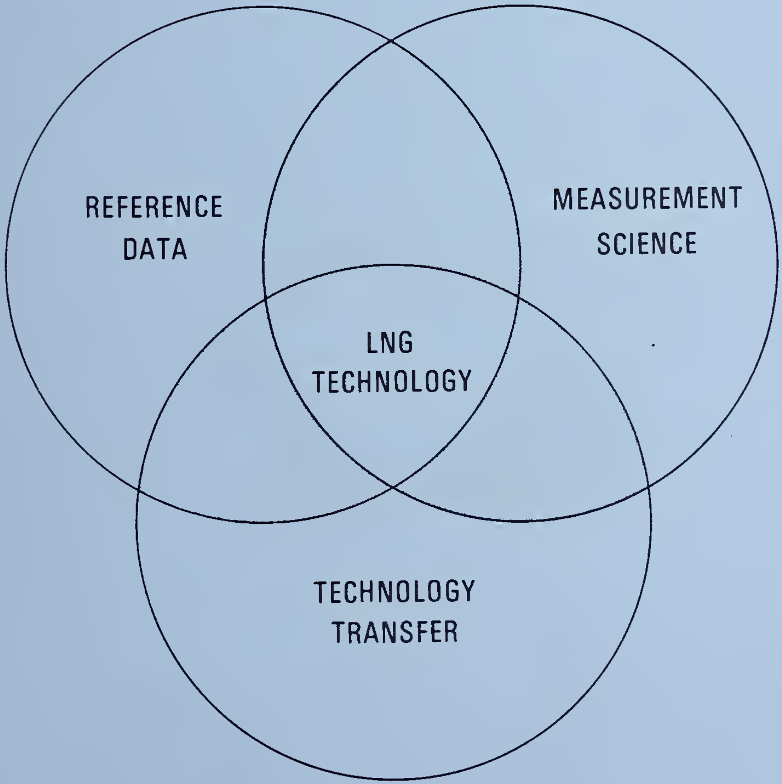
NBSIR 74-373

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

PROGRESS REPORT FOR THE PERIOD
1 JAN - 30 JUNE, 1974

D. B. Mann, Editor



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

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D. B. Mann, Editor

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

Progress Report for the Period
1 Jan - 30 June, 1974

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

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Prepared for:

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

Pipeline Research Committee
(American Gas Association)

Federal Power Commission
Bureau of Natural Gas
Washington, DC 20426

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

U. S. Department of Commerce
Maritime Administration
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National Bureau of Standards
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Washington, DC 20234

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

ABSTRACT

Seventeen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over $500,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.
2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.
3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paper work at the cost center level.

The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.

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

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III. Technology Transfer

1. Title. Refractive Index of Fluid Methane

   Principle Investigator. James D. Olson

2. Cost Center Number. 2750122

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

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

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

6. Background. The high precision interferometric technique used to measure the refractive index was developed in this laboratory by D. E. Diller (J. Chem. Phys. 49, 3096 (1968)). An improved optical data gathering method was the principal modification of this technique. Prior to this reporting period, a literature survey of Lorenz-Lorentz and Clausius-Mossotti virial equation data was conducted. A cryostat was constructed using the design of Diller. The temperature measurement problems described in the previous report were eliminated after modification of the apparatus in December and January.

7. Program and Results. All of the essential measurements of the refractive index of fluid methane were completed during this reporting period. These data include the saturated liquid and vapor and the gas isotherms above the critical point. Table 1 lists the saturation data. The measurements were made at the Hg^{198} green line, λ = 546.22705 nm.

   The refractive index data were combined with the experimental densities of Goodwin and Prydz[1] to calculate the Lorenz-Lorentz function,

$$LL = \frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} .$$

Figure 1 is a preliminary sketch of the trends exhibited by the LL function. A_r is the zero density limit of the LL function at 300 K. The saturated vapor LL data may be about 0.3%-0.5% too small because uncertainties in the vapor densities. The saturated liquid LL function decreases sharply at higher densities in contrast to the Clausius-Mossotti function previously obtained by Straty and Goodwin[2]. The LL data for all the gas isotherms are represented within 0.05% by the fitted equation, $LL = 6.6081 + (0.00679)\rho - (0.0003439)\rho^2$.

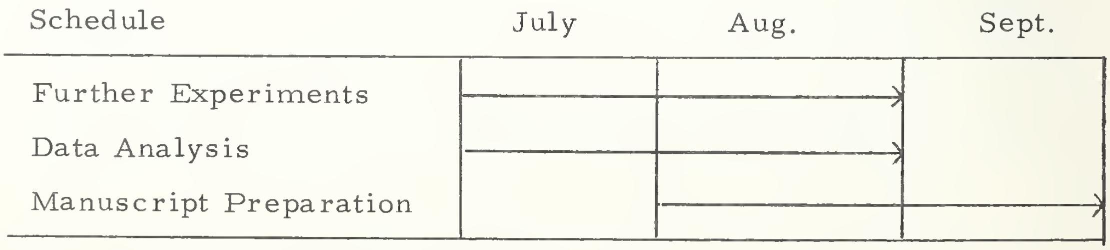
The critical refractive index, n_c, was obtained by use of the rectilinear diameter law on the saturated liquid and vapor refractive index data ($T_c = 190.555$ K). The critical refractive index was combined with an estimate of the critical LL function, indicated by the diamond on Figure 1, to calculate an estimate of critical density; $\rho_c = 10.15_5 \pm 0.01$ mole/ℓ. The critical density uncertainty was calculated from the error bounds on LL_c in Figure 1. This is a preliminary value and differs from that currently used. Further analysis will be necessary to determine the best value for the critical density.

