NBSIR 75-817 (R)

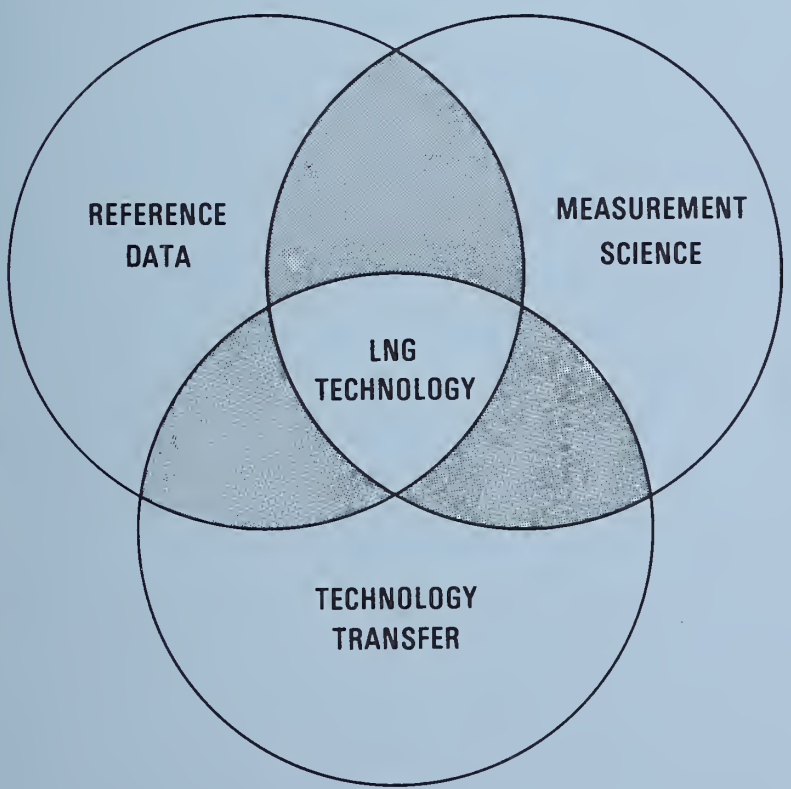
LIQUEFIED NATURAL GAS RESEARCH

at the

NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 JANUARY - 30 JUNE, 1975

D. B. Mann, Editor



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

NBSIR 75-817

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

D. B. Mann, Editor

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

Progress Report for the Period
1 January - 30 June, 1975

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John K. Tabor, Under Secretary
Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology

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(in cooperation with the American Gas Association)

Pipeline Research Committee
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National Aeronautics and Space Administration
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ABSTRACT

Nineteen cost centers supported by six 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 $500,000. 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 Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.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. 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 (beginning in 1975 the publication became biweekly) 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 120 subscriptions going to AGA Member Companies and 148 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 January 1975.

B-1262 THE THERMOPHYSICAL PROPERTIES OF METHANE AND DEUTERO-METHANES IN THE SOLID, LIQUID AND GASEOUS PHASES - A SELECTED BIBLIOGRAPHY. Indexed by property, phase and author, 68 pages (Feb 1975). ($8.00)

B-1263 THE THERMOPHYSICAL PROPERTIES OF METHANE MIXTURES - A SELECTED BIBLIOGRAPHY. Indexed by property, system and author, 118 pages (Feb 1975). ($10.00)

B-1264 PROCESSES AND EQUIPMENT INVOLVING LIQUEFIED NATURAL GAS AND METHANE - A SELECTED BIBLIOGRAPHY. Indexed by subject and author, 76 pages (Feb 1975). ($8.00)

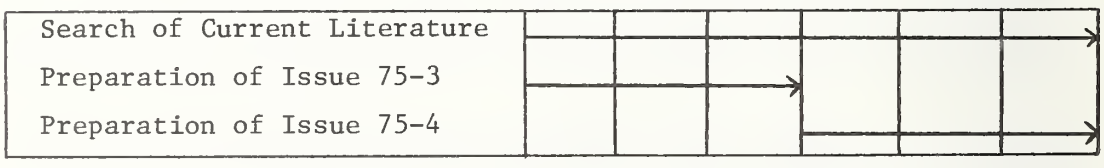
During the period January through June 1975, we have distributed 20 copies of these and the comprehensive bibliographies. A bibliography on LNG Patents was supplied to AGA in May. A supplement to this is in preparation and will be completed in July.

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

9. Funding. January 1 - June 30, 1975

Labor	7.3 K$
Other Costs	3.2 K$
Total	10.5 K$
Remaining	10.0 K$

10. Future Plans. Issue 75-2 of the LNG Quarterly was mailed to the National Technical Information Service for printing and distribution on July 2, 1975. Issue 75-3 will be published in October. The three comprehensive bibliographies discussed in Item 7 above are available for distribution.



