrication of the LNG ships were reviewed and the problems associated with welding of the ship plates for the low temperature (0 to -50° F) portion of the ship were discussed. The overall conclusion of these visits was that productivity was limited by the weldability of the base metal. Thus, the program should be directed towards improving the base metal--as opposed to improving the welding procedures or the consummables such as fluxes, rods and wires.

Visits were made to the two regulatory agencies that control the construction of LNG tankers in the U. S.: the American Bureau of Shipping (ABS) and the U. S. Coast Guard (USCG). Their viewpoints of the requirements on the properties required in the steel weldments were solicited. ABS indicated that the requirements might be unrealistictly severe and favored a program that would lead to the establishment of more rational requirements. The USCG emphasized the permanence of the standards as they currently exist because of the international acceptance of the requirements as they stand. The conclusion of these visits was that the program to develop an improved ship steel should be conducted using the current requirements as the property goals; however, parallel program to evaluate the rationality of these requirements should be formulated in conjunction with ABS.

The four leading steel plate producers and two other companies were visited to assess the applicable steel making technology:

Armco Steel Co.	Middletown, OH.
Bethlehem Steel Co.	Bethlehem, PA.
Lukens Steel Co.	Coatesville, PA.
U. S. Steel Co.	Monroeville, PA.
Linde Division of Union Carbide	Ashtabula, OH.
Climax Molybdenum Co.	Ann Arbor, MI.

At each steel company, an overview of the MarAd program was given by NBS, and the steel companies reviewed their experience with low temperature steels and advised NBS on the technology available to provide ship plate with improved low temperature toughness in the heat affected zone. The conclusions of these visits were that the most promising steel making practices were sulfide shape control and columbium treated steels. In addition, the advisability of purchasing steels to guaranteed transverse toughness requirements was emphasized.

A literature search is being conducted to further assess the technology available to improve ship steels. The basis for this search was bibliographies obtained from DDC, NTIS and the American Society of Metals. This task is still in progress and will be reported on in the next issue of this document.

8. Problem Areas. None

9. Funding.

Cost to 12/31/74	$10,000
Balance	25,000

10. Future Plans. The results of our survey will form the basis of a program to be formulated and recommended to MarAd on February 12, 1975. Approximately one month later, the program will be presented to the MarAd Welding Panel for their consideration.

1. Title. Heating Value of Flowing LNG

   Principal Investigators. J. A. Brennan and J. M. Arvidson

2. Cost Center Number. 2756579

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

4. Introduction. This project will draw on information and facilities generated by other sectors of the NBS LNG effort. Thus the calibration of a densimeter used will be traceable to the NBS density reference system being constructed by Younglove under cost center 2751361. Mixture density data produced under 2751574 by Haynes and Hiza will also provide a necessary input to the proper interpretation of results.

5. Objectives. The original objective of this program was to set up a LNG flow facility and to evaluate selected flowmeters in LNG service. In November 1973 the objective was expanded to demonstrate the accuracy of measurement of the heating value of LNG flowing in a pipeline through integration of state-of-the-art instrumentation for flow, density and heating value. The expanded project has been conceived of in a three-year time frame. In the first year individual components will be calibrated and installed in the NBS LNG flow facility.

6. Background. The need for accurate flowmetering of LNG provided the original impetus for the work in this program (unpublished NBS Report [1972], NBSIR 73-300). Since liquid natural gas may be sold on the basis of heating value the program was broadened to include the necessary instrumentation for determining heating value of LNG, this expanded program to commence early in 1974. The objectives are based on scaling small flowmeters capable of laboratory testing up to full line size components. Appropriate intermediate sizes are included with field tests scheduled as part of the overall project.

7. Results. Liquid nitrogen tests on both four-inch vortex shedding flowmeters referred to in the last report [NBSIR 74-373] have been completed. One of the meters was installed in a test section and sent to an LNG facility for installation preparatory to conducting the LNG tests. These tests were originally scheduled to be completed in 1974 but have had to be rescheduled for early in 1975.