8. Problem Areas. There are no problems at this time.

9. Funding. January 1 - June 30, 1974

Labor	0.5 MY	17.0 K$
Other Costs		4.0 K$
	Total	21.0 K$
	Remaining	8.5 K$

10. Future Plans. The data will be reduced and a manuscript prepared during the next two months. Some additional experimental data will be taken as well. This is an NRC-Postdoctoral Appointment which terminates near the end of September 1974 and thus, this effort will be completed prior to that time.



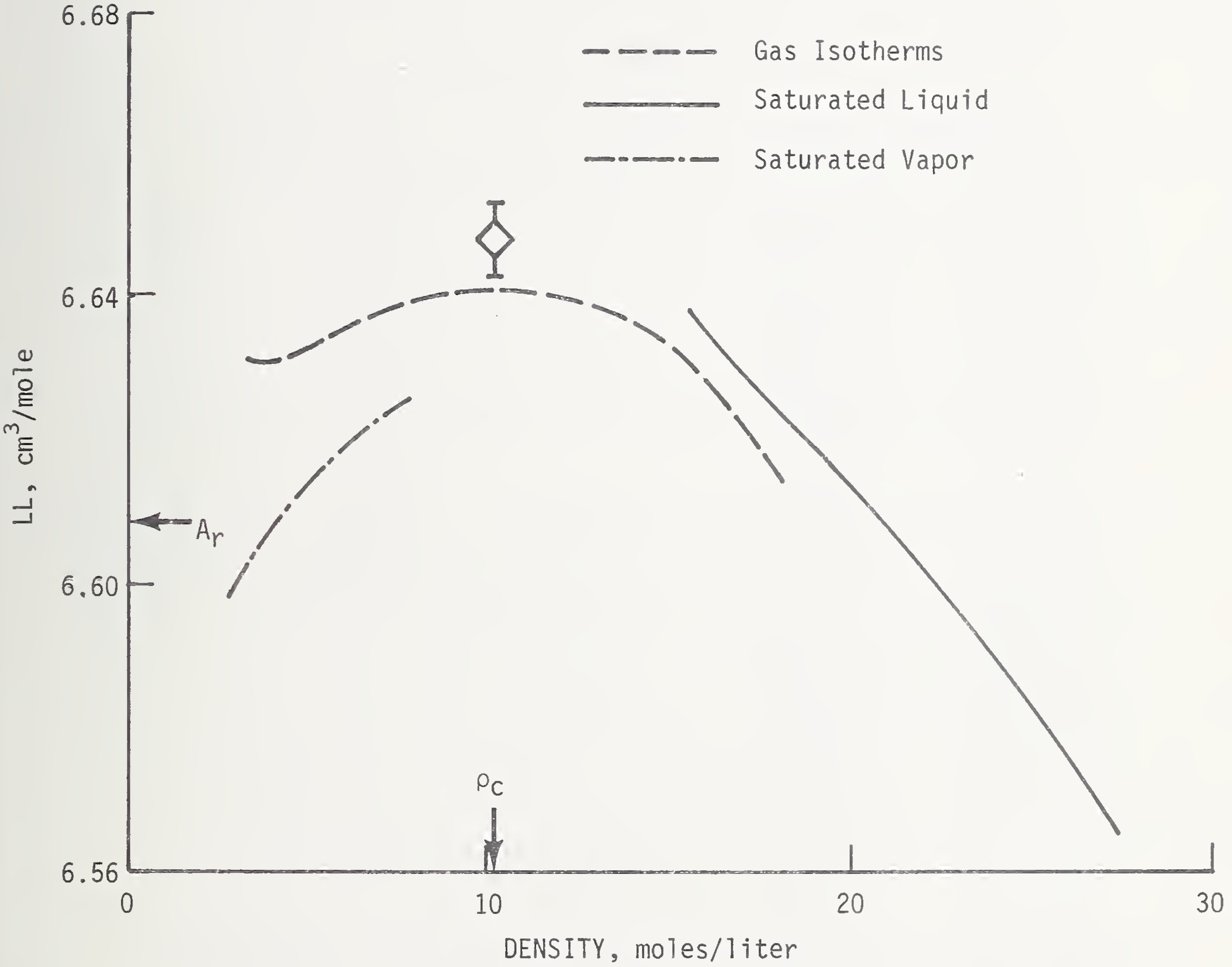


FIGURE 1. LL Function vs. Density

References.

1. R. D. Goodwin and R. Prydz, J. Res. NBS 76A, 81 (1972).
2. G. C. Straty and R. D. Goodwin, Cryogenics 13, 712 (1973).

Table 1. Refractive Index of Methane at Saturation

Saturated Liquid		Saturated Vapor	
T(K)	n	T(K)	n
95.000	1.291925	99.290	1.00041
100.000	1.287281	114.403	1.00139
105.000	1.282518	129.865	1.00374
110.000	1.277639	139.649	1.00622
115.000	1.272646	150.000	1.01016
120.000	1.267505	160.000	1.015746
125.000	1.262206	172.386	1.026976
130.000	1.256717	176.928	1.033134
135.000	1.251031	180.000	1.038404
140.000	1.245083	182.000	1.042540
145.000	1.238853	186.000	1.053738
150.000	1.232279	190.000	1.078959
155.000	1.225270		
160.000	1.217739		
165.000	1.209538		
170.000	1.200455		
175.000	1.190055		
178.000	1.182914		
180.000	1.177615		
181.000	1.174749		
182.000	1.171708		
183.000	1.168460		
184.000	1.164957		
185.000	1.161138		
186.000	1.156889		
187.000	1.152056		
188.000	1.146359		
189.000	1.139107		
189.404	1.135383		
190.555	1.10326_7*	190.555	1.10326_7*

*extrapolated n_c

1. Title. Fluid Transport Properties

   Principal Investigator. Howard J. M. Hanley

2. Cost Center Number. 2750124

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

4. Introduction. Studies of mixtures have not received the attention or support that have been given to equivalent studies of pure fluids. This is especially true for transport properties where the mixture effort has been negligible. Yet from the standpoint of the liquefied natural gas industry mixtures are more important than pure fluids. At this time there is no adequate method in existence for predicting the transport properties of fluid mixtures even in the dilute regions. Properties cannot be measured for all possible mixtures, thus adequate predictions methods are needed in order to supply the necessary design data needed to increase efficiency and reduce costs.