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 seeminly 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. Publication has been delayed awaiting a decision as to publishing the thesaurus separately or combined with one in fire safety and one in the mechanics of structural failure. Most of the terminology unique to LNG safety is now incorporated into this thesaurus.

   During the period January 1, 1975 through June 30, 1975, we have indexed 275 papers, reports, etc. dealing directly with LNG safety, and properties of methane and LNG. Of these, 204 were sent to ASRDI in machine-readable form on magnetic tapes.

8. Problem Areas. None

9. Funding. January 1 - June 30, 1975

		NASA/ASRDI
Allocation (9/30/74 - 10/1/75)	50 K$	
Labor	0.5 MY	26.6 K$
Other Costs		3.3 K$
	Total	29.9 K$
	Remaining	8.9 K$

10. Future Plans. We will continue to index safety-related papers and should complete approximately 250 of these in the next reporting period.

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

Principal Investigators. R. D. Goodwin, G. C. Straty, L. A. Weber, and H. M. Roder

2. Cost Center Number. 2750574 (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, 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 pressures P is determined by expanding the fluid from the calibrated cell into large calibrated volumes maintained near room temperature (~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 measurments on ethane, relatively high density fluid would reside in external parts of the system which could not be accurately accounted for in a conventional apparatus.

During previous reporting periods, 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. 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 [1] was obtained. Ethane vapor pressures were also measured and found to be in agreement with available published data.

During this reporting period, PVT measurements on ethane have been essentially completed. Data have been obtained along approximately 50 isochores at uniformly spaced temperature intervals from near the triple point to 320 K at pressures to 350 bar. Data appear to be consistent with other available data within the combined experimental error. A manuscript reporting the results of the ethane measurements is in preparation.

[1]. R. Prydz and R. D. Goodwin, J. of Chemical Thermodynamics 4, 127 (1972).

7.2 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. Measurements in the regions of overlap with the ultrasonic data indicate excellent agreement, and overall agreement with calculated sound velocity data is satisfactory. The data have been combined with previously measured PVT data to obtain the isentropic compressibility and specific heat ratio C_p/C_v. A manuscript reporting the results of the hypersound velocity measurements has been prepared and submitted to Cryogenics for publication.

7.3 Ethane, Dielectric Constant Data--L. A. Weber.

Previous dielectric constant data for ethane have been limited to the saturated liquid near the triple point and to the saturated liquid and vapor in the region of the critical point. New experimental work has been completed on the measurement of the dielectric constants of ethane as a function of temperature and density over a wide range of densities in the saturated and compressed fluid. The present data include the saturated liquid in the temperature range 95 - 300 K and seven isotherms

at temperatures between 120 and 323 K and at pressures up to 390 bars. The capacitance measurements were made with a commercial three-terminal a-c bridge having a resolution of one part in 10^6. The capacitor is made up of a pair of concentric cylinders and has a stability of one part in 10^5. Dielectric constant measurements are being combined with accurate density data to form the Clausius-Mossotti (CM) function, $1/\rho\ (\varepsilon-1)/(\varepsilon+2)$ which for ethane, like other non-polar fluids, is nearly independent of the temperature and density. This work has been very valuable for examining the consistency of the available density data for ethane, including the new equation of state (PVT) data discussed above and the new magnetic densimeter measurements discussed under "Densities of LNG Mixtures." Data analysis and report preparation are in progress.

7.4 Ethane, Specific Heat Data--H.M. Roder.

Specific heat data (C_v) are required to accurately define the derivatives of the equation of state (PVT), which in turn are used to calculate other thermodynamic functions such as enthalpy. Measured values of C_v are particularly valuable to cross-check thermodynamic calculations for the compressed liquid states. We are preparing for a series of C_v and C_{SAT} measurements on ethane similar to those completed on methane under this program [1]. Measurements of the heat capacity of the empty calorimeter will be extended from 300 to 330 K to permit C_v measurements of compressed gaseous ethane at temperatures above critical. Since the critical temperature of ethane (305.3 K) is well above room temperature, fluid of relatively high density will reside in the filling capillary part of the system, and will have to be accounted for accurately.

During this reporting period the heat capacity apparatus has been checked out electrically, and for vacuum, and some heat capacity measurements have been made on the empty calorimeter. Accuracy and consistency checks on methane are planned next.

[1]. B. A. Younglove, J. Research. NBS 78A, 401 (1974).

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 measurement 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 and compressed liquid ethane in certain temperature regions have not been measured previously and have only recently been completed at this laboratory. The melting line is known only with low accuracy and attempts to measure it using existing apparatus continues to be unsuccessful.

The recently completed (PVT) and dielectric constant measurements together with specific heat measurements now underway will help overcome some of the deficiencies. Additional attempts to measure the melting line more accurately are planned.