   The orifice meter used in the gas phase measurement at the LNG facility was calibrated in water at the NBS flow facility in Gaithersburg, Maryland. This calibration will help in determining the actual orifice flow coefficient which will be used in comparing the liquid measurement with the vaporized gas measurement.

   Refurbishing of the surplus calorimeter has been completed. The calorimeter and the gravitometer have been connected to the flow facility and are now operational.

8. Problem Areas. No problem areas have been encountered that would have an adverse effect on the project.

9. Funding.

Man Years Expended	1.25
Major Equipment Purchased	$ 8,000
Total Reporting Period Costs	73,000
Balance on Hand	26,000

10. Future Tests. The flowmeter tests at an LNG peak shaving plant are now planned for early 1975. The next phase of the flowmeter scaling will be started after the LNG tests. Tests of the NBS integrated flow facility will also be started in early 1975.

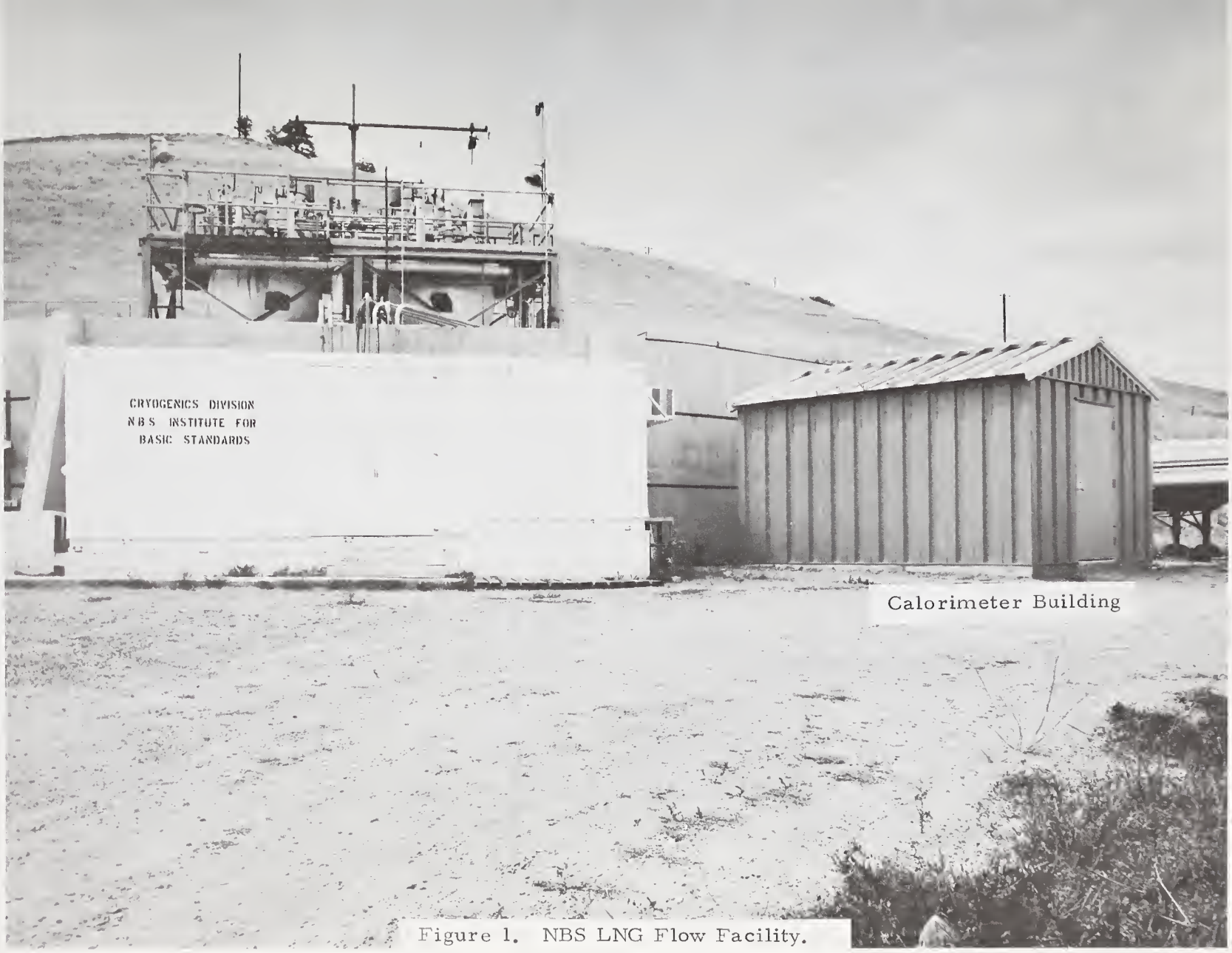


Figure 1. NBS LNG Flow Facility.

1. Title. LNG Density Reference System.

   Principal Investigator. Ben Younglove

2. Cost Center Number. 2751361

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

4. Introduction. The emphasis of the LNG effort of NBS is in providing technical support to industry in meeting the energy needs of our economy with natural gas.

   The density reference system will evaluate the ability of commercially available instruments to measure densities of LNG. Density is an essential measurement in performing total energy content determinations of natural gas reservoirs. While this effort is oriented towards metrology, the output from cost center 2751574 will provide basic reference data on pure liquids and mixtures which will serve as density standards.

5. Objectives. This research will provide a system for evaluating the density measurement capability of commercially available meters. We will evolve a density reference system capable of generating accurate densities for this evaluation. From the commercial meters we will attempt to select one capable of performance as a transfer standard in order to provide traceability of accuracy to field density measurement systems.

   The first year will be devoted to construction and testing of the density reference system. In the second year we will concentrate on evaluation of commercial meters, while the final year will involve selection testing and application of the transfer standard.

6. Background. In early 1973 a proposal was made to the American Gas Association for research in several areas of LNG technology to be done at this installation. Part of this program was the density reference system. Initial scheduling indicated for the first year of work, starting in April, to be design, fabrication, and testing of a density system. Work actually commenced in August as a result of staffing difficulties. Since this initiation, we have conducted extensive study on the feasibility of various techniques for such a system, deciding finally on an application of Archimede's principle (see 7. below). The reference system is now in the latter stages of construction and evaluation.

