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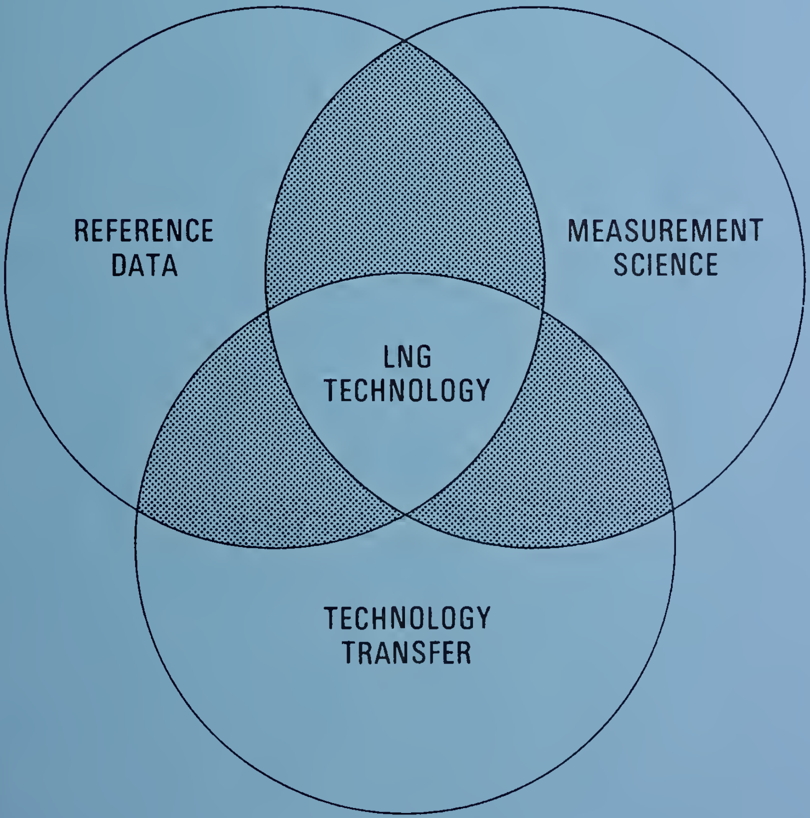
NBSIR 80-1626 R

LIQUEFIED NATURAL GAS RESEARCH
at the
NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT FOR THE PERIOD
1 JULY - 31 DECEMBER, 1979



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

NBSIR 80-1626

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

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

Progress Report for the Period
1 July - 31 December, 1979

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LNG Custody Transfer Measurements Supervisory Committee

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ABSTRACT

The objective of this report is to:

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

The work is supported by NBS and seven other agencies and represents the collective expenditure of $676,900 during the 6-month reporting period. The contents of this report augment quarterly progress meetings for certain of our sponsors and provide a perspective which is missing when the parts are viewed individually. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished, and therefore not for citation in the open literature.

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

CONTENTS

I. REFERENCE DATA

II. MEASUREMENT SCIENCE

III. TECHNOLOGY TRANSFER

CONTENTS (continued)

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

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

2. Cost Center Numbers. 7360574, 7360548

3. Sponsor Project Identification. Gas Research Institute Grant No. 5014-361-0131. National Aeronautics and Space Administration, Lewis Research Center,
   Purchase Order C-78014-C.

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

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

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

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

   Accurate thermodynamic properties data for liquefied gas mixtures must be based on precise compressibility and calorimetric measurements; compressibility data give the dependence of thermodynamic properties on pressure and density (at fixed temperatures); calorimetric data give the dependence of thermodynamic properties on temperature (at fixed pressures and densities). It is impossible, however, to perform enough compressibility and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation of the data to arbitrary compositions, temperatures and pressures. Instead, thermodynamic properties data for multicomponent mixtures must usually be predicted (extrapolated) from a limited number of measurements on the pure components and their binary mixtures. This project was initiated to provide the natural gas and aerospace industries with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, "Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar," by Robert D. Goodwin (April 1974), and National Bureau of Standards Technical Note 684, "Thermophysical Properties of Ethane, From 90 to 600 K at Pressures to 700 Bar," by Robert D. Goodwin, H. M. Roder, and G. C. Straty (August 1976). These reports contain the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane and ethane, and provide an accurate basis for calculating thermophysical properties data for LNG and other hydrocarbon mixtures.

7. Program and Results.

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

PVT and dielectric constant measurements have been carried out in the following regions for propane and isobutane:

Propane: Isotherms at 90, 100, 110, 120, 130, 140, 160, and 180 K at pressures to 35 MPa; saturation curve at 5 K increments from 90 to 200 K and at 228.4 K

Isobutane: Isotherms at 120, 140, and 160 K at pressures to 35 MPa; saturation curve at 5 K increments from 115 to 200 K and at 228.4 K.

7.2 Calculational Methods -- R. D. McCarty

As was mentioned in the last report, the work on the extension and optimization of the corresponding states method for the calculation of the thermodynamic properties of mixtures has been the subject for a Master's thesis at the University of Colorado. This particular phase of the study is now complete, but copies of the resulting thesis are still not available. Since the completion of the above mentioned graduate work, very little work has been done on the subject of calculational methods, however, work on the extended corresponding states method will resume in the near future.

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

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

7.4 Normal and Isobutane, Thermophysical Properties -- R. D. Goodwin

Interagency reports have been printed, as follows:

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

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

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

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

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

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

All planned measurements and data analysis have been completed. A report, PVT Properties of Saturated and Compressed Fluid Nitrogen, has been submitted to the Journal of Chemical Thermodynamics for publication. A second report, PVT Properties of Compressed and Liquefied Nitrogen-Methane Mixtures, has also been submitted to the Journal of Chemical Thermodynamics for publication. A poster paper entitled PVTx Properties and Equation of State for Compressed and Liquefied Nitrogen-Methane Mixtures is being prepared for presentation to the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Industry, Berlin, Germany, March 17-21, 1980.

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

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

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1979.

Staff-years expended	1.0
Equipment and/or Services Purchased	12.5K$
Approximate expenditures, total	77.6K$

10. Future Plans.

	Quarter	
Objectives and Schedule:	1	2
Optimize existing calculation methods for the thermodynamic properties of methane-nitrogen mixtures and LNG mixtures.	————	————→
Measure, analyze and report PVT and dielectric constant data for propane.	————	————→
Publish experimental sound velocity data for propane.	————	————→
Measure, analyze, and report PVT and dielectric constant data for isobutane	————	————→
Measure, analyze, and report PVT and dielectric constant data for normal butane.	————	————→
Prepare and publish Standard Reference Data and final equations of state for propane thermodynamic properties.		————→

1. Title. FLUID TRANSPORT PROPERTIES

Principal Investigator. Howard J. M. Hanley

2. Cost Center Number. 7362290, 7362291, 7360125

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

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

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

6. Background. A continuing program has successfully expanded the state-of-the-art of transport phenomena for pure fluids. Information for pure fluids is required as a prerequisite for mixture studies. The theory of transport phenomena has been developed and applied to produce practical numerical tables of the viscosity, thermal conductivity and diffusion coefficients of simple fluids: Ar, Kr, Xe, N_2, O_2, F_2, He, H_2(1), CH_4,(2) C_2H_6,(3) C_3H_8.(4)

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

7. Program and Results. A correlation of the properties of ethylene(4) and hydrogen(1) is in the manuscript stage. Significant results from computer similarities relating to the structure of mixtures have been reported.(6) Our computer program to predict the transport properties of fluids and mixtures to include hydrocarbons to C_{20} is near completion.

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

9. Level of Effort. July 1 - December 31, 1979.

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

10. Future Plans. The thrust of the effort for the next several months will be to extend the computer simulation studies of mixtures. The studies will yield information on the structure of the mixtures which will, in time, lead to better methods to predict their properties.

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2. B. J. Ackerson and H. J. M. Hanley (in preparation).

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

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

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

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7. L. Van Poolen, R. D. McCarty and H. J. M. Hanley (in preparation).

8. D. J. Evans and H. J. M. Hanley, Phys. Rev. A (1979)(in press).

1. Title. PROPERTIES OF CRYOGENIC FLUIDS

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

2. Cost Center Numbers. 7360122, 7360124, 7360125

3. Sponsor Project Identification. NBS

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

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

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

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

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

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

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

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

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

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

7. Program and Results.

7.1 Transient Hot-Wire Apparatus - H. R. Roder. The thermal conductivity system is in the final stages of debugging to define both accuracy and precision of our experimental measurements. Preliminary results on oxygen encompass isotherms at 294 and 307 K from 0.4 to 60 MPa covering a density range up to twice critical (640 kg/m^3). Deviations from the correlation of NASA SP 3071 are systematic and run from -5% at low densities to +15% at the very highest. Experimental values by Ivanova, et al. for temperatures between 294.8 and 306.7 K differ from the present values by 12% at the lowest density and are less than that at the other densities. Comparison to the highest isotherm of Ziebland and Burton at 200 K reveals similar curvatures. Ziebland and Burton's highest pressure is 13.4 MPa which at 200 K corresponds to 438 kg/m^3. Assuming exact correspondence at zero density, the deviation between present values and the Ziebland and Burton measurements is about 5 percent at the highest density. The differences may arise from errors in the various experimental systems, because the isotherms compared are not truly isotherms, or because there exists some fine-structure in the behavior of thermal conductivity vs. density along isotherms.

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

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

7.4 Mixture Composition Determination Using Raman Spectroscopy - D. E. Diller. A joint project on in-situ mixture composition determination was carried out while Diller was on an exchange visit with NML, NBS, Gaithersburg during October 1978 - June 1979. The feasibility of using Raman spectrometry for determining the composition of mixtures of natural gas components was examined. Raman intensity measurements were carried out on eight, gravimetrically prepared, binary gas mixtures containing methane, nitrogen and isobutane at ambient temperature and at pressures to 0.8 MPa. The repeatability of the molar intensity ratio, $(I_2/j_2)/I_1/y_1)$, where y_1 is the concentration of component 1 in the mixture, and I_1 is the intensity of the related line in the mixture spectrum, was examined. The compositions of two gravimetrically prepared methane-nitrogen-isobutane gas mixtures were determined spectrometrically with an estimated precision of about 0.001 in the mole fraction. Typical differences from the gravimetric concentrations were less than 0.002 in the mole fraction. The Raman spectrum of a gravimetrically prepared, eight component, hydrocarbon gas mixture was obtained to show that the Raman spectrometric method has potential for being applicable to natural gas type mixtures.

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

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

7.5 Methane, Viscosity Measurements - D. E. Diller. The torsional piezoelectric crystal apparatus has been performance tested on gaseous and liquid methane. Tests has been carried out on five isotherms at temperatures between 100 and 300 K at pressures to 10 MPa. Differences between the measurements and the extended corresponding states model of H. M. A. Hanley, et al. are within experimental error. Measurements on additional isotherms and at pressures to 35 MPa are in progress. The objective of this work is to provide accurate data for testing and improving models for calculating the viscosity of hydrocarbon mixtures.

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

8. Problem Areas. The measurements using the hot-wire apparatus continue to be delayed because of experimental problems.

9. Level of Effort. July 1 - December 31, 1979

Staff-years expended	2.2
Equipment and/or Services Purchased	21.0K$
Approximate expenditures, total	176.0K$

10. Future Plans.

Objectives and Schedule:	Quarter 1	Quarter 2
Complete performance test transient hot-wire thermal conductivity apparatus	——→	
Design, construct and performance test high temperature-high pressure PVT apparatus.		
Measure, analyze and report viscosity data for methane in compressed liquid and gas region.	————	———→
Complete computer program for predicting mixture phase equilibrium.	———	→
Develop accurate model for thermophysical properties of polar-nonpolar mixtures.	————	———→

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2. B. J. Ackerson and H. J. M. Hanley, The Thermal Diffusivity of Methane in the Critical Region, Chem. Phys. Lett. 53, 596-8 (Feb 1978).