9. Funding.

Man-years expended (January to June 1975)	1.0
Equipment and/or Services Purchased	11.5K$
Total Reporting Period Cost	61.9K$
Balance Remaining (June 30, 1975)	10.0K$

10. Plans for Future Work.

Objectives and Schedule:	year	1975	
	quarter	3	4
Report equation of state (PVT) data for ethane.		→	
Measure, analyze and report dielectric constant data for ethane.			
Measure, analyze and report specific heat data for ethane.			

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.

7. Program and Results. An apparatus has been assembled for laser light scattering spectroscopy on compressed and liquefied gases (76 - 300 K, 350 bars). The apparatus consists of a high pressure optical cell, a cryostat for refrigeration with 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 pressure scanned Fabry Perot interferometer for the measurement of the Doppler frequency shifts associated with the scattering from propagating density (pressure) fluctuations (Brillouin scattering).

Data on the hypersound velocities in pure methane have been obtained by Brillouin scattering techniques at low densities (< 14 mol/ℓ) where the large sound absorption in methane prohibits more conventional 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. The data have been combined with previously measured PVT data to obtain the isentropic compressibility and ratio of the specific heats. A manuscript reporting the results of these measurements has been prepared and submitted to Cryogenics for publication.

We are currently working on equipment modifications to permit the determination of the thermal diffusivity, $\lambda/\rho C_p$, of pure methane. The most accurate method of doing this is to use photon-counting and digital autocorrelation techniques to measure the temporal behavior of the spontaneous temperature fluctuations occurring in the fluid which is governed by the bulk fluid thermal diffusivity. This is equivalent to measuring the very narrow Rayleigh line width and requires a resolution of about one part in 10^{12}.

Preliminary checks of the modified apparatus on a well-characterized test fluid appear to have been satisfactory. Further testing with methane is planned.

8. Problem Areas: None.

9. Funding.

Man-years expended (January to June 1975)	0.3
Equipment and/or Services Purchased	4.7K$
Total Reporting Period Cost	17.5K$
Balance Remaining (June 30, 1975)	0.0K$

10. Future Plans.

Objectives and Schedule:	year / quarter	1975 3	1975 4
Methane:			
Measure, analyze and report thermal diffusivity coefficient data for methane.			

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 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, N2, O2, F2, He, He. Recent work has extended this approach to methane. It is felt that a successful mixture program will emerge from combining the results for pure fluids with equation of state studies. The equation of state work is being carried out by other investigators in this laboratory.

7. Program and Results. Statistical mechanics has been applied to predict and correlate the dilute and moderately dense thermophysical properties of carbon dioxide.[1] Carbon dioxide was selected as a typical polyatomic molecule to study. The self-diffusion coefficients of methane have been correlated and tabulated.[2] Results for the dilute gas transport properties of oxygen and nitrogen have been published.[3] The well-known critical point anomaly in the thermal conductivity can now be predicted to within experimental error.[4] Equations to calculate the dense gas and liquid transport properties of methane are in press.[5]

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

9. Funding. January 1 - June 30, 1975

Allocation	57.5 K$	OSRD
Labor	0.5 MY	28.0 K$
Other Costs		2.7 K$
	Total	30.7 K$

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

References

1. J.F. Ely and H.J.M. Hanley, Mol. Phys. (Sep 1975).

2. K.R. Harris, H.J.M. Hanley et al., "The Self-Diffusion of Simple Fluids," Australian National Univ. Press., DRU-RR 2 (1974).

3. H.J.M. Hanley and J.F. Ely, J. Chem. Phys. Ref. Data 2, 735 (1973).

4. H.J.M. Hanley, J.V. Sengers and J.F. Ely, Proc. 14th Int. Conf. Thermal Conductivity (to be published).

5. H.J.M. Hanley, W.M. Haynes and R.D. McCarty, Cryogenics (In Press 1975).

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 entitled "Equilibrium Properties of Fluid Mixtures: A Bibliography of Cryogenic Data" was updated to January 1975. A camera-ready copy was transmitted to Plenum Press during the first part of April and publication is expected by mid-summer 1975.

   b) Work is continuing on the compilation of liquid-vapor equilibrium data and derivation of the excess Gibbs functions and Henry's constants for binary systems containing methane with the light hydrocarbons, argon and nitrogen. A paper, "On the Consistency of Liquid-Vapor Equilibria data for Binary Mixtures of Methane with the Light Paraffin Hydrocarbons," which covers a portion of this work, will be presented at the 1975 Cryogenic Engineering Conference.

   c) A paper has been submitted to Cryogenics entitled "Liquid-vapor Phase Equilibria in the System N_2 + CH_4 from 130.00 K to 180.00 K." This paper includes an evaluation of available data for this system, as discussed in (b), as well as the new measurements.

   d) Preparations have also been made to start liquid-vapor equilibrium composition measurements at selected conditions for the methane + ethane system. Measurements are expected to begin during the next quarter.