7. Program and Results. Vibrating cylinder and vibrating plate densimeters have been received and installed in the test apparatus. An additional vibrating cylinder device has been withdrawn from the test program due to vibrating instabilities. The capacitance meter is ready for delivery and will arrive on commencement of the liquid nitrogen test.

There is some uncertainty regarding the delivery of the magnetic buoy device. We will be advised on this soon by the manufacturer.

A microwave cavity is being modified for installation and evaluation; this is an NBS device. We also are assembling a vibrating hollow-tube densimeter for evaluation.

The vibrating plate device has been checked in distilled water, also alcohol, acetone, hexane and in air as a preliminary evaluation and pre-calibration at room temperature. The vibrating cylinder densimeter was checked in liquid nitrogen in a similar test. No malfunctions were noted.

The capacitance device was checked in liquid nitrogen on its first arrival and showed reasonable behavior but suffered from an intermittent open circuit. The device was returned to the manufacturer for inspection. The electronic read-out unit was replaced by a more up-to-date version.

The weighing head has arrived in this reporting period and has shown some malfunctioning in the electronics. The weight loader is being rebuilt as the initial design was too position sensitive. The density monitor device has been checked in distilled water.

It is expected that the density reference system will be operational by 15 February 1975 and that significant testing can be initiated at that time. Preliminary considerations have been made concerning statistical test procedures.

8. Problem Areas. The weighing head had several malfunctions including an unintentional short to ground in the sensing circuit and improperly installed knife edge. One vibrating cylinder device and possibly the magnetic buoy may not be available for test; the magnetic buoy system is large enough to require separate testing from the other transducers.

9. Funding. July 1 - December 31, 1974.

Man-Years this period:

Principal	0.42
Technician	0.16
Equipment	$ 550
Total Cost	31,700
Balance on hand end December	24,500

10. Future Plans. First three months. Check monitor performance using liquid nitrogen and methane. Run tests on assembled densimeters using binary mixtures of methane with ethane, propane, and butane. Develop a statistical test plan in cooperation with the NBS statistical group.