1. Title. PROPERTIES OF CRYOGENIC FLUID MIXTURES

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

2. Cost Center Numbers. 7360123, 7362290, 7368574

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

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

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

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

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

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

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

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

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

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

7. Program and Results. A summary of recent progress is as follows:

a) The paper(1) discussing compilation, evaluation, and correlation of liquid-vapor equilibria data for methane + ethane system appeared in the Journal of Physical and Chemical Reference Data.

b) A similar paper(2) on the methane + propane system has been accepted for publication in the same journal

c) The updated and expanded version of the bibliography(3) on equilibrium properties of fluid mixtures is now being typed. The new version will be current to January 1980, and will include systems containing all saturated and unsaturated hydrocarbons through C_3, the saturated straight and branch C_4's and C_5's, and water.

d) A systematic effort has just been undertaken to reexamine consistency tests relative to each other and some new statistical methods with the goal of determining the sufficiency of the tests for liquid-vapor equilibria, and the extension to solid-liquid, liquid-liquid, and possibly PVTx in general. Most probably testing of data for nitrogen + methane mixtures will follow.

e) Experimental measurements have been completed on the system nitrogen + ethene principally to explore the liquid-liquid-vapor equilibrium region. In the process, some measurements were made in the nitrogen + ethane system as well. Measurements were made at NBS by a graduate student/guest worker from the Colorado School of Mines. A paper on this work is in preparation.

8. Problem Areas. None

9. Level of Effort. July 1 - December 31, 1979

Staff-years expended	1.4
Equipment and/or Services Purchased	15.0K$
Approximate expenditures, total	112.0K$ (13.5 K$ - GRI)

10. Future Plans.

Objectives and Schedule:	Quarter 1	 2
Complete preparation of updated and expanded bibliography on equilibrium properties of fluid mixtures	————	—→
Continue systematic study of consistency test, apply to data for nitrogen + methane.	————	————→
Complete paper on liquid-liquid-vapor experimental data for nitrogen + ethene and nitrogen + ethane	————	—→

References

1. M. J. Hiza, R. C. Miller, and A. J. Kidnay, A Review, Evaluation, and Correlation of the Phase Equilibria, Heat of Mixing, and Change in Volume on Mixing for Liquid Mixtures of Methane + Ethane. J. Phys. Chem. Ref. Data, 8, No. 3, 799-816 (1979).

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1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

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

2. Cost Center Number. 7361574

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

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

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

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

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

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

7. Program and Results.

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

Papers describing the apparatus, experimental procedures, and the data and its analysis, from the last series of measurements are being prepared for publication.

7.2 Calculational Methods. Final optimization on revision to all of the models is now complete and two manuscripts are in preparation. The final draft of the paper to appear in the Journal of Chemical Thermodynamics is complete. Some changes to the manuscript need to be made prior to sending it to the Steering Committee for final review. The preparation of the NBS document which will contain computer code and detailed instructions on their use is in progress.

8. Problem Areas. None

9. Level of Effort. July 1 - December 31, 1979

Staff-years expended	None
Equipment and/or Services Purchased	
Approximate expenditures, total	

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

1. Title. MATERIALS FOR LNG APPLICATIONS

   Principal Investigators. L. L. Sparks

2. Cost Center Number. 7363574

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

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

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

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

6. Background. The Thermophysical Properties Division, previously known as the Cryogenics Division, has been involved in the development and application of cryogenic insulations since being established in 1951.

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

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

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

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

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

Assessment of materials and specimen acquisition. Commercially produced foams and their applicability as low temperature insulations have been screened using information from company literature and technical reports. The material chosen for initial testing and characterization was a 32 kg/m^3 polyurethane foam supplied by the Office of Standard Reference Materials of NBS. Specific information on chemistry, process, etc. for this material is being sought through the Products Research Committee. Other materials for our evaluation are being obtained from a shipyard and an aeroscape company. The cooperation of several commercial foam producers has been assured and will allow us to obtain materials on request. Since many of the properties in question are somewhat time dependent, specimens will not be stockpiled, but rather obtained as near to the time of use as practical.

Test Methods. All procedures for mechanical and thermal testing have been outlined. These procedures are based on experience, existing standards for similar tests at room temperature, and discussions with numerous testing facilities. Continuous evaluation and refinement of our procedures may lead to extensions and modifications of existing standardized methods to include the cryogenic temperature range. Specifically, all mechanical tests will be done using capacitance gauge techniques, controllable testing environment, and programmable loading machines. Thermal contraction, $\Delta L/L$, of large inhomogeneous specimens will be accomplished utilizing a recently completed system designed for this purpose. This system also includes an environmentally controllable test space. The contraction will be measured relative to a copper reference standard by deflection of an incident laser beam. This system was chosen because, in addition to allowing accurate yet simple measurements, it avoids the necessity of attaching a length or strain measuring device to the specimen. For lightweight foams the results are influenced by the mechanical constraints imposed by these devices. Thermal conductivity in the temperature range $76 \leq T \leq 373$ K was determined using an ASTM sanctioned guarded hot plate system.

Specimen Characterization. This area has been emphasized during this period. A technique utilizing a metallographic microscope for determining cell size and orientation has been developed. The foam stock being used for the initial specimens has been thoroughly examined with respect to the morphology of the material. We are now in the process of evaluating reproducibility and observer influence. Microphotographs necessary to do an extensive cell size and shape study have been made. Cell-gas constituents have been determined using the mass spectrograph facility at a nearby industrial plant. This cooperative venture involved constructing a system which could be used to free the cellular gas, could be transported between labs without contaminating the gas specimen, and could be integrated into the Rockwell systems. The work to date has been free to NBS since it was of an exploratory nature: subsequent work in this area will be on a contract basis.

Testing. Thermal conductivity of a hydrocarbon filled 32 kg/m^3 polyurethane foam has been determined in the temperature range $76 < T < 373$ K. Computer programs necessary to analyze the data have been developed, and final results are imminent.

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1979

Staff years expended	0.74
Equipment and/or Services purchased	$ 2,617
Appropriate Expenditures, Total	$60,300

10. Future Plans. During the next reporting period we will complete the thermal and mechanical testing programs for the material now being considered. We will also refine our cellular study techniques and expand our analysis capability in this area. A crucial phase of the program, relating observed cryogenic properties to foam structure, chemistry, and processes, will begin. Thermal contraction, L/L, is extremely important in applications involving insulating foams, and measurement of this property will be stressed. L/L for additional specimens will be determined as possible. Our cooperation with other government agencies and industrial users of foams will continue and expand as relevant opportunities come to our attention.

1. Title. LNG MATERIALS RESEARCH, CONCRETES

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

2. Cost Center Number. 7361403, 5621511

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

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

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

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

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

as was determined in a thorough literature evaluation of concrete at cryogenic temperatures (LNG Materials Handbook, second supplement, funded by MarAd).

The Properties of Solids group at NBS-Boulder has successfully examined the thermal and mechanical properties of a wide variety of materials: metals, polymers, insulations, and composites. The group, as a whole, has the equipment and expertise to perform cryogenic tests to determine the mechanical and thermal properties of concretes. Close working relationships with private companies, universities, and professional associations provide guidance in the areas of material selection and quality control of field-erected structures.

7. Program and Results. The extended program calls for establishment of an understanding of the low-temperature behavior observed for two different, "ordinary" concretes (portland cement, sand and gravel aggregates). This understanding must include the effects of parameters such as moisture and air content, water to cement ratio, additives, aggregate type and size, and age. Properties to be used in this study include thermal conductivity and contraction, and the strengths and moduli. Field poured concrete and alternate types of concrete will be studied using the procedures and understanding developed for ordinary concretes.

   The compressive strength of the initial, well characterized concrete mix has been determined in the temperature range $76 \leq T \leq 300$K. Test temperatures were 295, 195, and 76K; four specimens were used at 195 and 76K and three were used at 295K. The specimens contained approximately 8% free water and the compressive strength increased by 400% when cooled from 295 to 76K. Modulus data were also obtained from these tests and from an additional test at 4K.

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1979

Staff years expended	0.35
Equipment and/or services purchased	$ 2,617
Approximate Expenditures, Total	$30,000

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

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

    Characterization of specimens, which includes obtaining detailed information of moisture content, aggregate type and distribution, air content, porosity, and chemical composition of the cement, will be required for each type of specimen. Methods for accurately determining these characteristics and for testing concretes in cryogenic environments will be developed or refined in this phase. Standardized testing procedures are essentially nonexistent for concrete at low temperatures.

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

1. Title. CUSTODY TRANSFER - LNG SHIPS

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

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

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

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

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

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

7. Program. The calibration reports have been completed and issued for all three of the membrane ships. The NBS determined volume height relationships for these tanks agree with those determined by the primary surveyor to better than ± 0.2%.

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

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

9. Level of Effort. July 1, 1979 to December 31, 1979

Staff years expended	0.2
Approximate expenditures, total	15 K$

10. Future Plans. The interim reports for the first two ships of the free standing tanks design will be formally issued and the interim report for the third ship will be completed. The bottom surveys of the third ship will be completed as soon as the tank insulation is modified. The results of other measurements related to tank calibration accuracy will be reported. These various reports will be combined into a final report estimating the calibration accuracy of the cargo tanks of these three ships.

1. Title. HEATING VALUE OF FLOWING LNG

Principal Investigators. J. A. Brennan

2. Cost Center Number. 7362570

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

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

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

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

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

7. Program and Results. One additional test was run on the densimeter and flowmeter installed at the LNG import terminal. This test was run to check new flowmeter electronics in an effort to eliminate the occasional poor signal quality referred to in the last report. During this test, extended time was allotted to repeat tests using the old electronics and well as the new. No signal quality problems occurred during any of the testing.

   There is no definite proof that the signal quality problems experienced are electronic in nature. Since they appear randomly, it has not been possible to do a good analysis of them. It is possible that the problem might be caused by foreign material in the LNG interferring with the vortex sensor. It has been difficult to isolate the problem because of its random nature, but it will be investigated one more time in conjunction with instrumentation check out for another project. If the poor signal quality occurs during those tests, some additional checks will be completed in an effort to determine the source of the problem.

   Densimeter tests were run each time the flowmeter was tested. After the necessary electronic component changes were made, the densimeter ran properly for the remainder of that test run. The output followed changes in density as calcuated from gas analysis and temperature and pressure measurements. During the next test however, the densimeter output was very unstable. The instability was not the same problem that had been experienced before the electronic components were changed, but did persist throughout the test.

Apparently the densimeter instability resulted from a higher flow rate. A constant high flow rate existed during this whole test. Although the velocities within the pipe were not excessive [0.3 m/s (10 ft/s)] apparently the combination of the higher flow rate and the location of the densimeter relative to a tee resulted in the poor performance. Another test was run at a later time when the flow rate was lower and the densimeter functioned properly again.

An attempt will be made to investigate the apparent flow rate dependence on densimeter performance during the instrumentation check out run referred to above. The ability to make this test is dependent on the gas send out rate from the terminal. Results from these tests will be reported in project "Large Scale LNG Measurement" in the next report.

This project has been completed and a final report to sponsor is in preparation.