8. Problem Areas. None.

9. Funding.

Man-years expended (January 1 - June 30, 1975)	0.7
Equipment and/or Services Purchased	4.0K$
Total Reporting Period Cost	52.0K$
Balance Remaining (June 30, 1975)	0.0K$

10. Future Plans.

Objectives and Schedule:	year / quarter	1975	
		3	4
Compile, evaluate, correlate and report liquid-vapor equilibrium data for methane-ethane mixtures.			
Measure, analyze and report liquid-vapor equilibrium data for methane-ethane mixtures.			

1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

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

2. Cost Center Numbers. 2751574, 2752574

3. Sponsor. LNG Density Project Steering Committee, American Gas Association, Inc., Project BR50-11.

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 mainly 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 gas in the following temperature ranges: (a) methane (105 - 160 K); (b) ethane

(100 - 270 K); (c) propane (100 - 280 K); (d) normal butane (135 - 300 K); (e) isobutane (115 - 300 K); and (f) nitrogen (95 - 120 K). Measurements have also been carried out for the following binary mixtures:

(a) 0.49 CH_4 + 0.51 C_2H_6 (105 - 140 K);

(b) 0.50 C_2H_6 + 0.50 C_3H_8 (105 - 140 K);

(c) 0.50 CH_4 + 0.50 C_3H_8 (105 - 130 K);

(d) 0.05 N_2 + 0.95 CH_4 (105 - 140 K);

(e) 0.49 N_2 + 0.51 CH_4 (95 - 130 K);

(f) 0.67 C_2H_6 + 0.33 C_3H_8 (125 - 140 K);

(g) 0.92 CH_4 + 0.08 nC_4H_{10} (105 - 140 K);

(h) 0.59 C_3H_8 + 0.41 nC_4H_{10} (110, 135, 140 K); and

(i) 0.61 C_3H_8 + 0.39 nC_4H_{10} (115 - 150 K).

The evaluation and optimization of predictive calculation methods for the densities of LNG mixtures has continued. The corresponding states model [1] has been tested and optimized using data for selected binary mixtures (e.g. methane-ethane, methane-propane, ethane-propane, etc.). The modified hard sphere equation of state model [2] has been tested using data for selected binary mixtures (e.g. methane-n-butane, propane-n-butane, etc.).

References:

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

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

8. Problem Areas. None

9. Funding.

2751574 (measurements)

Man years expended (Jan. 1 - June 30, 1975)	0.8
Equipment and/or services purchased	6.1K$
Total reporting period cost	42.3K$
Balance remaining (June 30, 1974)	20.0K$

2752574 (calculation methods)

Man years expended (Jan - Jun 1975)	0.25
Equipment and/or services pruchased	3.4K$
Total reporting period cost	10.1K$
Balance remaining (June 30, 1975)	32.4K$

10. Plans for Future Work.

Objectives and Schedule:	year / quarter	1975 3	1975 4
Measure orthobaric densities of binary mixtures containing methane, ethane, propane, butanes and nitrogen.			
Evaluate and optimize available density calculation methods.			

1. Title. LOW TEMPERATURE MATERIAL BEHAVIOR

Principal Investigators. H. I. McHenry and R. P. Reed

2. Cost Center Number. 2750430

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

4. Introduction. For cryogenic applications, the ASME Boiler and Pressure Vessel Code and the API Standard 620 Appendix Q Code specify the same design allowable stress level for 5Ni steel as for 9Ni steel. Since 5Ni steel costs approximately 20% less than 9Ni steel, significant cost savings could be achieved by using this material for LNG applications. At the present time, 5Ni steel cannot be used in place of 9Ni steel for marine applications because the U. S. Coast Guard has not approved it. The principal reasons that the USCG has delayed approval are lack of service experience in land based tankage and concern that the fracture resistance of the weld heat affected-zone is inadequate.

5. Objectives. This program is being conducted to evaluate the fracture resistance of the heat affected zone of 5Ni steel weldments at room temperature, 111 K and 76 K.

6. Background. This program is a continuation of the program conducted by NBS for MarAd to determine the mechanical properties of candidate materials for LNG tankage. Their work demonstrated that 5Ni steel plate has adequate mechanical properties for LNG applications. Further work was recommended to verify that the plate properties would be retained in the weld heat affected zone.

7. Program and Results. The program to evaluate 5% Ni steel weldments consists of evaluating the weldment toughness in accordance with the USCG requirements for weld procedure qualification and determine the fatigue crack growth and fracture toughness properties of the weldment.