Second three months. Complete binary bests and conduct tests on more complex mixtures according to the test plan. Initiate the preliminary tests on the magnetic buoy device depending on its availability and the scheduling of the above tests.

1. Title. Liquefied Natural Gas Technology Transfer

   Principal Investigator. D. B. Mann, R. S. Collier

2. Cost Center Number. 2750401

3. Sponsor Project Identification. Maritime Administration, Project 55-330-15-011.

4. Introduction. The NBS support of the Maritime Administration (MarAd) LNG ship program is divided into two areas. These are a materials experimental program (Cost Center 2750430) and cryogenic technology transfer. In addition to those objectives listed below this program provides a cohesive structure for the coordination of the NBS LNG program.

5. Objectives. Cryogenic Technology Transfer is designed to provide cryogenic technical information, data, and advice to the Maritime Administration (MarAd), its contractors and other agencies performing work of interest to, or for, MarAd in the design, development, testing, construction and operation of LNG ships and ship components.

6. Background. The Merchant Marine Act of 1970 restructured federal maritime policies to make bulk carrier vessels, such as tankers and LNG ships, eligible for construction and operating subsidies. In December 1973 the keel was laid for a 926 foot long LNG vessel carrier at Quincy, Mass. The keel laying initiated the construction of the first LNG tanker to be built in the United States. American ship builders have orders for a total of 15 of these complicated ships. Various future projections indicate a total of from 25 to well over a 100 ships will be required to handle the LNG importation within the next 10-15 years. LNG marine technology is presently foreign dominated. As a matter of fact, many of the ships being constructed in U. S. shipyards are using designs under license from foreign industrial groups or governments. LNG is a cryogenic fluid and the massive technology developed over the past 15-20 years in cryogenics as applied to industrial gases and the aerospace effort provides a resource which could be applied profitably to improving the U. S. competitive position in the construction and operation of LNG shipping. Because of its historical association with broad based cryogenic technology over a period of 20 years, the NBS Cryogenics Division was requested to provide support to the MarAd LNG ships program in order to aid in the transfer of cryogenic technology where it could enhance the effectiveness of maritime LNG shipping. Therefore, on April 17, 1973 we submitted a work statement which was confirmed by the establishment of a program in May.

7. Program and Results. In the initial phases of the LNG Cryogenic Technology Transfer Program emphasis was placed on establishing the level and degree to which we could interface with MarAd, MarAd Research

Centers and MarAd contractors. Progress, therefore, is measured as specific responses to MarAd and MarAd contract requests and NBS generated output felt necessary for the overall program.

7.1. Data and Information -- LNG. Thermophysical property data and measurement methods for LNG are necessary for design and performance evaluations of major structural ship containment systems, insulation and major components such as valves, piping, pumps and safety oriented and operational instrumentation. This data is also necessary to establish ship operational efficiencies by accurately relating the volume of LNG carried to the actual quality of the LNG as a fuel -- its heating value. This latter quantity is the contract designation which the ship owner or operator is obligated to establish both on purchase and delivery of the cargo.

Thermophysical property data and related measurement methods must be of high accuracy and precision and the information must be put in the hands of those who need it. This information must be accepted for its validity on an international basis, but with emphasis on first availability to U. S. maritime industry.

Emphasis during this reporting period has been to establish the necessary mechanism for acceptance of previously generated data as well as the results of current research. The thermophysical properties of methane (see AGA project BR-50-10, cost center 2750364) generated under the NBS program have been accepted and approved by the three AGA standing committees charged with LNG responsibilities. In addition, the data has been submitted as an ASTM standard by NBS and will be recommended as an ANSI standard by the AGA. Other data on ethane, propane, butane, and nitrogen and their mixtures (LNG) will follow this procedure (see AGA project BR-50-11, cost center 2751574, 2752574).

Measurement methods to establish cargo value are also being established (see AGA project PR-50-48 and paragraph 7.2 below) and will be submitted to shipbuilders, owners and operators for their comments and approval.