8. Problem Areas. Discussed in section 7.

9. Level of Effort. July 1 - December 31, 1979

Staff years expended	0.2
Equipment and/or services purchased	none
Approximate Expenditures, Total	$9200.00

1. Title. LARGE SCALE LNG MEASUREMENTS

   Principal Investigators. J. A. Brennan

2. Cost Center Number. 7360570

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

4. Introduction. This project is an extension of the work started on the project "Heating Value of Flowing LNG." Flowmeter scaling work will be extended to a line size of 32 inch (81 cm) diameter. Tank volume will be used as the flowmeter comparison value rather than gas flow rate values. Liquid level measurement in and volume determination of large storage tanks will be an important element in this investigation. Previous work on LNG densimetry will also be continued under actual LNG terminal operations.

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

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

7. Program and Results. The major effort has been in selecting and specifying instrumentation required to fulfill the project objectives. Some preliminary testing of components in the NBS liquid nitrogen flow facility will be completed wherever possible, but because of the size requirements, this testing will be limited.

   New recording instrumentation will be utilized on this project which will permit on line computations to be performed. This new instrumentation will be tested and debugged at Southern Energy Company's import terminal as soon as possible, and then it will be moved to the new import terminal.

   The new recording system will permit more timely problem identification in any of the test instruments and allow corrective measures to be implemented. Many of the problem areas associated with the previous projects at the LNG test sites were not identified until after the recorded data were returned and analyzed. Obviously, this procedure can result in considerable time waste which should be eliminated with the new system.

8. Problem Areas. No major problems have been encountered. Some problems have arisen in getting the required instrumentation modified so that it will meet the requirements of the terminal. It is anticipated that these problems can be favorably resolved.

9. Level of Effort. July 1 - December 31, 1979

Staff years expended	.35
Equipment and/or Services Purchased	none
Approximate Expenditures, Total	$14,500.00

1. Title. LNG DENSITY REFERENCE SYSTEM

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

2. Cost Center Number. 7367574

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

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

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

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

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

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

   The work has also been presented in the following papers:

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

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

7. Program. The DRS densimeter using a new electronic balance has been completed and is in operation. The shift of the density readings noted after the DRS was rebuilt has continued supporting the earlier assumption that the shift resulted from a balance corner loading maladjustment in the earlier work. The reference weight is not required for the density measurement with this new balance and thus can serve as a monitor of the balance calibration. The DRS densimeter is now much less sensitive to noise and the readings are more stable than with the earlier model. A similar reference densimeter, designed after the DRS densimeter but for use in an industrial lab, has been compared to the DRS densimeter in the DRS. The electronic balance and the weighing procedure differ but both use a silicon single crystal as a denisity sensor. Simultaneous density measurements with this densimeter and the DRS densimeter agree to better than 0.02%.

Measurements have been completed on four vibrating element densimeters both for evaluation and for calibration as transfer standards. The instrument by one manufacturer shows a velocity of sound dependence. The densimeters by a second manufacturer seem to be stable when the filter screens are removed and insensitive to velocity of sound or cycling. A densimeter by a third manufacturer is on hand for testing and calibration.

A calibration method was devised for the Archimedes densimeters during the course of tests of several of these densimeters. Three were also tested for repeatibility after handling and all were found to be sufficiently stable.

A portable densimeter similar to the DRS densimeter has been designed and is under construction. This will provide a standard densimeter based on a silicon single crystal that can be installed in other calibration systems to test the system accuracy.

An updated accuracy report for the DRS will be issued as will a report of recent tests of commercial densimeters.

8. Problem Areas. None

9. Level of Effort. July 1 - December 31, 1979

Staff Years Expended	0.6
Equipment and/or Services purchased	$ 8,000
Approximate Expenditures	$40,000

10. Future Plans. We will analyze and calibrate the vibrating plate densimeter as a transfer standard. The portable DRS will be completed, tested, and will be transported to other laboratories to determine relative accuracies of calibration facilities. A comparison of the DRS and the Gaz de France densimeter calibration system via this portable densimeter is planned. An updated accuracy report for the DRS will be issued as well as a report of the tests of commercial densimeters completed since the issuance of Technote 697.

1. Title. BASIC NATURAL GAS METERING

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

2. Cost Center Number. 7360571, 7362571

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

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

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

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

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

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

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

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

7. Program and Results. Under previous NBS funding, the new gas flow reference system was completed and the concept demonstrated. A description of the method and apparatus is appended to this report. In summary, nitrogen in both liquid and gas phases is circulated in a closed loop pump system. At 0.41 MPa and 288 K, the nitrogen is metered as a gas in the experimental gas flow test section. The nitrogen fluid is then cooled and expanded to 0.68 MPa and 90 K where its liquid density allows accurate and precise weight measurement. The liquid test draft is measured in such a way as to not disturb the steady state flow through the system. After weighing, the fluid nitrogen is again pumped to 0.41 MPa, warmed to 288 K and circulated through the gas meter test section.

A standard 4 inch diameter AGA-3 orifice meter run has been installed in the gas test section and preliminary test data indicates stable flow rates over a range of 2900 to 9000 kg/hr nitrogen gas. Temperatures at the gas test section can be varied from 273 K to over 316 K and pressures vary from .37 to .42 MPa. Initial test data have been taken using 3.8 cm and 5 cm (1.5 and 2 inch) gas orifice plates and five separate runs have giving nearly 80 test points over the weight flow range. Bore Reynolds Numbers of 4 million have been achieved and are believe to be above values used in orifice meter correlations.

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

8. Problem Areas. Original planning called for immediate testing of 5, 7.6 and 10 cm (2, 3, and 4 inch) orifice meter runs to develop new discharge and expansion coefficient values. This plan has been delayed in order to define more fully the characteristics of the system and to aid in the development of credibility of the results.

9. Level of Effort. October 1 - December 31, 1979

Staff-years expended	0.25
Equipment and/or services purchased	$ 1,500.00
Approximate expenditures	$24,000.00

10. Future Plans. During the next reporting period, a 10 cm (4 inch) gas turbine meter previously calibrated on natural gas using nozzels as the proving device will be installed in series with the 10 cm (4 inch) orifice run. Tests will be conducted to intercompare the reference weight system, gas turbine meter and gas orifice meter. This will provide necessary information to establish the total uncertainty of the new gas flow reference system. As a result, an Uncertainty Statement will be issued as an NBS report which will provide the values of total uncertainty of mass flow measurement in the gas phase and supporting data. Methods of maintaining statistical control of measurement process will also be given.

A master orifice meter test plan will be developed to allow new test data to be accumulated on this system and other reference systems using both liquid and gas as the test fluid. The original objective of generating new data on orifice discharge and expansion coefficients will be resumed after Steering Committee review.

ON A NEW METHOD OF GAS FLOW MEASUREMENT USING CRYOGENIC TECHNIQUES

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Direct comparison of ambient temperature gas flow measurements to mass is made possible by a new continuous closed-loop measurements method. The direct comparison is made possible by modification of a proven flow reference system based on mass-time.

The complete gas flow reference system has, as yet, not been demonstrated physically; however, the liquefied gas portion has been continuously proven over a period of six years and is the flow standard for the recently developed cryogenic flowmeter code. Modifications are state-of-the-art additions of heat exchangers and process control. It is believed that the accuracy of the liquid system (less than ± 0.2%) will be maintained after modification.

If implemented, the method would be extremely valuable in improving and redefining many of the present gas flow measurements and standards. Gas and liquid meter coefficients could be related directly to mass and to each other without the tedious reliance on state equations and accurate pressure and temperature measurements. The validity of liquid calibration for gas service could be confirmed on a mass basis. Current codes and recommended practices could be supported and improved with new, more accurate empirical data. The method can be extended to mixtures such as natural gas and would improve the accuracy of these measurements.

It is believed that this modification is a significant and timely improvement within measurement science which could have major impact on custody transfer and energy conservation.

Key words: Cryogenic; flow; gas; liquid; mass flow; measurement.

Paper presented at the 1977 NBS Flow Symposium, February 23-25, 1977, Gaithersburg, Maryland.

1. Introduction

A new and more accurate method of measuring gas flow in terms of mass is possible using existing, well developed cryogenic techniques. The method, which could be used to redefine present gas flow measurement codes and standards, is a natural and logical development from codes and standards measurements of cryogenic liquids such as oxygen, nitrogen, argon and hydrogen. The method is closed-looped allowing extended periods of observations at set gas pressures, temperatures and flow rates. Gas pressures above 1000 psi and gas temperatures above ambient temperatures are possible. The method is suitable for air, oxygen, nitrogen, argon, methane and natural gas mixtures of methane, ethane, propane, butanes, and nitrogen, and could be extended to neon, hydrogen, helium and other fluids.

Total uncertainty in mass flow is based on an existing cryogenic flow reference facility having over six years of operational experience. If successfully applied to gas flow measurements, gas flow measurements and standards could be improved by a factor of from five to ten.

Other studies made possible with this new method are:

a) Direct comparison of gas to liquid flow on a mass basis.

b) Intercomparison of gas to water or other fluid flow on a mass basis.

c) Performance of gas flowmeters operating on low temperature gases.

d) Investigation of Reynolds number variations at constant mass flow.

The new method will be described in general terms with several operating modes followed by a detailed description of the existing Cryogenic Flow Facility and modifications necessary to prove the new method.

2. Gas-Mass Flow Reference System

The system is shown in an elementary schematic in Figure 1 and thermodynamically in figure 2. The cyclic process is continuous with only power to the pump and refrigerant to the subcooler as requirements. Liquefied gas subcooled under moderate pressures (0.7 MPa) is fed to the inlet of the pressure pump 1. The pump is of the turbine type to minimize flow pulsations and capable of pressurizing the liquefied gas to above critical pressures ($\sim$ 4 MPa) at 2. This single phase compressed fluid is then fed to the first pass of the counter flow regenerative type heat exchanger where it is heated to ambient temperature or above at 3. An electric heater is installed at this point to stabilize the gas temperatures. The gas meter test section contains all necessary upstream and downstream flow conditioning such as pipe length, flow straighteners, the meter and all other standard meter run equipment. Gas leaving the gas meter test section will be at a lower pressure (depending on the meter type) and at a different temperature (depending on test and ambient temperatures) at 4. The gas