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

6. Background. A program was started in 1965 with the goal of producing tables of fluid transport properties through many approaches; e. g. , data correlation and evaluation, statistical mechanics, kinetic theory, thermodynamics and statistics. A theory was developed based on a modification of the Enskog theory. In addition, a systematic study of new potential function, the M-6-8. The theoretical studies along with data analysis results in prediction techniques for the dilute gas region for monatomic and polyatomic fluids. These techniques were then successfully extended to the dense gas and liquid regions. To date tables of transport properties have been prepared for argon, krypton, xenon, oxygen, nitrogen, fluorine and hydrogen. In addition an analytical representation of the anomalous behavior of the thermal conductivity coefficient in the "critical region"

has been developed. As a precursor to the study of fluid mixtures we have started a task to apply numerical techniques such as molecular dynamics to transport properties. To this end the Principal Investigator is in Australia gaining experience in advanced theoretical techniques. During the current reporting period a molecular dynamics model has been modified and applied to methane. The program has been run for a system of 108 methane molecules. The resulting output are, in effect, experimental data and will be compared with methane data and equations of state from the Cryogenics Division.

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

9. Funding. January 1 - June 30, 1974

Allocation	53.5 K$	OSRD
Labor	0.5 MY	20.3 K$
Other Costs		0.4 K$
	Total	20.7 K$
	Funding FY 75	53.5 K$

10. Future Plans. The mixture part of the program will begin after August 1974. If the methane calculations prove successful, it may be possible to make preliminary calculations on binary systems of methane with ethane and nitrogen during the next year.

1. Title. LNG Fuels Safety

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

2. Cost Center Number. 2750427

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

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

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

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

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

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

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

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

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

7. Program and Results. This NASA-funded program is not due to start until September 30, 1974, however, some preliminary work is being done on the thesaurus as well as some literature searching. We expect to locate some 400 safety-related papers which will be processed during the succeeding year. We also plan to publish, under a companion ASRDI Contract, a comprehensive thesaurus for Cryogenic Fluid Safety. This will include terminology pertinent to LNG safety.

8. Problem Areas. None

9. Funding. September 30, 1974 - October 1, 1975

   Allocation - FY 75 50 K$ - NASA/ASRDI

10. Future Plans. We will begin processing safety-related documents in October and complete over 400 of them by October 1975. In addition, we will process carefully selected LNG/Methane/Methane Mixtures documents. Selection of these documents will be done in cooperation with other LNG projects within NBS.

1. Title. Properties of Cryogenic Fluids: Hypersonic (GHz) Velocity and Thermal Diffusivity Measurements

   Principal Investigator. G. C. Straty

2. Cost Center Number. 2750141

3. Sponsor. NBS

4. Introduction. Laser light scattering spectroscopy techniques will be used to obtain accurate thermophysical properties data for compressed and liquefied pure methane. This work will complement related work on the thermodynamic properties of the pure components of LNG mixtures (2750364). This work will provide data for the development of LNG technology at NBS and throughout the fuel gas industry.

5. Objectives or Goals. The objectives of this project are to obtain accurate sound velocity and thermal diffusivity data for pure methane (90-300 K, 350 bars) by using laser light scattering spectroscopy techniques. Sound velocity data are useful for testing the consistency of volumetric, calorimetric and thermodynamic properties data, and are potentially useful for density gauging applications. Thermal diffusivity data are useful for calculating transport properties data for LNG mixtures, required for performing heat transfer calculations.

6. Background. When light is incident on a perfectly homogeneous fluid, the reradiated (scattered) light field sums to zero in all but the exact forward direction. For a "real" fluid however, fluctuations, arising through various mechanisms, destroy the perfect homogeneity and results in the scattering of light in other directions as well. For example, thermally activated density fluctuations (phonons), propagating with the characteristic velocity of sound, give rise to scattered light which is doppler shifted in frequency from the incident light frequency and whose spectrum contains information on the sound velocity and attenuation. Local non-propagating temperature fluctuations, which decay diffusively, give rise to scattered light in a narrow frequency band about the incident light frequency and whose spectrum contains information on the lifetime of the fluctuations (thermal diffusivity). Since the frequency shifts are generally very small, it was not until the advent of the lasers with their extremely well defined frequency, that practical experiments using these phenomena were possible.

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

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

7. Program and Results. Preliminary data on the hypersound velocities in pure methane have been obtained at low densities (< 14 mol/ℓ) where the large sound absorption in methane prohibits ultrasonic measurements. Data have been obtained along several isotherms from 210 K to 300 K at densities down to 1 mol/ℓ. Agreement with previously measured ultrasonic velocities in the regions of overlapping data is good. Agreement with values calculated directly from PVT data is satisfactory.

8. Problem Areas. No significant problems have been encountered. Progress on the light scattering experiment has been determined primarily by our assignment of priorities to other LNG related efforts. The program to measure the hypersound velocities in pure methane is, however, progressing satisfactorily and on schedule.