Additional methods of disseminating cryogenic technology are also being explored. The American Bureau of Shipping (ABS) was visited in November of 1974. The ABS is a ship classification society which establishes standards known as "Rules" for the design, construction and periodic survey of ships and other marine structures. Classification certifies adherence to these rules providing assurance that a vessel posseses the structural and mechanical fitness for its intended service. The visit by NBS personnel was at the request of ABS staff for the presentation of the total NBS LNG program with particular emphasis on materials of construction information. We will continue to provide them with program information and ABS will certainly be closely associated with the ships hull material study (cost center 2751430).

7.2. LNG Custody Transfer Systems. As part of a program to provide information and assistance to the shipbuilding companies of the United States, NBS was requested to give an independent evaluation of custody transfer systems for ships designated by MA Design LG8-S-102a MA Hulls 289, 290, 291.

In general, the scope of work for system component evaluation includes transducers and instrumentation for liquid level, density, temperature and pressure, and also the sampling of mole fractions of LNG components; advanced techniques may include direct measurements of the total mass and the total potential heat of combustion of the fluid (heating value or "therm" metering).

In addition to design and evaluation of system components (which would possibly be common to several different types of systems), there is a need to consider the integration of these components into a custody transfer system. This may require knowledge of the system independent of instrumentation. For example, tank capacity tables relating liquid level to liquid volume rely on the accuracy of survey procedures for measuring the inside tank dimensions, also on calculations of list and trim corrections, the effect of thermal contractions, and tank loading factors. Also, since LNG is a mixture, there is normally a selective vaporization of the fluid causing space and time variations of the fluid mixture and its properties (tank "weathering"). These effects extend the conditions under which sensors and transducers must operate.

As part of Phase I of this evaluation (System Design Review) NBS has received from the ship contractors and builders information, plans, and drawings regarding the following:

1) Overall layout of the ship tank and piping system.

2) Basic tank construction materials.

3) Drawings and information on the locations and use of Resistance Thermometer Devices (RTD's).

4) Preliminary drawings and block diagrams concerning the capacitance liquid level and density measuring devices.

5) An error analysis of tank measurements using conventional strapping techniques.

6) Information on the probable range of LNG mixture constituent fractions.

In addition, informal discussions have been held with the shipbuilder, owner and subcontractors concerning the capacitance level measurement, heat leak and convective patterns within the tank, ship operating procedures, possible new tanks trapping procedures, potential heat of combustion (heating value) and its measurement, and alternate (future state of the art) gauging techniques.

Using this and other sources of information NBS has completed the following:

1) Calculated the changes in dimensions of the tank due to thermal contractions and tank loading.

2) Made preliminary calculations of heat transfer and system thermodynamics concerning the spacial and time variations of LNG mixture fractions (tank weathering).

3) Completed preliminary evaluation of the capacitance level and density measurement techniques.

4) Conducted a detailed evaluation of the relationship between dielectric constant and density using the relevant range of mixture fractions and current (provisional) equations of state.

5) Reviewed various tank strapping procedures.

Based on these studies NBS has identified the following major sources of uncertainty:

1) A non-unique relationship between dielectric constant and density.

2) Measurement of tank inside dimensions (tank strapping).

3) Possible density variations within the tank.

The systematic uncertainties for these factors are estimated as follows:

1) Density - ±1.2% or less; this number may be reduced if thermodynamic conditions in the tank are known and mixture constituent fraction data is applied as a correction factor. Technical details of these considerations will be contained in a separate report.

2) Tank strapping - ±0.4% or less depending on the surveying technique used.

3) Non-uniform density - it is not possible to give a good estimate of this uncertainty at the present time, some calculations show that this effect is negligible but more work should be done in the area of heat transfer and convective patterns of fluid within the tank.

The uncertainty estimate for the total mass will be at least the r.m.s. value of these three factors. Other factors mentioned above are considered small or calculable-and-correctable. Uncertainties in liquid level and density output, electronic signal conditioning, and readout have not been calculated and are considered to be relatively small at the present time; more information on this point is needed and could possibly be considered as part of a testing program.