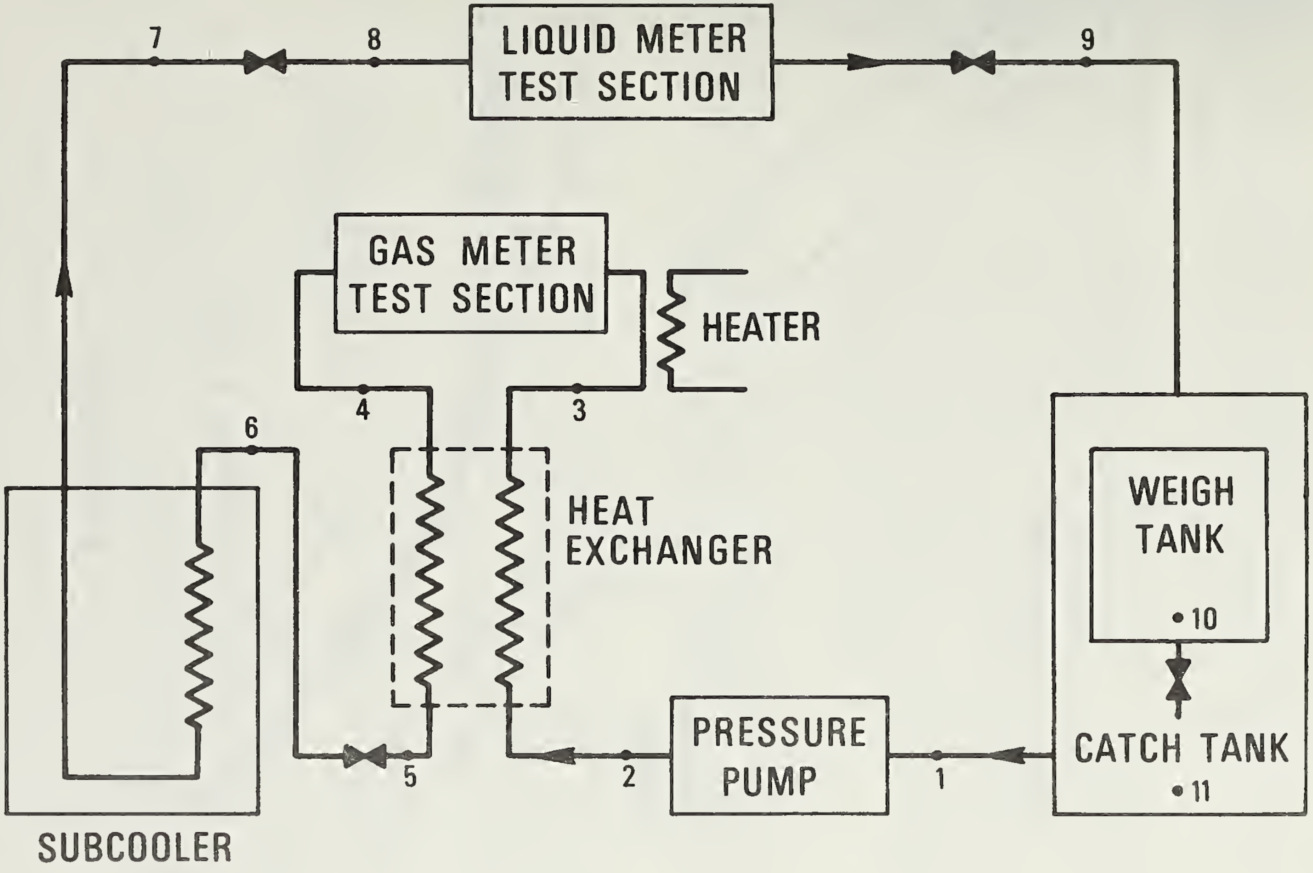

Figure 1. Gas flow measurement system schematic for operation at greater than critical pressures.

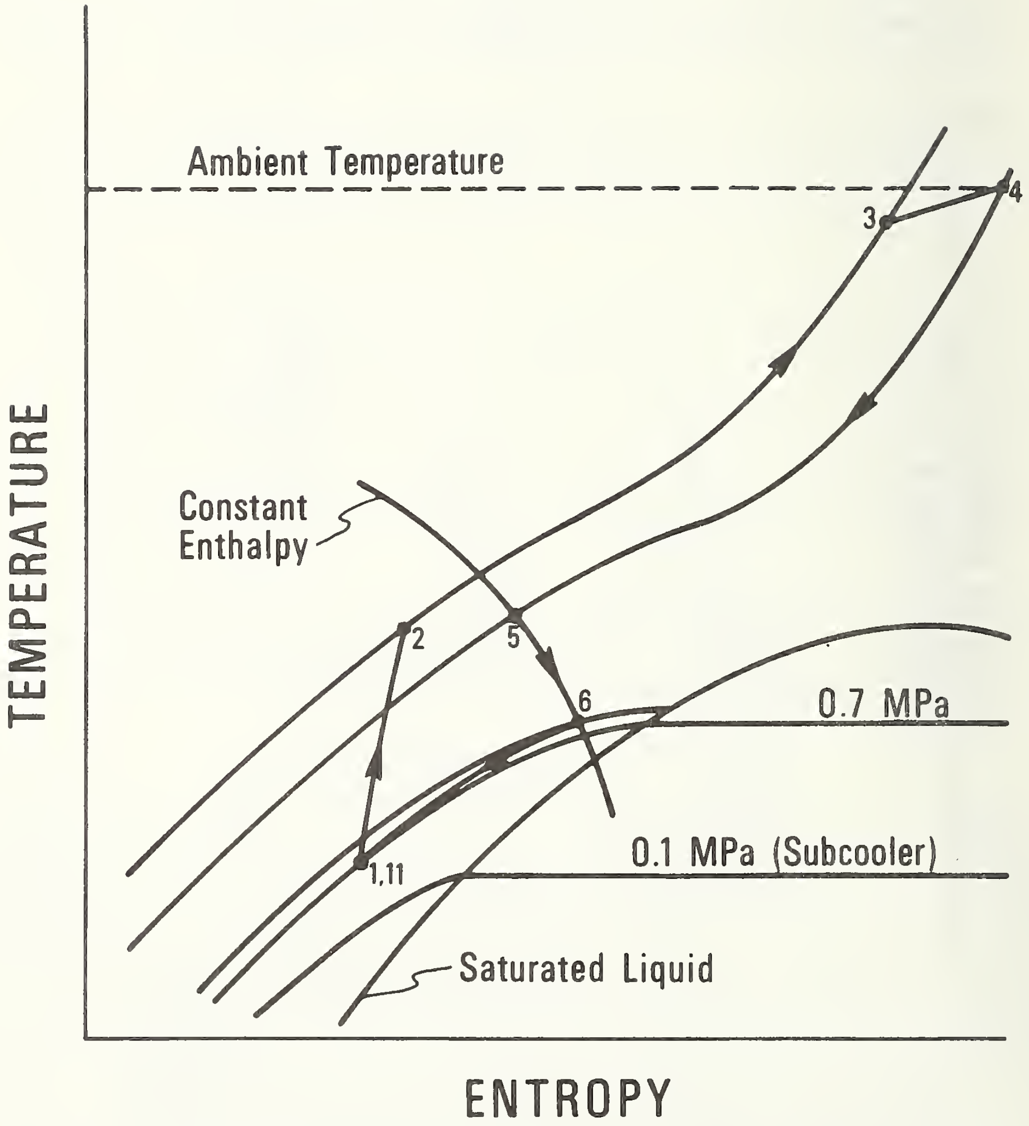

Figure 2. Operation of flow measurements system at above critical pressures.

will then be fed to the second pass of the counter flow heat exchanger where it leaves as a compressed fluid at cryogenic temperatures at 5. The pressure of the fluid is reduced by a simple expansion through an expansion valve to moderate pressures ($\sim$ 0.7 MPa) and fed to the subcooler at 6. The subcooler provides a controlled liquid temperature prior to the liquid meter test section.

The liquid meter test section contains all necessary liquid flow treatment and the cryogenic flowmeter. This meter can be of the same type and design as the gas meter or can be a proven cryogenic meter used as a secondary standard.

After metering, the liquid enters the catch and weigh system which are shown as concentric containers. The weigh tank is supported on a load string and a load cell. Load cell calibration is maintained with standard weights referenced to NBS standards of mass.

At periodic intervals the drain valve in the weigh tank is closed and a quantity of cryogenic fluid is accumulated in the weigh tank 10. The time required to accumulate a given weight of liquid is measured and the mass flow rate calculated. The weigh tank drain valve is then opened and the liquid cryogen is released to the catch tank 11.

Pressures within the catch and weigh tank are maintained above the fluid saturation pressure by inert gas pressurization to maintain subcooling and to eliminate flashing after expansion at point 6. The actual pressure selected will also depend on the pressure ratio available from the pressure pump.

The schematic of figure 1 is the simplest equipment arrangement and will allow operation of gas meters above the critical pressure and with low pressure drop through the gas meter. These conditions can be met with flowmeters with 100 in. water pressure loss such as orifice meters, venturi meters, some turbine meters and most non-intrusive type flowmeters.

For operation at pressures below critical pressure, some additional equipment must be added. Figures 3 and 4 show these modified arrangements.

In figure 3, a low-head high-volume flow circulation pump is used in place of the pressure pump. A boiler and heat source are added to vaporize the liquid prior to heating to ambient temperatures and a condenser is required to reliquefy the gas prior to subcooling. This additional equipment is made necessary because the temperature of condensation of the fluid from the gas meter test section is equal to or less than the boiling point temperature of the fluid discharged from the circulation pump. A high capacity blower could be installed at the outlet of the gas meter test section to increase the pressure and therefore the saturation temperature, but this would defeat one of the advantages of the method which is low power requirements and simplicity.

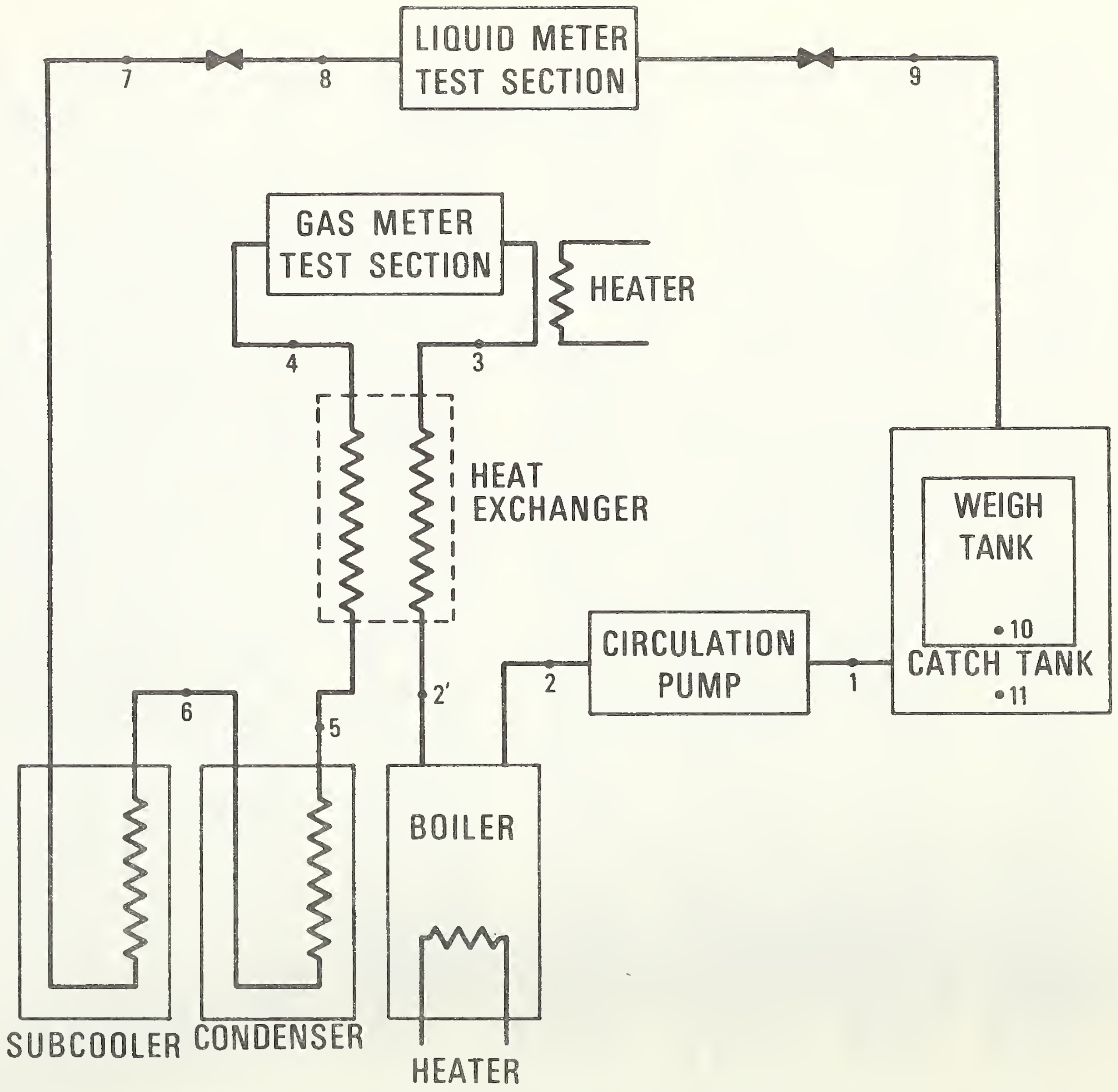

Figure 3. Gas flow measurements system schematic for operation at less than critical pressures.