Weld procedure qualification involves testing three Charpy impact specimens at five locations within the weld zone: at the weld centerline, the fusion line, and the heat affect zone at 1, 3 and 5 mm beyond the fusion line. The fatigue crack growth properties will be determined for the case of a crack growing through the thickness. Bend specimens will be used to enable definition of the part of the heat affected zone most susceptible to crack growth. Fracture toughness will be determined using J-integral procedures.

To date, the weldments have been fabricated by the Armco Steel Company; and the Charpy impact specimens for task one and the fatigue crack growth specimens for task two have been machined.

8. Problem Areas. None.

9. Funding. January 1 - June 30, 1975

Expended as of June 30, 1975	$ 5,000
Remaining	$45,000

10. Future Plans. All testing will be completed in the next six months.

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

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

2. Cost Center Number.

2753430 - LNG Ship Hull Materials (Shipyard Contracts)
2751430 - LNG Ship Construction Materials (Metallurgical Evaluation)
2752430 - LNG Ship Hull Materials (Fracture Properties)

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.

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

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

6. Background. Early in 1974, the Welding Panel of MarAd's Ship Production Committee recommended that a program be conducted to reduce the cost of ship hull construction. NBS was requested by MarAd to propose such a program to the LNG subcommittee of the Welding Panel at a meeting in Boulder in 1974. In mid-October, MarAd approved the initial phase of NBS's recommended program, i.e., to survey the problem and the technology available for its solution. On the basis of this survey and as the result of a meeting of the Welding Panel in March, 1975, a coordinated program involving the LNG shipyards, the steel suppliers, and NBS was recommended to MarAd and to the Welding Panel. This program was approved and work started in May 1975.

*American Bureau of Shipping.

7. Program and Results. The Ship Steel Improvement Program consists of three primary tasks:

Material Acquisition
Shipyard Evaluation
Metallurgical Evaluation

Currently, the program is in the material acquisition phase. The steel procurement plans are summarized below:

Shipyard	Steel Company	Test Temperature	Steel Grade*
Avondale	Armco	-25°F	V-051
Avondale	Armco	-50°F	V-051 (SCC)**
Newport News	Bethlehem	-25°F	V-051 (SCC)
Newport News	Bethlehem	-50°F	V-051 (SCC)
General Dynamics/Quincy	U.S. Steel	-25°F	CS (SCC)
General Dynamics/Quincy	Bethlehem	-60°F	EH (SCC)
Sun Ship	Luhens	-40°F	EH (Cb)***
Sun Ship	Luhens	-60°F	EH (Cb,SCC)

*The steel grades V-051, SC and EH are American Bureau of Shipping (ABS) steels.
**SCC - Sulfide Shape Control
***Cb - Columbium Treated

Procurement is contingent upon completion of the contractual arrangements between the shipyards and NBS.

Upon receipt of material, each participating shipyard will evaluate the steel plates by qualifying optimum weld procedures in accordance with USCG requirements. The welding processes being qualified are submerged arc, gas metal arc, and shielded metal arc. The test weldments will also be subjected to a metallurgical evaluation to determine the effect of microalloying and sulfide shape control on heat affected zone toughness.

8. Problem Areas. Contract negotiations with each of the shipyards have not yet been completed. Thus, the steel procurement has been delayed.

9. Funding.

Cost Center	Cost to 6/30/75	Balance
2753430	$40 K	$150 K (obligated)
2751430	$40 K*	$ 35 K
2752430	$ 5 K	$ 35 K

*Includes phase I costs.

10. Future Plans. Steel procurement should be completed and the shipyard and metallurgical evaluations should be started during the next reporting period.

1. Title. CUSTODY TRANSFER - LNG SHIPS

Principal Investigators. R. S. Collier and P. J. Giarratano

2. Cost Center Number. 2750460

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

4. Introduction. In response to a request from the U.S. shipbuilding industry, NBS is conducting an independent design review of the shipboard custody transfer systems under the sponsorship of the Maritime Administration and in cooperation with the major U.S. shipbuilding companies.

5. Objectives. The objectives of this program are to 1) Identify the major technical areas relating to uncertainties in the measurement of total mass and total heating value, 2) Estimate uncertainties in the total mass and total heating value due to these identified factors, 3) Develop a proposed testing program for custody transfer system components, and 4) Investigate improved gauging techniques.

6. Background. Calendar year 1974 funding provided for the initial review of ships designated by MA Design LG8-S-102a MA Hulls 289, 290, 291. The current funding provides for an extension of this program to include ships of other designs which are being built by the major U.S. shipbuilding companies.