If the problem of tank strapping is solved the ultimate (least possible) uncertainty will most probably rest on fluid sampling and the resulting measurement of mixture fraction; possible non-uniform

density within the tank and liquid level measurement may also be a factor. Thermometry may also become an important factor if mixture constituent fraction is not well known or if density is not measured directly.

A testing program to verify this design review is suggested as follows:

1) A complete rangeability test of the capacitance densitometer in the LNG density reference system over the operating ranges of temperature, pressure, and mixture constituent fractions.

2) A test of the capacitance liquid level vernier in a convenient LNG test facility.

3) An independent check of the strapping technique which is ultimately decided upon.

4) Instrumentation of at least one of the tanks in operation, to measure possible density variations within the tank.

In addition, an experimental program should be conducted to develop gauging techniques which are less sensitive to tank strapping and possible fluid variations within the tank; e.g., RF gauging (see NBSIR 73-346) and the strain gage technique proposed by General Dynamics. Possible direct measurements of potential heats of combustion (heating value or "therm" metering) should also be considered.

8. Problem Areas. None.

9. Funding.

July 1 - December 31, 1974

Labor	.6 MY
Costs	$42,000
Balance	0

10. Future Plans. A preliminary work statement has been submitted to MarAd for continuation of this program in the areas of cryogenic technology transfer, a study of cryogenic custody transfer systems (2750401), and the completion of the materials experimental program (2750430). Particular emphasis will be on maintaining present methods of information dissemination and establishing new contacts with such groups as the coast guard and additional shipbuilders.

1. Title. Federal Power Commission Consultation

   Principal Investigators. D. B. Chelton and A. F. Schmidt

2. Cost Center Number. 2750404

3. Sponsor. Federal Power Commission - Bureau of Natural Gas -- letter agreement dated 4 June 1973.

4. Goals. The Cryogenics Division will provide consultation and advisory services to the Federal Power Commission on the cryogenic safety and the design aspects of several current applications before the FPC for authorization of LNG terminal and storage facilities. These services cover properties of cryogenic environments, insulation systems, cryogenic safety, thermodynamics, heat transfer, instrumentation and cryogenic processes such as refrigeration and liquefaction.

5. Background. Cost Center initiated July 7, 1973.

6. Program and Results. The results and status of those facilities presently under the jurisdiction of the Federal Power Commission and subject to our review are outlined in the following table.

   Elements of the facilities that are subject to review are the land-based cryogenic storage tank components, bounded by the tanker or barge, the vaporizer and the liquefaction units (if any). These include, but are not limited to the transfer lines, the storage tanks, the vaporizers and the process piping as it interacts with the storage tanks. It is essential that the reviews cover the operation, maintenance and emergency procedural philosophies for each terminal. Based upon these studies, reports are submitted to the staff of the FPC setting forth the technical evaluations and conclusions on each proposal. In addition, NBS may provide expert witnesses on behalf of the staff of the FPC in any hearings on the aforementioned applications.

   Emphasis is placed on the safety aspects of the facilities including their possible interactions with the surrounding areas. The impact of engineering design such as appropriate use of existing technology and material selection for structural integrity must be assessed. The basis of review includes various codes and standards, prior experience, precedent and engineering knowledge.

7. Funding.

Funding FY 75	$50,000
July 1 - December 31, 1974	14,000
Anticipated Man Years of Effort FY 75	0.8

8. Future Plans. At the present time there are several pending applications, but detailed information is not yet available. It is anticipated that additional facilities will be reviewed as applications are made to the Federal Power Commission.