9. Funding.

Man-years expended (Jan. -June 1974)	0.3
Equipment and/or Services Purchased	1.4 K$
Total Reporting Period Cost	15.0 K$
Balance Remaining (June 30, 1974)	0.0 K$

10. Future Plans.

Schedule:	year	1974	
	quarter	3	4
Methane:			
Measure hypersonic (GHz) velocities in methane		———	
Assemble and test apparatus for Rayleigh line-width (thermal diffusivity) measurements on methane			———

1. Title. Properties of Cryogenic Fluid Mixtures: Equilibrium Properties Data, Compilation and Evaluation, Prediction Methods

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

2. Cost Center Numbers. 2750142; 2750145

3. Sponsors. NBS; NBS-OSRD

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

5. Objectives or Goals. The overall objective of this project is to provide critically evaluated data, original and from other sources, on the phase equilibria and thermodynamic properties of cryogenic fluid mixtures. The program has been divided into the following elements:

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

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

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

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

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

6. Background. A physical equilibria of mixtures research project was established in the Cryogenics Division in 1959. The initial effort, based on a bibliographic search and other considerations, was directed toward the acquisition of new experimental data on the solid-vapor and liquid-vapor equilibria and physical adsorption properties for a limited number of binary and ternary mixtures of components with widely

separated critical temperatures. Most of the systems studied included one of the light hydrocarbon species -- methane, ethane, or ethylene (ethene) -- with one of the quantum gases -- helium, hydrogen, or neon. The data for these systems led to significant improvements in the predictions of physical adsorption equilibrium and a correlation for the prediction of deviations from the geometric mean rule for combining characteristic energy parameters. In addition, significant new information was obtained for interaction third virial coefficients which was used in a correlation by one of our consultants, J. M. Prausnitz. The approach taken in this work has been as fundamental as possible with the intention of having an impact on a broad range of mixture problems.

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

Preceding this reporting period, an expanded bibliography was prepared to update NBS Technical Note 56, published in May 1960 (objective a). Experimental liquid-vapor equilibria measurements were also completed at selected temperatures on the argon + methane systems.

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

a) A comprehensive bibliography of experimental data for ten equilibrium properties has been completed, reviewed, and revised. The final manuscript has been sent to a publisher selected by the OSRD. The bibliography includes sections on solid-liquid, solid-vapor, solid-liquid vapor, liquid-liquid, liquid-vapor, and gas-gas equilibria, as well as sections on liquid mixture densities, Joule-Thomson coefficients, and calorimetric measurements. The materials considered are hydrogen, helium-3, helium-4, deuterium, neon, carbon monoxide, nitrogen, oxygen, hydrogen sulfide, fluorine, argon, carbon dioxide, krypton, xenon, and the staurated and unsaturated hydrocarbons through the C_4's.

   Because of its importance, the section on liquid-vapor equilibria was published as a survey paper in Cryogenics 13, 575 (Oct. 1973). It is anticipated that the complete bibliography will be published and available by late summer of this year.

b) Work is currently in progress on the retrieval and evaluation of equilibria data for the methane + ethane system. Data for both argon + methane systems have been retrieved and evaluated. To maintain this phase of the program within reasonable bounds, the only properties under study are liquid-vapor equilibria, liquid mixture densities, and gas or vapor mixture densities. This effort also requires selection of the pure vapor pressure and saturation densities. The new vapor pressure measurements of Wagner (Cryogenics 13, 1973) for nitrogen and argon have been programmed and compared with other data sets. As expected, there are significant discrepancies between data sets for the pure fluids which must be resolved.

c) Our most recent liquid-vapor equilibria measurements for the nitrogen + methane system between 95 and 120 K are now being extended above the critical point of nitrogen to approximately 180 K. Preparations for these experiments were started during the last week of this reporting period.

8. Problem Areas. The major problem that may affect progress on the evaluation of mixtures data is the lack of generally accepted, rigorous methods for critically evaluating phase equilibria data. Each binary system poses special problems of its own, and it may be necessary to tailor the techniques employed.

9. Funding.

Man-years expended (Jan. -June 1974)	0.6
Equipment and/or Services Purchased	3.0 K$
Total Reporting Period Cost	38.0 K$
Balance Remaining (June 30, 1974)	0.0 K$

10. Future Plans.

year	1974	
Schedule: quarter	3	4
Retrieve phase equilibrium data for methane-ethane mixtures	——→	
Select pure component ethane data	——→	
Calculate excess Gibbs energies for methane-ethane mixtures		——→
Compare calculated excess Gibbs energies for different sets of data		——→
Compare calculated excess volume V^E for different sets of data		——→
Complete phase equilibria measurements for the nitrogen-methane system between 120-180 K	——→	
Analysis of nitrogen-methane data, comparisons, preparation of paper	———	———
Prepare for new L-V equilibrium measurements on methane-ethane mixtures		——→
Examine the prospects for new experiments on heats of mixing and virial coefficients of selected binary mixtures		———

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

   Principal Investigator. Neil A. Olien

2. Cost Center Number. 2750362

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

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

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

6. Background. In 1969 we made a thorough review of the world's publications to determine which periodicals and abstracting services should be scanned cover-to-cover to adequately encompass the LNG field. The result is that we now scan over 300 primary publications and nearly 30 secondary publications. Of these approximately one-third are directly related to LNG. In addition, within the past year we have increased our coverage of the energy field to include hydrogen as a future fuel. Much of this information is also pertinent to LNG and as such is listed in our LNG-related publications. Our Current Awareness Service has been published weekly since 1964 and the Liquefied Natural Gas Survey has been published quarterly since 1970.

7. Program and Results. Two issues of the LNG Quarterly were prepared and distributed. There are now 118 subscriptions going to AGA Member Companies and 191 to other subscribers. In September and October we updated the three bibliographies covering methane properties, methane mixtures properties and processes and equipment involving methane and LNG.

For some time we have realized that the above mentioned comprehensive bibliographies had grown to such a large size as to limit their usefulness (e. g. , B-965 covering processes and equipment listed over 1500 references). With this in mind we have reviewed the individual references in each bibliography and selected those which were most useful either from the standpoint of accuracy of the data or the appropriateness of the subject matter. These are now complete and copies have been printed and are available for sale as listed below.