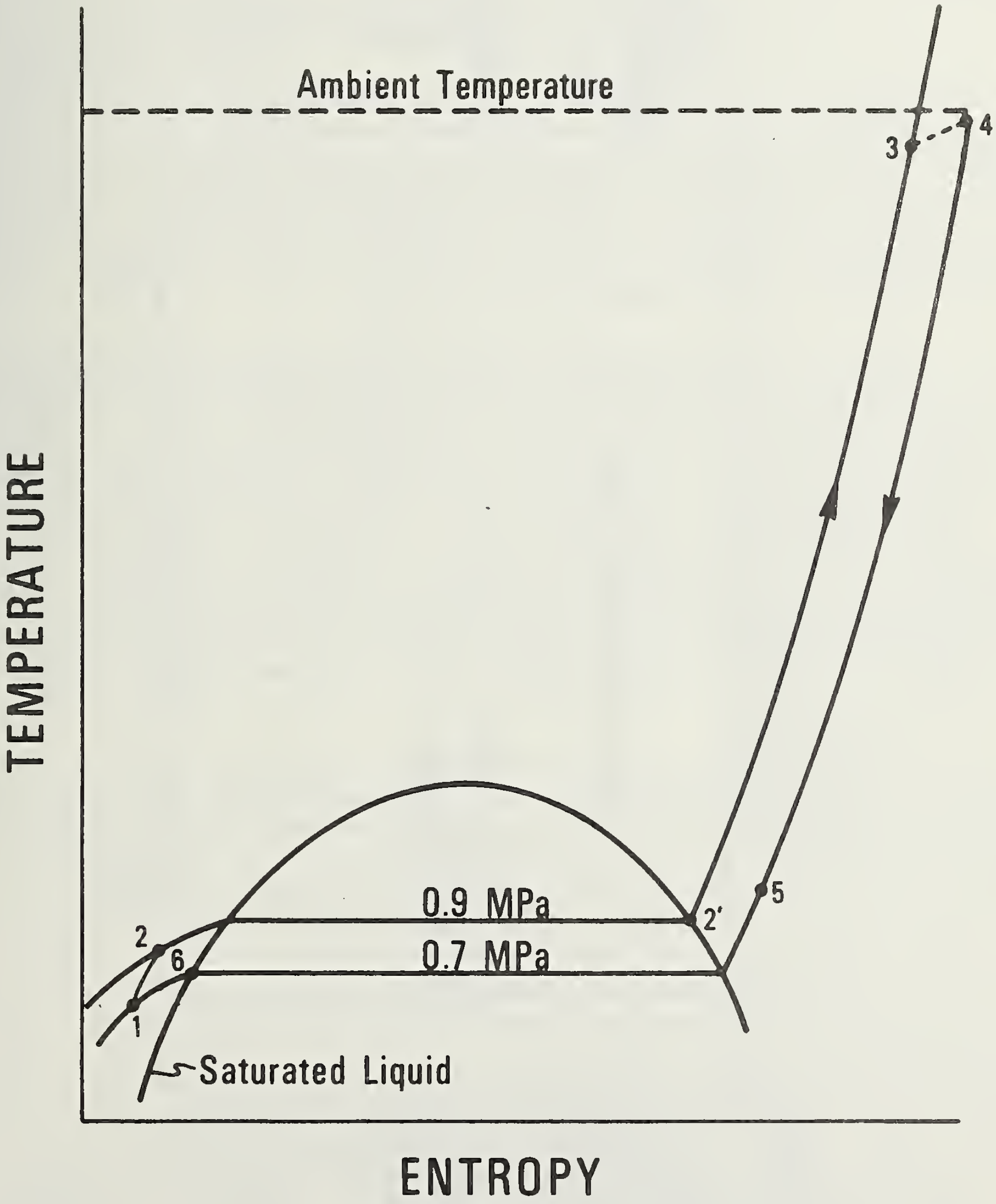

Figure 4. Operation of flow measurements system at less than critical pressures.

For the special case of large meter pressure losses, such as choked nozzle flow, a combination of the two cycles would be necessary. The pump must be a pressure pump, as in figure 1, to provide the necessary high pressur at the gas meter inlet; however, a condenser and heater will be necessary as in figure 3, to provide external heating of the high pressure stream and condensation of the low pressure stream. No pressure reducing valve would be required.

3. Liquid Mass Flow Reference System

In the gas mass flow measurement system just described, the actual mass flow measurement takes place while the gas is in its liquid phase. For commercial industrial gases such as oxygen, nitrogen, argon, methane and natural gas mixtures, the liquid phase is in the cryogenic temperature region. This is a fortunate situation because we can establish the potential limiting accuracy of the gas mass flow system by referring to an existing cryogenic liquid mass flow measurement system.

The cryogenic flow measurement reference system was established in 1968 in a joint government-industry program on cryogenic flowmetering. Under that program, NBS joined with the Compressed Gas Association and state regulatory agencies to establish a flow reference system, to evaluate existing flowmeters used in commercial service, to evaluate new measurement methods and to establish a national model cryogenic flow measurements code through the National Conference on Weights and Measures. A schematic of the facility constructed under that program is shown in figure 5. The similarity to the previously described gas mass system is obvious. The basic operating principles of the two systems will be very similar and the basis for the estimate of uncertainty in mass flow measurement should be identical.

The cryogenic flow measurement program was completed in 1976 with the acceptance of a permanent cryogenic flow measurement code by the Conference on Weights and Measures. The description of the facility and program are well documented in the literature (see references). The most pertinent reference to this discussion of the gas mass flow system is the work of Dean, et al. (1971). This report is a summary of an 18-month study to determine the accuracy of the flow reference system, "At this time the uncertainty of the measurement of totalized mass flow is estimated to be ±0.18%. This figure includes an uncertainty of ±0.12% for known sources of systematic errors plus an uncertainty of ±0.06% for random error. The estimated uncertainty due to the random error is three times the standard deviation calculated from 23 applications of the calibrated masses over a period of three months." The report provides a complete description and data on how this accuracy statement was determined and, in addition, provides a description of the process control which allows the reference system to be kept under statistical control.

Over sixty flowmeters based on five different generic types were included in the evaluation program. Transfer standards were developed for field certification of commercial meters as well as being used in inter-laboratory

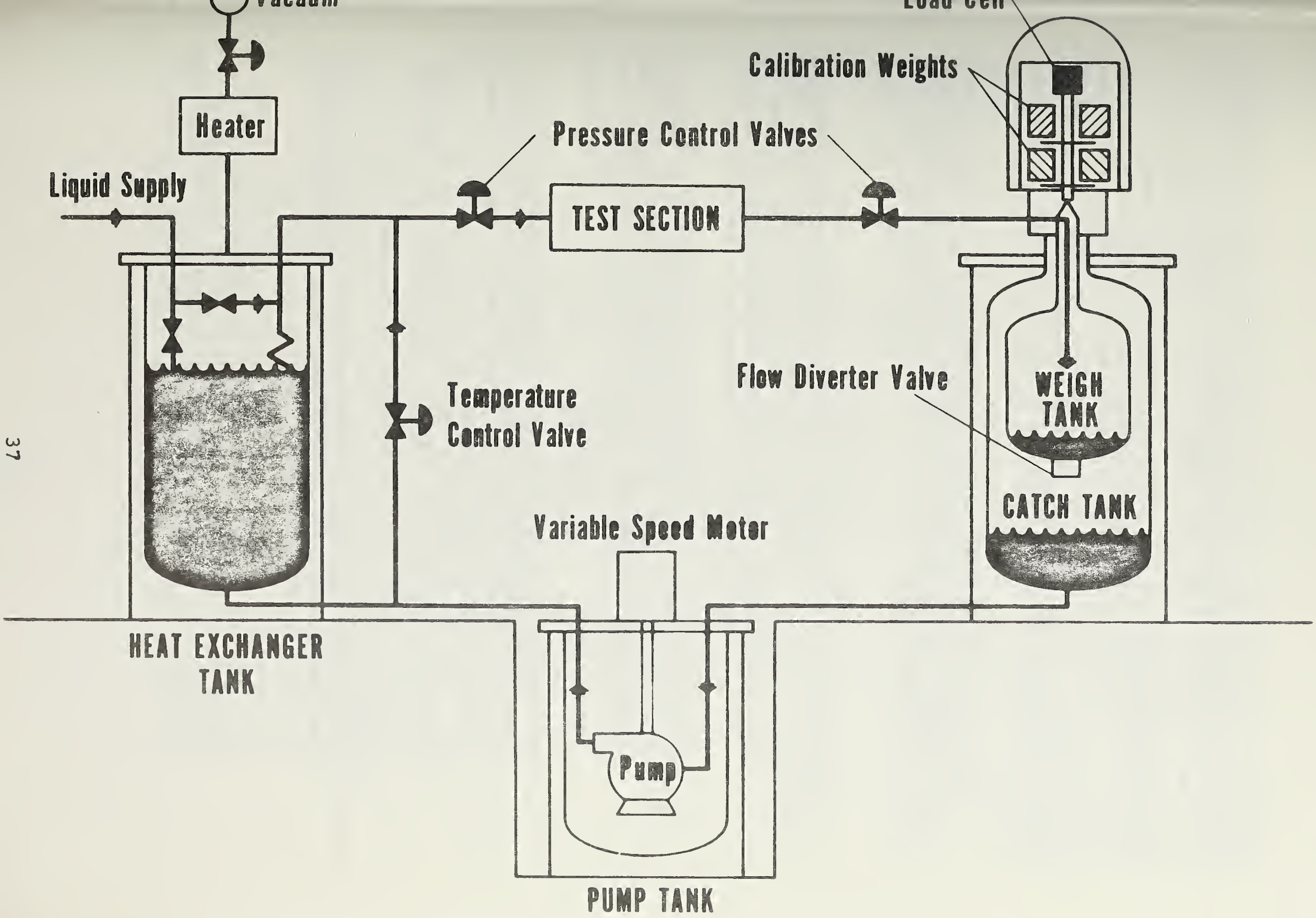

Figure 5. Cryogenic flow measurements reference facility schematic.

comparisons which provided additional validity to the accuracy statement. Confidence in the ability of this system to provide a mass flow measurement was established in almost 4000 hours of operational experience. The report itself was a provisional accuracy statement and during the six years of operation, more precise measures of systematic error have been made which should allow the uncertainty statement to be improved significantly. However, if the accuracy of this system could be maintained while adding a regenerative heat exchanger and gas flowmeter test section, the improvement in measurements of a gas mass flow reference would be significant. Present estimates of the latter are between plus or minus one and two percent, therefore, an improvement could be realized of between five and ten over present methods.

The process fluid used in the facility of figure 5 is nitrogen although argon has also been used successfully. The system itself could be adapted to other cryogenic fluids such as air, oxygen, hydrogen, methane, ethane, propane and liquefied natural gas.