7. Program and Results. Working relations between three of the four major U.S. shipbuilders have been established. Most of the problem areas which are common to custody transfer systems of all types have been identified and are listed as follows:

1. Density
   a) accuracy
   b) rangeability
   c) stability
2. Tank Strapping
   a) thermal effects
   b) loading factors
   c) measurement techniques
3. Convection (Non-Uniform Density)
   a) density or composition stratification
   b) possible isolation of measurement stillwells
4. Tank Weathering
   a) time changes in composition, stratification, etc.
   b) composition measurement
   c) sampling

5. Liquid Level/Total Volume Measurement

6. Pressure and Temperature Measurements (gradients included).

7. Electronic Signal Conditioning, Data Reduction, Analysis and Readout.

In addition, further progress was made in calculating uncertainties in density measurement, variations in composition due to tank weathering and thermal effects associated with hydrostatic head pressure within the tank.

8. Problem areas. One of the most difficult estimates to make is the degree of density or composition stratification within the tank; this could also include the effect of stillwells and remote access areas within the tank. It will probably not be possible to estimate these effects to the desired accuracy. It is therefore recommended that some of these ship tanks be fitted experimentally to measure density, temperature and composition at various locations within the tank during the normal course of checkout of these systems.

9. Funding. January 1 - July 1, 1975

Man-Years this Period	0.5
Total Cost	$29,887
Balance (July 1, 1975)	$45,113

10. Future Plans.

1. Conduct a complete rangeability test of the capacitance type densitometer.

2. Continue a program of exchange of information with the U.S. shipbuilding companies.

3. Recommend procedures and facilities for testing a 15 meter capacitance type liquid level vernier.

4. Conduct further experiments on RF gauging in large tanks.

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

6. Background. The LNG flow facility at NBS will be utilized to evaluate the response of the individual elements in the heating value measurement. Different compositions of LNG will be prepared to provide a range of densities sufficient to determine any dependencies. A limited amount of sampling work is included to determine the relative importance of this parameter to the overall measurement.

   Flowmeter scaling is being done utilizing the cryogenic and the water flow facilities at NBS and private LNG peak shaving facilities. This portion of the program is behind schedule because of scheduling problems at the private LNG facilities.

7. Results. LNG tests on the four-inch flowmeter that had been scheduled at an industrial LNG plant for early 1975 were not completed because there was no LNG send out. It now appears that a brief test might be possible during late November or early December 1975. Therefore, this critically important phase of the program has been delayed approximately one year from the original plan. In order to keep the delay in the flowmetering phase of the program as short as possible it was decided to go ahead with the necessary plans for the next larger size flowmeter (eight inch) and try to test both sizes during the next send-out season.

   An alternate industrial LNG plant was also selected which has a higher probability of sending out LNG during the next send-out season. This change in sites might also provide test data on the four inch meter that

would not have been available before. To get this additional data, the four-inch meter will be left installed in the original facility until after the tests in November or December. The flowmeter will then be moved to the alternate site for additional testing in conjunction with tests on the eight inch flowmeter.

Tests on the NBS flow facility are now scheduled for the summer months. This schedule was necessitated when an adequate supply of LNG was not available and it was necessary to assemble a natural gas condenser. A minimum amount of interference with the flowmeter field tests will result by conducting these tests during the summer months.

8. Problem Areas. Major problem areas encountered have been in scheduling tests as described above. Locating a suitable supply of LNG resulted in some delay but the resulting solution should provide more flexibility in later stages of the program.

9. Funding.

Man-Years Expended	1.0
Major Equipment Purchased	$10,000
Total Reporting Period Costs	$55,000
Balance on Hand (to Dec. 31, 1975)	$70,511

10. Future Tests. The flowmeter tests at an LNG peak shaving plant have been rescheduled for November or December 1975 (4-inch) and January or February 1976 (4- and 8-inch). Tests on the NBS integrated flow facility are scheduled to start during July 1975.

1. Title. LNG DENSITY REFERENCES 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.

6. Background. The density reference system was initiated in 1973 with a proposal to the AGA for research on LNG technology. Since that time the reference system has been selected, designed, constructed, and is now in operation, evaluating density metering systems.

7. Program and Results. The density reference system has shown consistent good agreement in density measurements to the densities of Haynes (ref. cost center 2751574) for liquid methane. That is, essentially all of the measurements are within 0.15% of Haynes.

Data on the performance of density measurement by the vibrating cylinder, vibrating plate, and capacitance meter in liquid methane have been taken.

The suppliers of the above densitometers have kept in close touch with the progress in evaluation of their meters. There has been some malfunctioning in these devices and some modifications made (see item #8 below). The capacitance meter was altered by its design engineer to include a temperature sensor (platinum thermometer) and a new set of electronics for readout. This device now features readouts of density, temperature, and capacitance. The designer's intent is that the temperature sensor will allow a more accurate measurement of density over variations in hydrocarbon composition.

We have had input from the NBS statistical group as to statistical approaches for testing, they have also been of significant help in advising on detailed operation of the weighing head.