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

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

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

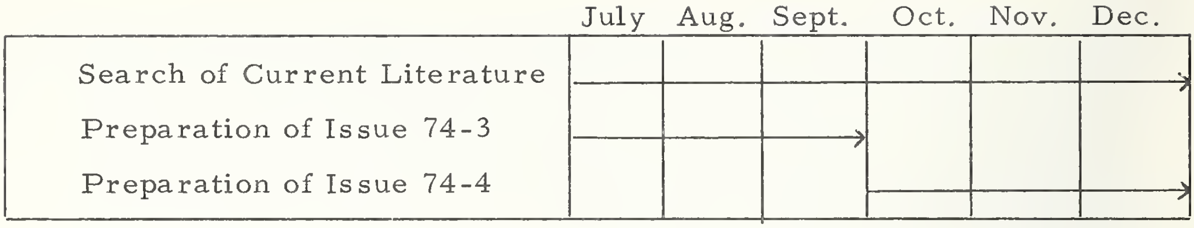
During the period January through July 1974 we have distributed 32 copies of these and the comprehensive bibliographies.

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

9. Funding. January 1 - June 30, 1974

Labor	7.5 K$
Other Costs	2.1 K$
Total	9.6 K$
Remaining	8.0 K$

10. Future Plans. Issue 74-2 of the LNG Quarterly was mailed to the National Technical Information Service for printing and distribution on June 19, 1974. Issue 74-3 will be published in late September or early October. The three bibliographies discussed in Item 7 above will be updated in October.


July
Aug.
Sept.
Oct.
Nov.
Dec.
Search of Current Literature
Preparation of Issue 74-3
Preparation of Issue 74-4

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

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

2. Cost Center Number. 2750364

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

4. Introduction. This cost center will provide comprehensive accurate thermophysical properties data to support the development of LNG technology at NBS and throughout the fuel gas industry.

5. Objectives or Goals. The objective of our work is the determination of comprehensive accurate thermophysical properties data for the major pure components (methane, ethane, propane, butanes, and nitrogen) of liquefied natural gas mixtures at temperatures between 90 K and 300 K and at pressures up to 350 atm (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.

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

6. Background. Liquefied natural gas is expected to supply an increasing percentage of the United States' energy requirements. It is likely that massive quantities of liquefied natural gas will be imported during the years 1976-1990. Ships and importation terminals are being built for transporting, storing, and vaporizing liquefied natural gas for distribution. Accurate physical and thermodynamic properties data for compressed and liquefied

natural gas mixtures are needed to support these projects. For example, accurate compressibility and thermodynamic properties data are needed to design and optimize liquefaction and transport processes; accurate data for the heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition, are needed to provide a basis for equitable custody transfer.

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

This project was initiated to provide the natural gas industry with comprehensive accurate data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. We have published National Bureau of Standards Technical Note 653, Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar, by Robert D. Goodwin, during this reporting period. This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating thermophysical properties data for LNG mixtures.

We have also published comprehensive accurate dielectric constant and Clausius-Mossotti function data for pure compressed and liquefied methane (Cryogenics 13, 712 (1973)). This data will provide a data base for mass and density gauging.

7. Program and Results.

7.1 Ethane, Thermodynamic Properties Data--R. D. Goodwin

We have completed a voluminous manuscript, "Provisional Values for the Thermodynamic Functions of Ethane," comparable with our report on methane in NBS Technical Note 653, "The Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar." The above ethane report covers the entire range of fluid states at temperatures from 90 to 600 K, and pressures to 700 bar. The purpose of this work has been twofold: to indicate those physical properties for which experimental data are inadequate; and to provide the AGA with useful results at an early date.

In this work on ethane we have achieved a long-sought goal, namely an equation of state for thermal computations of such simplicity that it virtually ensures a correct qualitative behavior of the $P(\rho, T)$ surface and of the important derivatives, especially about the critical point. It also gives qualitatively acceptable extrapolation to pressures at least twice those of P-ρ-T data used for adjusting constants in the equation of state. A manuscript on the above unique equation of state has been prepared for open publication. It is our hope that complex computations on LNG mixtures may be simplified by use of this equation in identical form for each pure component.

In appendices to the present report we give copies of our unpublished work on the physical properties of ethane, namely--

Appendix J	R. D. Goodwin, The Vapor Pressure of Ethane, Laboratory Note 73-3, July 9, 1973.
Appendix K	R. D. Goodwin, Ethane Virial Coefficients and Saturated Vapor Densities, Laboratory Note 73-4, Aug. 14, 1973.
Appendix L	R. D. Goodwin, The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine, Laboratory Note 73-5, Sept. 18, 1973.
Appendix M	R. D. Goodwin, Liquid-Vapor Saturation Temperatures of Ethane and Methane, Laboratory Note 73-6, Nov. 28, 1973.

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

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

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

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

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

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

A newly constructed light scattering spectroscopy apparatus has been employed to obtain hypersonic (GHz) velocity data at the lower densities where measurement by ultrasonic techniques were impossible. Preliminary data have been obtained to densities as low as 1 mol/ℓ along several isotherms. Measurements in the regions of overlap with the ultrasonic data indicate excellent agreement,and overall agreement with calculated sound velocity data is satisfactory.

7.4 Methane, Thermophysical Properties Data

AGA Project BR50-10 was initiated to provide the natural gas industry with comprehensive accurate thermophysical properties data for pure compressed and liquefied methane, the most abundant component in LNG mixtures. The final report of this work, "The Thermophysical Properties of Methane, From 90 to 50 K at Pressures to 700 Bar", was published as NBS Interagency Report (NBSIR) 73-342 in

October 1973. It has been reprinted as NBS Technical Note 653, by R. D. Goodwin, in April 1974. This report contains the most comprehensive and accurate tables available for the thermophysical properties of pure gaseous and liquid methane, and provides an accurate basis for calculating accurate thermophysical properties data for LNG mixtures. (For example, see references [1] in the section on Densities of LNG Mixtures in this report.)