4. Applications

The potential for such a system, if the total uncertainty can be maintained at ±0.2% or less, is impressive and would allow the following studies:

- Redefinition of gas flowmeter factors relative to mass flow directly and continuously. No intermediate calculations or approximations are required.
- Gas flow pressures and temperatures could be controlled independently of the mass flow reference and would allow wide variations in experimental conditions. An added benefit, particularly in the case of nitrogen as the process fluid, would be that the Reynolds number can be increased by a factor of 4 or 5 by reducing the temperature and therefore the viscosity of the gas.
- Gas flowmeter performance could be compared directly with existing codes and standards which are based on volumetric or water calibration predictive calculations. Errors in predictive correlations could be identified and corrected.
- The working hypothesis that water calibration may be transferred directly to gas flow can be tested to an accuracy not previously possible. Errors in this hypothesis can be identified and corrected.
- The effects of upstream and downstream meter flow conditioning (straight runs and/or flow straighteners) can be redefined with gas flow with greater accuracy than previously available.
- Evaluations of potential gas flow transfer standards on a long term mass flow basis. This would include such devices as the choked nozzle and other new devices such as the laser Doppler velocimeter or ultrasonic meters, the success of which would make gas flow or water flow reference systems increasingly unnecessary.

- An evaluation of velocity effects on direct reading densitometers. This work would be in support of the development of a natural gas energy meter.
- As a precision reference system, test sections could be used to investigate the development of boundary layer and turbulence, and the effects of these phenomena on gas meter size.

Component design would be heavily influenced by the selection of the fluids to be used. If multiple fluids were to be tested, then components must be designed for the most severe conditions. This would particularly be the case in the selection of pressure pump and regenerative heat exchanger. Table 1 is the result of calculations made on two different applications. The methane/LNG system was based on a flow rate of 16.4 cubic meters per second (50 MMCFD). It is believed that a system of this size would meet many of the natural gas industry requirements for flow calibration in meter studies.

The nitrogen example is basically a modification of the existing cryogenic flow facility to demonstrate the feasibility of the gas flow measurement reference system. The gas flow rate of 1.2 cubic meters per second (2750 SCFM) would be of such a capacity as to allow testing of existing codes and practices and at the same time would not require a large investment in heat exchange or pressure pump equipment.

Other applications are also possible and a reduction in size of the facility for small flow should also be feasible. This suggests that a small portable gas measurement mass flow standard could be constructed and used routinely for field calibration and certification of meters.

5. Summary

Direct comparison of ambient temperature gas flow measurements to mass is made possible by a new continuous closed loop measurement method. The direct comparison is made possible by modification of a proven flow reference system based on mass–time. The anticipated total uncertainty in mass flow of gas at operating conditions should not exceed ±0.2%. This is an improvement of a factor of 5 to 10 over existing gas flow standards.

At a time when natural resources and raw materials are decreasing in quantity and increasing in cost, it is believed that new measurement methods, such as proposed, are essential to provide the necessary measure of accuracy and precision for establishing product quantity and value.

Table 1. Examples of application of gas mass system.

	Methane/LNG	Nitrogen
Gas Side		
* Flow rate (m^3/s)	16.4	1.2
Pressure (MPa)	5.5	3.4
Temperature (K)	289-300	289-300
Pipe diameter (cm)	20-25	10-15
Heat Exchanger		
Heat transfer load (MJ/s)	9.27	0.52
Liquid Side		
Weigh tank capacity (m^3)	3.8	0.379
Catch tank capacity (m^3)	5.7	0.433
Pressure (MPa)	0.83	0.69
Temperature (K)	100.0	80.0
Pipe diameter (cm)	10.0	7.6
Pressure Pump		
Flow rate (m^3/s)	0.027	0.0019
Pressure ratio	6.6	5.1
Power Requirement (kJ/s)	395.0	16.04

* @0.1 MPa and 289 K(14.73 psia and 60 F)

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

   Principal Investigator. Neil A. Olien

2. Cost Center Number. 7369574

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

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

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

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

7. Program and Results. Four issues of the LNG Quarterly are prepared each year and distributed. There are now 131 subscriptions going to AGA Member Companies and 153 to other subscribers.

   The size of the four comprehensive bibliographies mentioned in section 5 above has grown to the extent that their usefulness is limited, therefore it was decided that they would not be updated and a series of more specialized bibliographies would be made available. The following list gives those currently available. Additional topics will be added as necessary. The listed bibliographies were updated in August 1979.

B-1820	LIQUEFIED NATURAL GAS STORAGE INCLUDING INSULATION SYSTEMS. 225 pages, 1264 references, author and subject indexes	$20.00
B-1821	LIQUEFIED NATURAL GAS PEAKSHAVING AND SATELLITE OPERATIONS. 39 pages, 230 references, author index	$10.00
B-1822	LIQUEFIED NATURAL GAS STRATIFICATION AND ROLLOVER. 10 pages, 40 references, author and subject indexes	$ 5.00

B-1823	LIQUEFIED NATURAL GAS SAFETY INCLUDING SPILLS. 82 pages, 421 references, author and subject indexes	$10.00
B-1824	LIQUEFIED NATURAL GAS PIPELINES AND TRANSFER LINES. 48 pages, 249 references, author index	$10.00
B-1825	LIQUEFIED NATURAL GAS SHIPS, BARGES AND OVERWATER TRANSPORTATION. 154 pages, 892 references, author index	$15.00
B-1826	LIQUEFIED NATURAL GAS VAPORIZORS INCLUDING COLD UTILIZATION. 64 pages, 356 references, author and subject indexes	$10.00
B-1827	LIQUEFIED NATURAL GAS HEAT TRANSFER. 38 pages, 170 references, author index	$10.00
B-1828	LIQUEFIED NATURAL GAS LIQUEFACTION AND REFRIGERATION. 102 pages, 585 references, author and subject indexes	$15.00
B-1829	LIQUEFIED NATURAL GAS ECONOMIC FACTORS. 92 pages, 513 references, author index	$15.00
B-1830	LIQUEFIED NATURAL GAS OVERLAND TRANSPORTATION. 15 pages, 81 references, author index	$ 5.00
B-1831	LIQUEFIED NATURAL GAS PATENTS. 250 pages, 1595 references, author and subject indexes	$20.00
B-1832	LIQUEFIED NATURAL GAS INSTRUMENTATION. 30 pages, 110 references, author and subject indexes	$ 5.00

8. Problem Areas. None.

9. Level of Effort. July 1 - December 31, 1979.

Staff-years expended	0.25
Equipment and/or Services Purchased	3.5K$
Approximate expenditures, total	9.4K$

10. Future Plans. Issue 79-4 was delivered to the printer the third week of January and should be distributed in early February.

79-WA/HT-19

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$3.00 per copy $1.50 to ASME Members

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345 E 47 St., New York, N.Y. 10017

Present and Future Sources of Fluid Property Data

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Fluid Property calculations for the design and operation of large process systems require that the data used by the engineer be in a computer compatible form. This, in turn, places complex demands on those of us in the data generation and correlation field. The responsibility of the producers of data, i.e., experimentalists, theorists or correlators, to the ultimate users of the data such as design engineers is discussed, because the efficient transfer of data from the originator to the ultimate user is absolutely essential. The specific requirements for data in the future will be for 'black box' type computer-compatible routines to calculate broad ranges of thermophysical properties for pure fluids and mixtures. Although calculational packages are very useful tools, reliance on them by the uninformed can lead to costly design errors and there is some evidence that the existence of the packages may tend to reduce future research in fluid properties. Generic solutions to the future data requirements of the chemical process and energy industries will place heavy reliance on theoretical approaches. Illustrations of the future data requirements of specific industries are given as examples.

ABSTRACT

Fluid Property calculations for the design and operation of large process systems require that the data used by the engineer be in a computer compatible form. This in turn places complex demands on those of us in the data generation and correlation field. The responsibility of the producers of data, i.e., experimentalists, theorists or correlators, to the ultimate users of the data such as design engineers is discussed, because the efficient transfer of data from the originator to the ultimate user is absolutely essential.

The specific requirements for data in the future will be for 'black box' type computer-compatible routines to calculate broad ranges of thermophysical properties for pure fluids and mixtures. Although calculational packages are very useful tools, reliance on them by the uninformed can lead to costly design errors and there is some evidence that the existence of the packages may tend to reduce future research in fluid properties. Generic solutions to the future data requirements of the chemical process and energy industries will place heavy reliance on theoretical approaches. Illustrations of the future data requirements of specific industries are given as examples.

INTRODUCTION

We have witnessed an increasing emphasis on more sophisticated forms of fluid property data over the past several decades. One large factor in this emphasis was the emergence of the aerospace industry and the many requirements imposed by NASA, some of which were described in the previous paper (1). The modern computer, of course, was another major factor, but NASA and its stringent demands for very high accuracy and reliability truly set us on a path from looking up discrete values in handbooks to representing a continuum of properties with computer programs. One of the pioneering efforts in this was the refinement of the Benedict-Webb-Rubin equation of state by Strobridge (2), an effort which was only possible because of the modern digital computer. Calculations, as such, however, are not new. James Conant, the former president of Harvard tells a story, perhaps apocryphal, that took place during World War I (3). When President Wilson appointed a board, with Thomas Edison as chairman, to give scientific advice to the Navy during the course of the war, one of the members chosen by Edison was a physicist from the National Bureau of Standards. Edison told the President that the reason for the presence of the physicist was, "we might have one mathematical fellow in case we have to calculate something out." I am not sure whether the story is appropriate or not in this centenary of Edison's greatest invention (4). Some things have changed since 1918. The direction we are taking in mathematical modeling and the concurrent rapid increase in speed and storage capacity of computers means that the changes will come at an even faster rate. The advent of the microprocessor and other offspring of large scale integration serve to magnify this trend. Those of us producing data must be prepared to be active participants in the introduction of our data and the form of our data into industrial automation. We must work with current and emerging industries to see that they have the best data and formulations available for their use. It is not enough to make excellent measurements, develop magnificent equations of state and the like. I can say from experience that the

Contributed by the Heat Transfer Division of The American Society of Mechanical Engineers for presentation at the Winter Annual Meeting, New York, N.Y., December 2-7, 1979. Manuscript received at ASME Headquarters August 10, 1979.

Copies will be available until September 1, 1980.

probability of use of data, models, etc. in industry approaches zero as the estoric nature of the data and models increases. To put it bluntly, if data are difficult to find or hard to use they just will not be utilized. The automation trend mentioned previously serves only to strengthen this tendency. I say this despite the large economic incentives of using more accurate data.

ECONOMIC IMPACT AND LEVERAGE

There have been several studies and estimates made of the economic impact on selected industries of inaccuracies in fluid property data (5,6,7,8,9). One such study is included in this meeting of the ASME. (10). David Zudketvitch has done a great deal in this field and has recently shown (11) that the capital and operating costs of several types of plants can be significantly reduced as a result of increased accuracy (reliability and reduced error bands) of thermophysical property data. Table 1 shows the relative importance of several kinds of data on the design of various parts of process plants.` The information in this table is taken from the pioneering work of Zudkevitch (12). It is readily apparent that phase equilibria data are the most vital. This is because the equipment (heat exchangers, distillation columns, compressors, etc.) associated with fluid separation processes is the most capital and energy intensive part of process plants. The large number of liquid-vapor equilibrium correlation techniques gives further credence to the industrial importance of this class of thermodynamic properties. It is reasonably well established, then, that the accuracy of the thermophysical property data of fluids can have a significant economic impact on the industries in which these fluids are used. Let us now look at the magnitude of this potential economic impact.