Colin McClune of Thornton Research Center (Shell Research Ltd.) has visited us and has given us the benefit of his knowledge on the qualitative behavior of two of the above devices. He intends to make further evaluations with his density system. It is our intention to keep in touch with his progress.

8. Problem Areas. The weighing head continues to be a challenge regarding reliability. Its electronic control circuit completely failed and was replaced by an improved circuit. The unweighing device has given some problems, but now the weighing head system appears to perform properly.

   The vibrating cylinder device was returned for repair of a pressure leak (at cold temperatures).

   The vibrating plate device has, on occasion, shown mode-locking errors. However the designer of this device has stated that this can be avoided by making an adjustment in the phase delay circuit. We intend to have him make this adjustment.

9. Funding. January 1 - June 30, 1975

Principal Investigators	0.72 man years	$37,700
Technician	0.12 man years	4,500
Equipment		5,400
Other		1,600
TOTAL		$49,200
Balance as of June 30, 1975		$ 1,600

10. Future Plans. First three months. Complete measurements of the installed densitometers on methane and its mixtures with the heavier hydrocarbons. Analyze data accumulated. Install magnetic buoy system and commence evaluation.

    Second three months. Complete density meter evaluation. Write summary of test results on all meters.

1. Title. LIQUEFIED NATURAL GAS TECHNOLOGY TRANSFER
Principal Investigator. D. B. Mann

2. Cost Center Number. 2750401

3. Sponsor Project Identification. Maritime Administration, Project 01 220 03 211, Purchase Order Number 400-58074.

4. Introduction. The NBS support of the Maritime Administration (MarAd) LNG ship program is divided into three areas. These are a materials experimental program, LNG ship custody transfer, 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. Recent proposals to liquefy and transport Alaskan gas to the U.S. only reinforced the importance of this new technology to providing a measure of energy self-sufficiency to the U.S.

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 some 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 of that year.

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 and MarAd contractors. Progress, therefore, is measured as specific responses to MarAd and MarAd contractor requests and NBS generated output felt necessary for the overall program. The materials experimental program is described under Cost Center 2750430. The problems associated with custody transfer of LNG ships is described under Cost Center 2750460 and the positive dissemination of information from these and other NBS programs is performed under this cost center. In addition, information developed under a program for reducing the cost of LNG ship hull construction is described under Cost Centers 27501430, 27502430, and 2753430.

A program for the standarization, dissemination, and utilization of LNG related property data has been formulated. It has the following three objectives:

1) To secure review, approval, and acceptance of the mechanical, thermophysical, and thermodynamic property data of interest to the LNG industry by the gas industry and voluntary and statuatory standards agencies.

2) To define and make available these data in a form most useful to the ultimate user.

3) To define the most economical and effective method of distributing this data to the ultimate user.

Support for this proposed program has been solicited from the sponsor (MarAd), the Pipeline Research Committee (AGA) LNG Supervisory Committee, the AGA Operating Section LNG Committee, the Research and Engineering Division of the American Gas Association and the National Gas Producer Suppliers Association. Assessment of the response to these presentations is in progress.

8. Problem Areas. The effective dissemination of information on cryogenic technology is basic to the overall ovjectives of this Cost Center. The main road block to achieving the objectives is definition by the user of the form in which the information should be available. Solution of this problem involves continued interaction between the Cryogenics Division and the ultimate user with the possible generation of a prototype of one or more methods for circulation, comments, and criticism.

9. Funding. January 1 - June 30, 1975.

Labor	0.2 man years
Cost	$10,000

10. Future Plans. Funding for this program extends to the end of calendar year 1975. During this period several prototype methods of data dissemination will be attempted. These would include a data book, simplified computer programs, and the outlining of symposia or conferences to achieve the maximum awareness of information generated under this program.

1. Title. ENERGY CONSERVATION POTENTIAL IN THE LNG INDUSTRY

Principal Investigators. D. B. Mann and T. M. Flynn

2. Cost Center Number. 2750103

3. Sponsor Project Identification. NBS Office of Energy Conservation

4. Introduction. By the end of 1975, there will be 166 LNG projects around the world in operation, under construction, planned, or proposed.

Peak shaving accounts for the largest number of LNG facilities with 106 being completed within the U.S. This number includes 55 actual peak shaving plants (which include liquefaction, storage, and gasification equipment) and 51 satellite facilities (which consist of storage and gasification equipment, but no liquefier). These 106 plants comprise a total storage capacity of approximately 65 billion cubic feet (equivalent gas volume) and a total liquefaction capacity of approximately 295 million cubic feet per day.

The impact of energy shortages world wide has underscored the need to utilize this resource (LNG) as efficiently as possible. Therefore, this program has been undertaken to provide the measurements and data base necessary for energy conservation in the Liquefied Natural Gas (LNG) industry. It will identify sources and degree of thermodynamic losses incurred during liquefaction, shipping, storage, and regasification of LNG and assure an adequate cryogenic measurement methodology and data base to facilitate the most effective use of Liquiefied Natural Gas.