The NBS Cryogenics Division has suggested that the report should become internationally accepted as "agreed on" standard reference data by the American Gas Association, Inc., and the natural gas industry. This suggestion has received approval from the AGA Pipeline Research LNG Supervisory Committee and the AGA Measurement Committee and is currently under consideration by the AGA-LNG Committee, E. L. Smith, Chairman. The report was recently brought to the attention of the international LNG industry at the Fourth Internationl Conference on LNG in Algiers, June 24-27, 1974 (see Paper VII-1 by L. A. Sarkes, AGA, Inc., and D. B. Mann).

8. Problem Areas. For ethane, the computation of an accurate thermodynamic network in liquid states is more difficult that for methane. Vapor pressure measurements of high accuracy are needed at low temperatures, where these pressures are so small that no accurate experimental technique so far has been developed. Heats

of vaporization are so large at low temperatures (17,000 J/mol) that the experimental error of greater than 1% in these data gives about 200 J/mol error in computations across the vapor liquid "dome." Densities of saturated liquid ethane in the mid-range of temperatures (160 to 250 K) apparently never have been measured. The melting line is known only with very low accuracy. Comparison of our calculated speeds of sound for saturated liquid ethane with experimental data suggests that derivatives of the $P(\rho, T)$ surface (via the equation of state) are not as accurate at low temperatures as desired. All of these deficiencies suggest the need for new highly accurate compressibility (P-ρ-T) measurements, sound velocity measurements in the homogeneous, single-phase domain, and possibly additional specific heat measurements, e. g. $C_v(\rho, T)$, over a wide range of (ρ, T).

Some delays in the modifications of the PVT apparatus have been encountered and are due almost entirely to delivery delays of purchased components. This lost time however has largely been made up and the PVT program is essentially on schedule.

9. <u>Funding</u>.

Man-years Expended, January-June 1974	0.9
Equipment and/or Services Purchased	$ 9.1 K
Total Reporting Period Cost	$ 58.9 K
Balance Remaining (June 30, 1974)	$ 9.6 K

10. Plans for Future Work.

Schedule	1974	
	3	4
Ethane:		
Complete editorial work on two major publications	——→	
Measure compressibilities (PVT) of liquid ethane		

1. Title. DENSITIES OF LIQUEFIED NATURAL GAS MIXTURES

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

2. Cost Center Numbers. 2751364, 2752364

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

4. Introduction. Accurate density data for liquefied natural gas mixtures are needed to provide a basis for custody transfer methods and equitable custody transfer agreements. This project will provide a data base for developing accurate methods for mass and density gauging at NBS and throughout the fuel gas industry.

5. Objectives or Goals. The objectives of this work are to perform accurate (0.1%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures, mainly in the temperature range 90-150 K, at pressures to 10 bar; and to test and optimize accurate methods for calculating the densities of LNG mixtures at arbitrary compositions and temperatures. 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. Methods for calculating the heating value of liquefied natural gas require knowing its density, which in turn depends on its composition and temperature. As the compositions of LNG mixtures vary considerably depending on the source of the gas and the processing conditions, methods are needed for calculating accurate densities at arbitrary compositions and temperatures. The accuracy (0.1%) is important because of the extremely large volumes of liquid involved. Each 1% error in density is equivalent to an inequity of \$15-20 thousand dollars per shipload of LNG (72,000 m^3 class).

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

A high precision (0.05%) magnetic densimeter (based on Archimedes Principle) was designed and constructed prior to this reporting period.

7. Program and Results. Density measurements have been completed for nitrogen from 95 to 120 K, for methane from 105 to 160 K, and for ethane from 105 to 220 K. Some measurements on propane and on normal and isobutane have also been made.

The scope of work for this project has been amended (January 15, 1974) to include testing and optimizing of computer programs for calculating accurate (0.1%) density data for LNG at arbitrary compositions, temperatures and pressures in the following ranges:

Composition: more than 70% methane, less than 10% of each of the minor components.
temperature: 90-140 K.
pressures: below 10 bar

Funds for this work have been placed in cost center 2752364.

Calculation methods will be compared with accurate density measurements as they become available. Several available methods for predicting the densities of LNG mixtures have been programmed for the NBS digital computer. These methods include a cell model [1], a hard sphere model [2] a corresponding states technique [3] and a computerized graphical interpolation scheme [4].

8. Problem Areas. A potential problem area is the delay in delivery of accessory equipment for the mixture studies.

9. Funding.

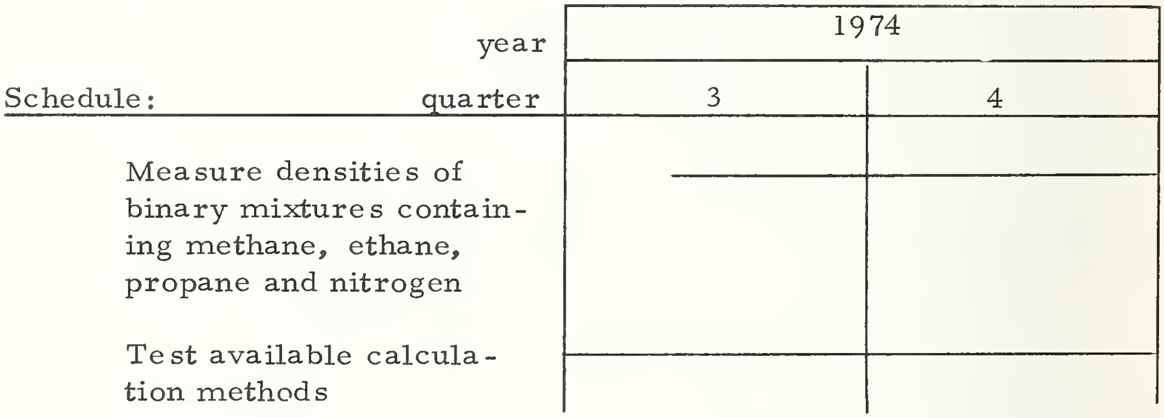
2751364 (Measurements)

Man years expended, January--June 1974		0.8
Equipment and/or Services Purchased	$	5.7 K
Total Reporting Period Cost	$	31.0 K
Balance Remaining (June 30, 1974)	$	4.0 K

2752364 (calculation methods)

Man years expended, January-June 1974		0.1
Equipment and/or Services Purchased	$	0.9 K
Total Reporting Period Cost	$	5.6 K
Balance Remaining (June 30, 1974)	$	14.5 K

10. Plans for Future Work.



References:

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

[2] Rodosevich, J. B. and Miller, R. C., Paper No. K-5, Advances, in Cryogenic Engineering, Vol 18, (in press, 1974).