The chemical process and fuels industries have current annual capital requirements in excess of $50 billion, with the bulk of this in conventional processes and feedstocks. The period 1979-2000 however is a period of transition for these industries with a change to unconventional base feedstocks (principally coal). As an example the American Gas Association has estimated the capital requirements for coal gasification/synthetic gas (SNG) for the period 1978-2000 to be $62.9 billion (see table 2). Liquefied natural gas (LNG) requirements will also be substantial with $7.9 billion for import terminal construction alone in the period 1978-1990. If we add to this the capital requirements for associated distribution and storage systems and dedicated auxiliary plants (e.g., air separation plants for coal gasification and LNG peak shaving facilities) we have projected total requirements in the period 1978-1990 of $83.6 billion and in the period 1991-2000 of $91.5 billion. This $175.1 billion in capital investment will be for process plants and associated equipment involving fluid mixtures ranging from six to eight component LNG to 20 plus component mixtures in coal gas plants. If we remember that this is for supplemental gas for the gaseous fuel industry we can get some idea of the magnitude of the projected capital costs for the total of industries involving mixtures. The potential savings in new plant construction and modification of existing plant as a result of the availability of more accurate data and models is of

Table 1.

RELATIVE IMPORTANCE OF SOME THERMODYNAMIC VARIABLES ON DESIGN AND PERFORMANCE - EVALUATION OF BASIC PETROCHEMICAL PROCESS EQUIPMENT

	VAPOR PRESSURE AND:						RATE DATA	
	DENSITY P-V-T	CRITICALS	PHASE DISTRIBUTION	ELECTROLYTE IONIZATION	ΔH And C_p	ΔS	TRANSPORT	REACTION
REACTORS	C	D	B	S	B	B	B	A
FRACTIONATORS	B	B	A	A	B	D	B	S
EXTRACTORS	B	D	A	D or S	C	D	B	S
HEAT EXCHANGERS	C	B	A	S	A	C	B	S
COMPRESSORS & EXPANDERS	A	A	A	...	A	B	D	S
METERING (AND SALES)	A	...	B	...	S	...	...	....
MATERIALS OF CONSTRUCTION	B	...	B	A	...	...	...	S
POLLUTION ABATEMENT	...	...	A	A	C	...	A	A

KEY:
A - Most important
B - Very important
C - Influences calculations, but accuracy not critical
D - Considered only in preliminary selection
N - Not applicable
S - Important in specific cases

Table 2. Capital Requirements - Supplemental Gas for U.S.
(Billions of 1977 Dollars)

	1978-1990	1991-2000	Total
Coal Gasification/SNG	20.4	42.5	62.9
LNG Importation	7.9	2.0	9.9
Transmission, etc.	55.3	47.0	102.3
Total	83.6	91.5	175.1

Source: Anderson, R., AGA Monthly 60, 30-3 (Apr 1978).

the order of tens of millions of dollars per year. The studies mentioned above also tell us that the savings in operating costs over the life of the plant can be even greater than the savings in capital costs.

EXISTING TABLES OF FLUID PROPERTY DATA

Although there is a strong trend today toward the use of computerized models for calculating fluid property data, tables of property data are still widely used. Table 3 lists some of the more useful of the existing collections which include data on many fluids. You will note that there is a lack of uniformity in the sources of these publications.

Table 3. Collections of Fluid Property Data

LNG MATERIALS AND FLUIDS - A USER'S MANUAL OF PROPERTY DATA IN GRAPHIC FORMAT, D. B. Mann, Editor, National Bureau of Standards, Thermophysical Properties Division, Boulder, CO 80303 (1977) (Supplement 1 - 1978; Supplement 2 - 1979)

THERMOPHYSICAL PROPERTIES OF MATTER/THE TPRC DATA SERIES, Y. S. Touloukian and C. Y. Ho, Editors, Plenum Press, N.Y.

SELECTED VALUES OF PROPERTIES OF HYDROCARBONS AND RELATED COMPOUNDS, Thermodynamics Research Center, Texas A&M Univ., College Station, TX 77843 (also a companion volume on other chemical compounds)

GAS ENCYCLOPAEDIA, L'Air Liquide, Division Scientifique, Elsevier/NorthHolland, Inc. (1976)

ENGINEERING DATA BOOK, Gas Processors Assn., Tulsa, OK (1972)

ASHRAE THERMODYNAMIC PROPERTIES OF REFRIGERANTS, Amer. Soc. of Heating, Refrigerating and Air Conditioning Engrs., 345 East 47th St., N.Y. 10017 (1969)

THERMODYNAMIC PROPERTIES AND REDUCED CORRELATIONS FOR GASES, L. N. Canjar and F. S. Manning, Gulf Publishing Co. (1967)

PHYSICAL PROPERTIES - A GUIDE TO THE PHYSICAL, THERMODYNAMIC AND TRANSPORT PROPERTIES OF INDUSTRIALLY IMPORTANT CHEMICAL COMPOUNDS, C. L. Yaws, McGraw-Hill (1977)

MATHESON GAS DATA BOOK, W. Braker and A. L. Mossman, Matheson Gas Products, East Ratherford, N.J. (1971)

They have been prepared by societies, government agencies, private firms and universities. There are also a number of sets of standard reference data or at least quasi-standard data for equilibrium properties for individual fluids (see table 4). You will notice that some of these are in the process of being revised or at least new versions are definitely planned. The argon and carbon monoxide publications are in great need of revision, but to my knowledge, no definite correlations or critical evaluations are underway. In the case of argon, we have a fluid of relatively small industrial importance, but argon is used so much as a standard for predictions as well as for testing new apparatus that its importance cannot be overemphasized. The state-of-the-art in equations of state has increased significantly since the publication of the Argon Standard Reference Data (13) by the NBS-Office of Standard Reference Data. In addition, a large number of new measurements have been made. The other fluid needing a new correlation is carbon monoxide. I recently completed an informal survey on CO and found to my surprise, that the best wide range tables (14,15) are nearly a quarter of a century old. Another set of tables (16), of slightly newer vintage, does exist, but is limited to the temperature region below 300 K.

METHODS OF CALCULATING FLUID PROPERTY DATA

Many of the references given in table 4 include calculational methods (equations of state). Table 5 lists some calculational methods, the broadest of which is the recently revised Reid, Prausnitz and Sherwood (17). A number of computer calculation packages are available on time-sharing networks for a user fee or for outright purchase. There is even a computer package available in the Soviet Union called AVESTA as illustrated in figure 1. AVESTA stands for Automatic Variable Engineering System of Thermophysical Advance. There are dangers in using computerized calculation packages, since the user can derive a false sense of security about the accuracy of the data returned. The danger is amplified when the data are used directly in computer calculations for plant design and operation. In the latter case the engineer never sees the data and he or she does not have a chance to apply good engineering judgement to the fluid property data. Often higher level managers in technical firms develop a feeling that the calculation packages provide data which have very small or non-existent error bars. This is both disquieting and dangerous. I have heard of a vice-president in the LNG industry who stated that they did not need any more work on LNG phase equilibria, because his company subscribed to a computer package which provided all of that. To illustrate the folly of such a pronouncement, let us examine figure 2. Elliott, et al. (18) made a comparison of K-value calculations from ten different

Table 4. Standard Data for Individual Fluids

Fluid		Source
H_2		McCarty, R. D., NASA SP-3089 (1975)
He		McCarty, R. D., J. Phys. Chem. Ref. Data 2, 923 (1973)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 4, Butterworths (1977)
N_2 *		Jacobsen, R. T. and Stewart, R. B., J. Phys. Chem. Ref. Data 2, 757 (1973)
O_2		Roder, H. M. and Weber, L. A., NASA SP-3071 (1972)
F_2		Prydz, R. and Straty, G. C., NBS Tech. Note 392 Rev. (1973)
Ar		Gosman, A. L., McCarty, R. D., et al., NSRDS-NBS 27 (1969)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 1, Pergamon (1971)
CO		Din, F., Thermodynamic Functions of Gases, Vol. I, Butterworths (1956)
CO_2		Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 3, Pergamon (1976)
NH_3		Haar, L. and Gallagher, J. S., J. Phys. Chem. Ref. Data 7, 635 (1978)
CH_4		Goodwin, R. D., NBS Tech. Note 653 (1974)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 5, Pergamon (1978)
C_2H_6		Goodwin, R. D., et al., NBS Tech. Note 684 (1976)
C_3H_8 *		Goodwin, R. D., NBSIR 77-860 (1977)
n-C_4H_{10}		Goodwin, R. D., NBSIR 79- (1979)
i-C_4H_{10}		Goodwin, R. D., NBSIR 79- (1979)
C_2H_4 *		Angus, S., et al., Intern. Thermodynamic Tables of the fluid State - 2, Butterworths (1974)
C_3H_6 *		Juza, J., et al., Acta Tech. (Prague) 23, 425 (1978)

*Newer versions underway or planned.

Table 5. Calculation and Estimation Techniques

THE PROPERTIES OF GASES AND LIQUIDS, Third Edition, Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., McGraw-Hill (1977)

PHYSICAL PROPERTIES - A GUIDE TO THE PHYSICAL, THERMODYNAMIC AND TRANSPORT PROPERTIES OF INDUSTRIALLY IMPORTANT CHEMICAL COMPOUNDS, C. L. Yaws, McGraw-Hill (1977)

A NEW TWO-CONSTANT EQUATION OF STATE, D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam. 15, 59 (1976)(For a review of this and other phase equilibria models, see Renon, H., Fluid Phase Equilibria 2, 101 (1978)

A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF LNG DENSITIES, R. D. McCarty, Nat. Bur. Stand. Interagency Report, NBSIR 77-867 (1977)

COMPUTER CALCULATION SYSTEMS, some examples are: CHEMTRAN/CHEMSHARE, CHESS, GPA CONV, SSI, FLOWTRAN, PDA, PPDS, TAP, etc.

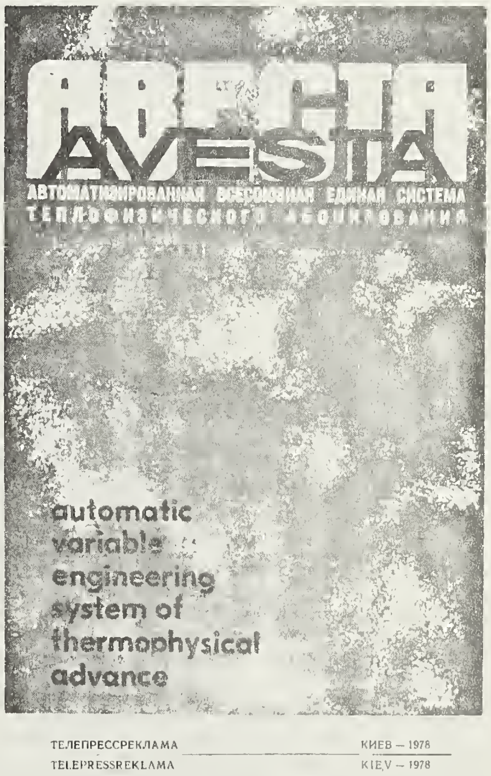

Figure 1. AVESTA-Automated Property Calculation Package from the USSR.

computer packages. K-values are very useful in designing separation plants and are defined as