FPC CONSULTATION - LNG FACILITY REVIEW

Applicant	Location	Type Facility	Storage Facility	Status		
				Site Tour	Technical Meeting	Review
Distrigas - New York Terminal	Staten Island, NY	Import Terminal	2-900,000 barrel	8/21/73	8/21/73	Complete
Distrigas - Everett Marine Terminal	Everett, MA	Import Terminal	1-600,000 barrel 1-374,000 barrel	8/23/73	8/23/73	Complete
Algonquin LNG, Inc.	Providence, RI	Import Terminal	1-600,000 barrel	8/24/73	8/24/73	Complete
Northern Natural Gas Co.	Carlton, MN	Peak Shaving	1-630,000 barrel 10.8 MMCFD liquefier	10/30/73	10/30/73	Complete
Northwest Pipeline Corp.	Plymouth, WA	Peak Shaving	1-348,000 barrel 6.0 MMCFD liquefier	10/31/73	10/31/73	Complete
East Tennessee Natural Gas Co.	Kingsport, TN	Peak Shaving	1-348,000 barrel 5.0 MMCFD liquefier	**	11/29/73	Complete
Transco Terminal Co.	Bridgeport, NJ	Import Terminal	3-600,000 barrel	1/23/74	1/23/74	Complete
Southern Energy Co.	Savannah, GA	Import Terminal	4-400,000 barrel	1/24/74	2/6/74	Complete
Alabama-Tennessee Natural Gas Co.	Greenbrier, AL	Peak Shaving	1-117,000 barrel 2.0 MMCFD liquefier	**	2/5/74	Complete
Trunkline LNG, Inc.	Lake Charles, LA	Import Terminal	3-600,000 barrel	2/7/74	5/14/74	Complete
Chattanooga Gas Co.	Chattanooga, TN	Peak Shaving	1-348,000 barrel 10.0 MMCFD liquefier	2/28/74	2/28/74	Complete
Tennessee Natural Gas Co.	Nashville, TN	Peak Shaving	1-290,000 barrel 5.0 MMCFD liquefier	2/27/74	2/27/74	Complete
Pacific Indonesia LNG Co.	Port Hueneme, CA	Import Terminal	2-550,000 barrel	5/15/74	*	In process
Northern Natural Gas Co.	Hancock Co., IA	Peak Shaving	1-630,000 barrel 10.8 MMCFD liquefier	**	***	Complete
Texas Eastern Transmission Company	Staten Island, NY	Peak Shaving/ Import	* 9.0 MMCFD liquefier	*	*	In process
El Paso Alaska Co.	Gravina Pt., Alaska	Export Terminal	4-550,000 barrel	8/19/74	*	In process
Pacific Alaska LNG Co.	Nikiski, Alaska	Export Terminal	2-550,000 barrel	*	*	Pending
Western LNG Terminal Co.	L. A. Harbor, CA Oxnard, CA Pt. Conception, CA	Import Terminal Import Terminal Import Terminal	4-550,000 barrel 4-550,000 barrel 4-550,000 barrel	* * *	* * *	Pending Pending Pending

* to be determined
** NBS visit not scheduled
*** technical meeting not scheduled

1. Title. LNG - Dual Fuel Auto

Principal Investigator. J. M. Arvidson, J. Hord and D. B. Mann

2. Cost Center Number. 2750590 (Reimbursable), 2750154

3. Sponsor Identification. Joint NBS and General Services Administration Requisition Number F4KE023, Case Number 66551.

4. Introduction. The work described relates to the general area of transfer of technology based on Division experience in the handling of liquefied combustible gases, instrumentation and systems analysis.

5. Objectives. To establish the degree of hazard to passengers and auto on the release of liquefied natural gas in the trunk area of the standard GSA dual fuel (natural gas and gasoline) sedan.

6. Background. The General Services Administration (GSA) dual fuel automobiles are equipped to run on gasoline or natural gas. In the initial GSA program the natural gas was compressed and carried in high pressure cylinders, which in sedans were located in the trunk space. To take care of accidental leakage, a large vent was installed in the roof of the passenger compartments, with two small air vents installed in the top of the trunk space. More recently, most of the dual fuel installations have been installed with liquefied natural gas (LNG) carried in an insulated tank at low pressure in the trunk compartment.