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

[4] Klosek, J. and McKinley, C., Proc. First Int. Conf. on LNG, Paper 22, Chicago (1968).

1. Title. Low Temperature Material Behavior

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

2. Cost Center Number. 2750430

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

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

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

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

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

specimens were made for tensile, fatigue and fracture tests for selected materials; a variable temperature cryostat was built; and the experimental procedures proofed, and fracture data obtained on selected Fe-Ni alloys.

Materials Properties Assessment

The literature data from some 60 references on the fatigue and fracture properties of the ferritic Fe-Ni steels (Ni < 18%) has been extracted, critically valuated, and compiled. The fracture data in the compilation are the impact energy; nil ductility transition, crack opening displacement, fracture toughness, and dynamic tear tests and their dependencies on temperatures, composition, and heat treating or cold working. Fatigue data include fatigue lifetime and fatigue crack growth rates at LNG temperatures. Also included are tensile properties, hardness, impact energies, explosion bulge tests, and other fracture data. The entire compilation will be sent as an interagency report and included in a review article on LNG materials in the open literature.

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

Experimental Program

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

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

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

Linear elastic fracture mechanics parameters (K_Q, K_{IC}) and J-integral (J_{IC}) test data have been measured for identical 1.25 inch thick compact tensile specimens. For the first time valid K_{IC} critical stress intensity data have been obtained for these Fe-Ni alloys. Also, for the first time a decided temperature dependence of the fatigue crack growth rate has been measured; the rate of crack propagation is higher at 76 K compared to room temperature for all alloys.

Program Publications and Talks

One talk was presented at the ASTM Special Symposium on Properties of Materials for LNG Tankage. This conference was held in Boston, Mass. on May 21-22, 1974.

One paper will be included in the Special Technical Publication of that ASTM conference, "Low Temperature Fracture Behavior of Ferritic Fe-Ni Alloy Steels," by R. L. Tobler, et al. (see Appendix P).

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

9. Funding. During this reporting period, about $75,000 has been spent. This leaves $40,000 for research during the next reporting period.

10. Future Plans. During the next three months the fatigue and fracture toughness properties of Fe-3-1/2Ni (heat treated), steel and 5083 Al will be measured at 300, 195, 111, and 76 K.

1. Title. Elastic Properties of Materials Intended for Use in Liquefied Natural Gas Applications

   Principle Investigators. H. M. Ledbetter, E. R. Naimon (NRC-NBS Postdoctoral Research Associate, 1973-74) and W. F. Weston (NRC-NBS Postdoctoral Research Associate, 1973-74).

2. Cost Center Number. 2750131

3. Sponsor Project Identification. NBS

4. Introduction. The elastic properties of structural and insulation materials must be known before such materials can be selected economically and safely. Proper material choice for cryogenic containers for the sea transport of LNG is a major economic problem.

5. Objectives. The objectives of this program were to determine the elastic properties of structural materials in the temperature range 4 - 300 K. These properties include: Young's modulus, shear modulus, bulk modulus, and Poisson's ratio. Measurements were made on a series of iron-nickel alloys and on some aluminum alloys.

6. Background. Depending on the type of tanker for sea transport of LNG, 500,000 to 7,000,000 pounds of expensive alloys are required. This large-scale consumption of costly metals demands careful material selection to insure economical, but safe, storage tanks. Since the goal is to reduce ship costs, it is essential to have relevant elastic property data for the best possible selection and design of tankers.

7. Program and Results. The program's general aspects, the experimental approach, the data analysis, and both tabulated and graphed results are given in a manuscript "Low-temperature elastic properties of aluminum 5083-0 and four ferritic nickel steels" by W. F. Weston, E. R. Naimon, and H. M. Ledbetter. This manuscript is included as Appendix N.

8. Problem Areas. Currently, there are no problems with the program.

9. Funding. The program cost is estimated at $15,000.

10. Future Plans. Currently, no additional measurements are planned in this program.

1. Title. Heating Value of Flowing LNG

   Principal Investigators. J. A. Brennan and R. W. Stokes

2. Cost Center Number. 2750361

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

4. Introduction. This project will draw on information and facilities generated by other sectors of the NBS LNG effort. Thus the calibration of a densimeter used will be traceable to the NBS density reference system being constructed by Younglove under cost center 2751361. Mixture density data produced under 2751364 by Haynes and Hiza will also provide a necessary input to the proper interpretation of results.

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

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

7. Results. A four-inch vortex shedding flowmeter was purchased and calibrated in water at NBS-Gaithersburg over the flow range 50 to 600 gallons per minute. The results of the calibration agreed very closely with the manufacturers predicted performance. A liquid nitrogen calibration was run at NBS-Boulder over a reduced flow range of 50-230 gallons per minute. Since it is not possible to test the meter in the actual piping configuration that will be used later in the LNG tests, a second liquid nitrogen test will be run with a different inlet piping configuration to determine what affect the piping may

have on meter performance. The results of both tests will be compared with the results reported earlier [NBSIR 74-358] on the 1-1/2 and 2-inch meters to see if the performance is similar.

A new sensor was supplied with the four-inch meter which did not require changing when changing test fluids from water to liquid nitrogen. It was still necessary to adjust the current through the sensor but this adjustment is easily made.