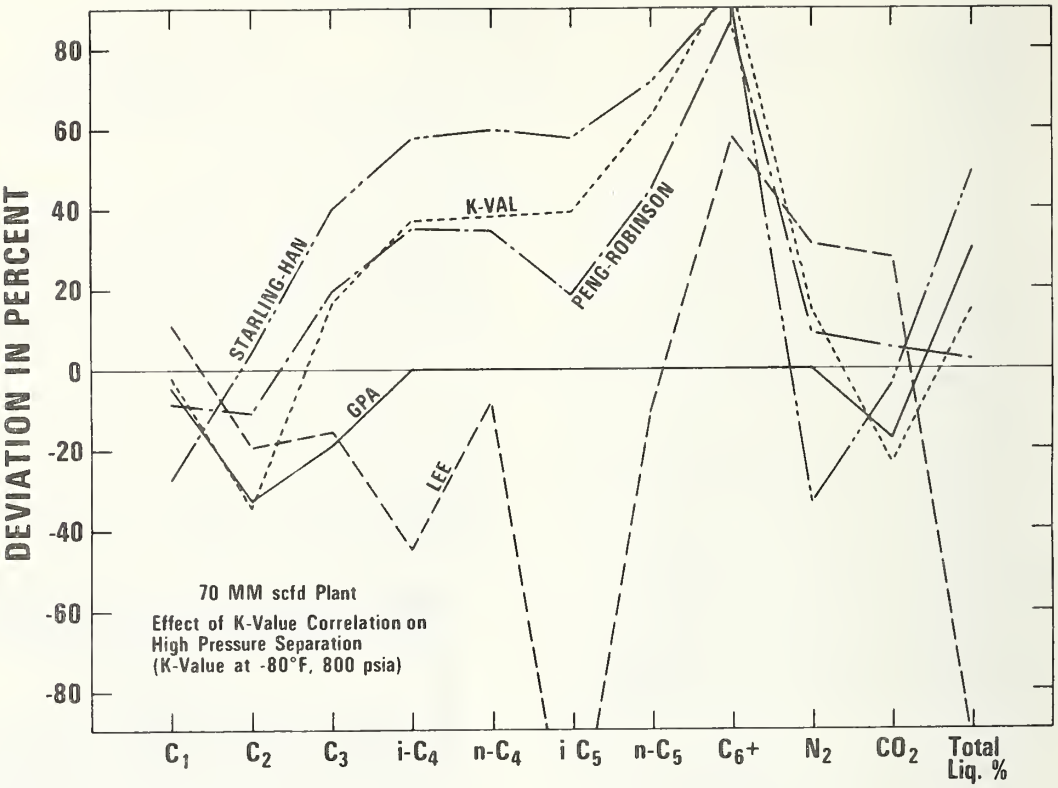

Figure 2. Comparison of K-Value Calculation Methods for Natural Gas.

K = y_i/x_i where: y_i = molar concentration of the i^{th} component in the vapor phase and x_i = molar concentration of the i^{th} component in the liquid phase.

In figure 2 I have shown the deviation of five of these methods from a sixth, arbitrarily chosen. The horizontal axis gives the molecular species (C_1=methane, C_2=ethane, etc.), and the last item is the total volume of all liquids condensed. I think it would be very difficult to maintain that any of those methods represents scientific truth. In fact, the methods examined by Elliott and presented here represent three different approaches to K-value predicting - i.e., conformal solution theory, van der Waals' techniques and empirical methods. One further disadvantage of the widespread availability of these packages was hinted at above. In a conversation with Professor Kobayashi of Rice University a few months ago, he and I agreed that the computer packages tend to stifle research. The attitude expressed by the vice-president mentioned above certainly does not encourage grants and contracts for needed research work. If it sounds as if I am advocating the elimination of calculation techniques, especially computerized methods, let me assure you that this is not the case.

DISSEMINATION OF FLUID PROPERTY DATA IN THE FUTURE

I firmly believe that computerized calculation methods for fluid properties, especially mixture properties, will become commonplace in the future. First, automation in design requires automation in data; second, data needs are so great as to demand the use of semi-automated calculations; and third, in the case of mixtures, tables are just not practical. How can we do this and still avoid the disadvantages described above? It is essential that calculational packages be accompanied by well documented and justified confidence limits, the existence and use of which is clearly understood by the users of the packages. In addition, the package should contain provisions for notifying the user when calculations are requested which are outside the range of the particular method used. What is needed is a 'truth in packaging' requirement for calculational techniques. A little earlier, I said that producers of data (experimenters, theorists or correlators) must be prepared to participate in the introduction of their data and models into industry. They must also do their part to prevent their data from being misused, i.e., unwarranted extrapolations. The objective should be wide-range and accurate models, which can be easily used and which, if they do not prevent improper use, at least clearly provide warnings of perils ahead. One of the blessings of the modern computer is the ease with which we can provide for warnings of this sort.

Often the engineer is either faced with a need for professional advice about calculational methods and data or is at a loss as to where to turn. In these cases, it is important to make a personal contact with knowledgable experts in fluid properties. Table 6 lists several 'Data' or 'Information Analysis Centers' which can be of great assistance to the engineer.

Table 6. Fluid Property Data Centers

Chemical Kinetics Information Center
NBS - Robert F. Hampson, (301) 921-1000, extension 2565

Chemical Propulsion Information Agency
Johns Hopkins, (301) 953-7100

Chemical Thermodynamics Data Center
NBS - Donald D. Wayman, (301) 921-1000, extension 2773

Cryogenic Data Center
NBS - Neil A. Olien, (303) 499-1000, extension 3257

Electrolyte Data Center
NBS - Bert R. Staples, (301) 921-1000, extension 3632

Thermodynamics Research Center
Texas A&M - R. C. Wilhoit, (713) 846-8765

Thermophysical Properties Research Center
Purdue - W. H. Shafer, (800) 428-7675

EXPANDED NBS PROGRAM IN FLUID PROPERTY RESEARCH

The Thermophysical Properties Division at NBS-Boulder has embarked on a long range effort to develop generic techniques for predicting the thermophysical properties of a broad range of industrial fluids. We are building on the experience we have gained through our participation in programs in liquefied natural gas (LNG) (primarily funded by the American Gas Association and the Gas Research Institute) and ethylene properties (a joint government-industry program, managed by the NBS-Office of Standard Reference Data). Our work has established a rational approach to the development of accurate and useful mathematical models. This approach involves the judicious marriage of experimental measurements, theoretical studies, mathematical modeling and a continuing interaction with current and future users of the models and data. The measurement aspect of this integrated program will occupy a substantial fraction of the available resources, but even at that we realize that the plan will be measurement limited. The measurements will be primarily on pure components and binary systems, with a strong need for very careful choice in fluids and measurement ranges. In addition the measurements must be of high quality, as the literature is replete with examples of measurements of little or no use because of the high uncertainty of the results. A purely experimental approach to mixtures properties rapidly leads to an infinite data requirement; therefore, theoretically based models must play a large role in the entire project. It is difficult to separate the theoretical efforts from the mathematical modeling work. We are conducting and have plans to accelerate our experiments wherein fluids are modeled in a computer by the techniques of molecular dynamics (19). These methods have the potential of becoming very powerful tools in the quest for a basic understanding of fluid behavior and the development of soundly based methods of predicting the properties of complex fluid mixtures. One area which requires a large amount of attention is the need for quantitative understanding of the interactions between unlike molecules. Included in this are molecules of disparate sizes (e.g., molecular mass ratios of 25 or greater) and even more complex interactions (e.g., polar-nonpolar interactions.)

All of this cannot be accomplished by one group in Boulder and we thus plan to continue a large number of very productive technical collaborations. Two of these are with the Thermophysics Division and the Office of Standard Reference Data, both located in the National Measurement Laboratory of NBS-Gaithersburg.

CONCLUSION

Even the person on the street is aware of the pervasiveness of the computer in all aspects of modern life, industrial and otherwise. This trend, will continue and people producing fluid property data and models must consider this trend in consideration of the future. These computerized mathematical models must be developed with a combination of intelligence and pragmatism. We must have a clear picture of our engineering customers and their requirements. They in turn must understand what they are getting from us and how best to use the tools we provide.

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1. Title. LIQUEFIED NATURAL GAS TECHNOLOGY TRANSFER

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

2. Cost Center Numbers. 7360403, 7364574, 7368574, 7360594, 5621510

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

4. Introduction. The liquefied natural gas program at the Thermophysical Properties Division of NBS Boulder represents an investment by industry and government agencies of over $7 million over the past six years. This investment was designed to develop reference quality properties data for both fluids and materials and instrumentation and measurement technology for the use of the LNG and related industries. Information developed under this program must be transmitted to the ultimate user in a timely and useful format. The classical publication methods of NBS most certainly provide the scientist and research engineer information in a form most useful to the academic or near academic community. However, as a result of extensive assessments of user requirements, it was found that an additional effective mode for technology transfer would be an LNG Materials and Fluids User's Manual. A complete outline and planned table of contents have appeared in previous semiannual reports. The Maritime Administration of the Department of Commerce and the American Bureau of Shipping agreeded to sponsor the first year's efforts on the materials section, and the American Gas Association, Inc. and the NBS Office of Standard Reference Data agreeded to sponsor the section on fluids and fluid mixtures. The project was begun on April 1, 1976.

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

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

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

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

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

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

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

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

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

7. Program and Results. The first edition of the User's Manual became available for distribution in September 1977. A complete description and ordering information are included as part of this report. Over 850 copies have now been distributed to sponsors and purchasers. New orders are currently coming in at the rate of about ten per week. The first supplement to the User's Manual is printed and 500 copies have been distributed

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

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

The second supplement has been completed. After some difficulty with extremely high bids, a reliable printer was engaged. The second supplement contains 28 graphs on composites, 6 on concrete, 27 updated graphs on structural materials, 15 graphs and 3 wall charts on propane properties and three graphs on mixture properties.

8. Problem Areas. Problems in compiling data and graph preparation delayed delivery of some of the materials property graphs to the printer by six weeks.

9. Level of Effort. July 1 - December 31, 1979

Staff-years expended	0.6
Equipment and/or Services Purchased	14.3K$
Approximate expenditures, total	46.7K$

10. Future Plans. This work is now essentially complete. We expect the final copy of the Second Supplement back from the printer in mid-January. A brochure, describing the supplement, will be mailed to current handbook owners shortly.

1. Title. OIML JOINT SECRETARIAT ON LNG MEASUREMENTS

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

2. Cost Center Number. 7360290

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

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

5. Objectives or Goals. Our objective is to accomplish the following goals.

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

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

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

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

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

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

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

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

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

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

Flow measurements of pure cyrogenic fluids will be the first of the recommendations generated under the proposed work plan. This will be accomplished by combining the existing U.S. and European codes for flow measurements. A working group has been formed of interested parties and the first draft of this recommendation should be ready for review by early 1980.

7. Program and Results.

8. Problem Areas. Staffing caused by press of other programs has caused some delay and has extended schedule, but does not cause additional problems.

9. Level of Effort. July 1 - December 31, 1979

Staff-years expended	0.06
Equipment and/or Services purchased	0.00
Approximate Expenditures	$5,000

10. Future Plans. Work will continue to combine the two existing codes. The codes have been reduced to specific subject elements and the element common to the two codes has been identified. Conflicting requirements are being noted and will be resolved by the working group. Requirements present in one code and absent in the other are also being identified and inclusion in the combined code will be resolved by the working group.

    Plans include preparation of the First Preliminary Draft by the working group.

NBS-114A (REV. 9-78)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 80-1626	2. Gov't. Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

LIQUEFIED NATURAL GAS RESEARCH AT THE
NATIONAL BUREAU OF STANDARDS

5. Publication Date

February 1980

6. Performing Organization Code

7. AUTHOR(S)

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, DC 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

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

See page ii

13. Type of Report & Period Covered

1 July 1979-31 Dec. 1979

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

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

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

The objective of this report is to:

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

2. inform all sponsoring agencies on related research being conducted at the NBS-NEL Themophysical Properties Division, NBS-NEL Mechanical Processes Division and NBS-NML Fracture and Deformation Division;

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

The work is supported by NBS and seven other agencies and represents the ollective expenditure of $676,900 during the 6 month reporting period. The contents f this report augment quarterly progress meetings for certain of our sponsors and rovide a perspective which is missing when the parts are viewed individually. istribution of this document is limited and intended primarily for the supporting gencies. Data or other information must be considered preliminary, subject to hange 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)*

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

18. AVAILABILITY ☐ Unlimited

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

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