5. Objectives. The objective of the project is to provide the technical basis for the planned management of the cryogenic aspects of liquefied natural gas to enable its more effective utilization and prevent its exploitation or neglect. It will include, for instance, thermodynamic analyses of representative LNG systems to define the thermodynamically "ideal" base for comparison to actual practice. It will identify and test instruments and measurement techniques in support of energy conservation, and analyze and test the feasibility of energy recovery through utilization of the cold in LNG.

6. Background. New project.

7. Program and Results. During this fiscal year, we completed the first four months of an intended three year study whose ultimate purpose is to provide the measurements and data base necessary for energy conservation in the Liquefied Natural Gas (LNG) industry. Progress made during these first four months include:

1) An historical perspective of the LNG industry;
2) The selection of peak shaving as the first subject for study, including a description of the process and essential components;
3) A thermodynamic analysis of peak shaving process;
4) and an identification of the most pressing measurement and instrumentation needs.

Specific objectives during this first period were to provide:

1) A documentation and definition of the LNG industry.
2) An LNG peak shaving process description.
3) A description of the variations among LNG peak shaving process components.
4) Thermodynamic analysis -- reversible process.
5) Thermodynamic analysis -- limitations.
6) Thermodynamic analysis -- applications to existing facilities.
7) An analysis of energy conservation through the potential of refrigeration recovery, or cold utilization.
8) An identification of tentative measurement instrument needs.
9) A base for measurement development for conservation requirements.

Among our first conclusions are the following:

1) LNG peak shaving is an established and growing U.S. industry.
2) Adequate technical information is available for conservation analysis.
3) The peak shaving process is subject to analysis using classical thermodynamics.
4) It is possible to establish a thermodynamically reversible process as an ideal.
5) Some irreversibilities are dictated by external requirements of the process.
6) Liquefaction is the largest single irreversibility, followed by storage losses.
7) Process efficiencies could be further enhanced if it were possible to build an integrated plant where cold utilization were a coordinated objective.
8) Tentative measurement requirements identified are: therm-meter, densitometer, flowmeter, liquid level and mixture fraction, all in gas or cryogenic liquid phases.
9) Thermodynamic, electrodynamic, transport, and phase quilibrium properties data are inadequate as of the reporting period. Existing experimental and analytical programs on property data will eliminate this inadequacy within the scope of the three year study.

8. Problem Areas. None

9. Funding. $40 K, NBS Office of Energy Conservation, Division 460.04.

10. Future Plans. Plans for the remainder of the study include the following elements:

1) Complete peak having plant efficiency analysis. Expected outputs would include:
   a. Complete ranking of major loss components.
   b. Quantify losses in terms of energy.
   c. Identify measurements, instrumentation, and process improvement opportunities.
   d. Quantify energy-benefit for each measurement, instrument, or process improvement.

2) Implementation
   a. Field testing of existing instruments in conjunction with energy conservation demonstration projects.
   b. Selection and analysis of new measurements and instruments.
   c. Field testing of new measurement devices and techniques in conjunction with demonstration projects.

3) Promote LNG Energy Conservation Program.
   a. Identify and document net energy to be saved.
   b. Identify and document additions to net energy supplies.

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 76	$50,000
January 1 - June 30, 1975	22,000
Anticipated Man Years of Effort FY 76	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	6/24/75	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.	Oxnard, 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

114A (REV. 7-73)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 75-817	2. Gov't Accession No.	3. Recipient's Accession No.

TITLE AND SUBTITLE

LIQUEFIED NATURAL GAS RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

5. Publication Date

6. Performing Organization Code 275.00

AUTHOR(S) D. B. Mann, Editor

8. Performing Organ. Report No.

PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No. 2750401

11. Contract/Grant No.

Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)

Same as Item 9.

13. Type of Report & Period Covered Semi-Annual - January through June 1975

14. Sponsoring Agency Code

SUPPLEMENTARY NOTES

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

Nineteen cost centers supported by six other agency sponsors in addition to NBS ovide the basis for liquefied natural gas (LNG) research at NBS. During this six nth reporting period the level of effort was at an 18 man-year level with funding penditures of over $500,000. This integrated progress report to be issued in nuary 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 onsors, but will not necessarily replace such meetings. Distribution of this document limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished; and therefore t for citation in the open literature.

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.

AVAILABILITY ☐ Unlimited

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☐ Order From National Technical Information Service (NTIS) Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)	21. NO. OF PAGES
UNCLASSIFIED	19
20. SECURITY CLASS (THIS PAGE)	22. Price
UNCLASSIFIED	

USCOMM-DC 29042-P74