Natural gas has a density less than air and therefore is buoyant and will rise at temperatures above about 151 K. It was anticipated that vents provided would be adequate for dilution of explosive concentrations of methane gas in the trunk and passenger compartments under conditions of operation. This was believed to be the case even if very cold gas was vented (at a temperature of less than 157 K) as the amount of the methane gas vented at this lower temperature would be minimal, would be heated rapidly above 157 K and then vented normally.

A recent explosion of a sedan, believed to be caused by migration of methane gas from a trunk area to the passenger area, raised the question of functional adequacy of the high level vents. In other words, can a combustible mixture of cold methane gas (at a temperature of less than 157 K) migrate from a leakage area in the trunk to the passenger compartment, and if so, can additional venting, relocation of vents, or other methods be incorporated in the sedan to eliminate this hazardous situation?

GSA has requested the Cryogenics Division of NBS to perform tests, analyze data, and make recommendations for the modification (if any) to be made in the vent system or any other aspect, method or design that would minimize the concentration of methane gas (or LNG vapor) in the trunk or passenger area to well below the lower explosion limit (at least to 50% LEL).

A test program and results were described in the previous reporting period (NBSIR 74-358). The potentially hazardous condition caused by release of methane or vaporized LNG in the trunk area was reported to the co-sponsor in the form of a progress report.

7. Program and Results. During this reporting period the General Services Administration concluded that the work done here on the venting of the GSA auto was adequate for their needs and that they did not intend to pursue the subject further. While these decisions were being made, NBS had requested use of the sedan for additional NBS experiments concerned with the venting of hydrogen in addition to methane gas.

These new tests were designed to add to the information previously collected and to answer the following questions:

a) What are reasonable inflow (leakage) rates, cumulative leakage quantities and leakage injection locations?;

b) What are experimentally reasonable gas residence times in the passenger compartment?;

c) What is the effect of increased roof vent area?;

d) What is the effect of leakage gas temperature and environmental temperature on test results?;

e) What is the effect of wind direction and velocity on the rate of efflux of gaseous fuels from the car interior?; and

f) What instrumentation is required?

The test vehicle was relocated into a test bay of a metal building equipped with explosion proof electrical fixtures and a roof mounted explosion proof exhaust fan. In place solid state combustible gas sensors were substituted for sample lines used in the previous test. Temperatures and pressures inside the vehicle were monitored as well as flow rates of combustible gas introduced to the passenger compartment. Both hydrogen and methane gas were injected into the passenger compartment.

A series of experiments were then performed to identify the explosion hazards, establish venting criteria, and obviate general safeguards for hydrogen or methane fueled passenger vehicles.

It was found that appropriately designed ventilation systems significantly reduced the safety hazards associated with accumulated combustible gases. Vents were recommended for all autos converted to burn hydrogen or methane and may possibly be eliminated in new cars that are designed for gaseous fuel operation. Combustible gas warning systems are recommended, at least in the interim, for all (converted and new design) gaseous fueled vehicles. Hydrogen and methane gases appear equally safe as vehicular fuels if used in properly designed vehicles.

The information developed under the joint NBS-GSA program has been compiled and will be published as an NBS report (TN 666).

This study indicates that gasoline powered vehicles converted to burn gaseous fuel should be equipped as follows:

1) The fuel system should be adequately designed for fuel containment in the event of collision;

2) The car trunk should be adequately vented if the fuel tank is located in the trunk;

3) The fuel tank vent should be ducted to the far rear exterior of the vehicle;

4) A trunk membrane should be provided to isolate the trunk or fuel and passenger compartments.

Optional but highly desirable equipment for such vehicles would include a positive ventilation system and an early warning combustible gas detector. Guidelines for the design of appropriate ventilation systems are given in the report. If used, a combustible gas sensor should be located in the passenger compartment at the highest point of the roof (vented or nonvented).

8. Problem Areas. None.

9. Funding.

Labor	.5 MY
Cost (includes some equipment)	$30,000

10. Future Plans. The program will be terminated with the publication of the NBS Technical Note.

NBS-114A (REV. 7-73)

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15. SUPPLEMENTARY NOTES

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.*)

Eighteen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at an 18 man-year level with funding expenditures of over $485,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.

2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.

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 contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. 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*)

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

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