A second four-inch vortex shedding flowmeter was obtained from a different manufacturer and calibrated in water at NBS-Gaithersburg. This meter is now being tested in the liquid nitrogen flow facility at NBS-Boulder. Results of the liquid nitrogen test are now being analyzed.

Test results from both four-inch meters will be used in testing techniques for predicting meter performance in liquid nitrogen. Testing of the second four-inch meter was not originally planned as part of the test program but the availability of a meter using the same principle but with different sensing elements was thought to be a worthwhile addition to the program. The additional testing required will add some expense to the program but the information available is already proving very beneficial.

All the components are on hand to fabricate the test section necessary for the LNG field tests on the four-inch meter. This section will be fabricated and ready for installation in July 1974. No installation date at the LNG facility has been determined at this time.

Static tests on the densitometer have been completed. Tests were run in liquids methane, propane and nitrogen using the same densitometer that had previously been tested in flowing liquid nitrogen on another program. Some adjustments to the electronics were necessary before testing in liquid methane but after the adjustment was made the densitometer worked properly in all three fluids.

It was decided to delay the purchase of new densitometers for this phase of the program until some additional information from the LNG Density Reference System is available. With that information selection of the most desirable densitometer should be easier. Since the older densitometer was available no program delay or other adverse affects will result from this decision.

The densitometer was intended to be used over small temperature limits but was used in these tests over the range 78 K to 277 K. Results obtained on each fluid independently were consistent but when all results were combined there was a definite degradation in overall performance. This degradation appears to be caused by covering such a broad temperature range with an instrument not designed for that use. Discussions have been held with the manufacturer about the performance and much of the above analysis came from that discussion. Since actual LNG measurements will not involve such wide temperature limits this problem should not occur in actual usage.

A surplus calorimeter was obtained from one of the sponsoring companies and some preliminary tests run. As a result of these tests and discussions with the manufacturer it was decided to have the manufacturer's service representative inspect the machine. The service representative suggested what would be needed to put the machine in good operating condition and the necessary parts have been ordered. Approximately $700 will be expended to refurbish the calorimeter.

A surplus trailer has been obtained and will be installed at the LNG flow facility for housing the calorimeter. After installation the trailer will require some renovation for proper calorimeter operation.

A gravitometer has been ordered and is scheduled for delivery the end of July. This gravitometer will be installed in the trailer with the calorimeter.

The two-inch flowmeter and the densitometer have been installed in the LNG flow facility in preparation for system integration tests. Installation of the calorimeter must await the trailer installation and refurbishing work.

In preparation for the system tests the electrical circuitry for the load cell system has been modified in an effort to improve performance. The flow control valve has also been modified for better control at low flow rates.

8. Problem Areas. No problems have been encountered that would have an adverse affect on the project.

9. Funding.

Man Years Expended	0.75
Major Equipment Purchased	$ 5,776
Total Reporting Period Costs	$45,000
Balance on Hand	$31,000

10. Future Plans. Flowmeter tests at an LNG peak shaving plant are planned late this calendar year. Actual test date depends on facility availability. The calorimeter will be refurbished and installed at the LNG flow facility after the necessary building arrangements have been completed. After the calorimeter is running, system integration tests will be started. It is planned to complete this phase of the program this calendar year.

1. Title and Principal Investigators. LNG Density Reference System - Ben Younglove.

2. Cost Center Number. 2751361

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

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

   The density reference system will evaluate the ability of commercially available instruments to measure densities of LNG. Density is an essential measurement in performing total energy content determinations of natural gas reservoirs. While this effort is oriented towards metrology, the output from cost center 2751364 will provide basic reference data on pure liquids and mixtures which will serve as density standards.

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

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

6. Background. In early 1973 a proposal was made to the American Gas Association for research in several areas of LNG technology to be done at this installation. Part of this program was the density reference system. Initial scheduling indicated for the first year of work, starting in April to be design, fabrication, and testing of a density system. Work actually commenced in August as a result of staffing difficulties. Since this initiation, we have conducted extensive study on the feasibility of various techniques for such a system, deciding finally on an application of Archimede's principle (see 7. below). Construction has begun on the various components of the system, and the automatic weighing head plus a precision gas balance for mixture determination are on order.

7. Program and Results. Two sample containers were built. A large one of approximately 8.9" O. D. x 17" deep is intended to house, at best, all of the densimeters that are anticipated. Another of the same diameter, but 7" deep will be used for preliminary testing and can also be used to house all but the largest of the densimeters. These vessels have been pressure tested to 200 psi at room temperature with water and the smaller has been pressure tested in liquid nitrogen to 90 psi with He gas.

A vacuum jacket large enough to house the pressure vessels was obtained.

A room temperature pressure vessel large enough to house the weighing head has been built and pressure tested to 200 psi with water. Various other items have been built such as vapor pressure bulbs and electrical feed throughs. The boule of single crystal silicon, donated by Texas Instruments, was cut to provide a buoy of approximately 127 grams and the ends polished. This will be suspended from the weighing heat via fine tungsten wire.

Manufacturers of densimeters have indicated willingness to loan working devices for test. One device is on hand and another is expected in about two weeks. Others will arrive later, the latest date mentioned for delivery was September this year.

8. Problem Areas. The weighing head being supplied by the manufacturer did not arrive during this reporting period. It is expected that this will be integrated in the system within the next two months.

9. Funding.

Man Year Expended	
Principal investigator	0.85
Technician	0.31
Equipment Purchased	$ 8,000
Total Cost	$70,300
Balance on Hand	$ 9,700

10. Future Plans. First three months. Continue assembly of density reference system. Install weighing head. Check ability of density monitor to measure water density at room temperature. Check system ability to provide reduced temperatures. Check system temperature regulation. Check density monitor performance with liquid nitrogen.

We will develop a test plan which will determine the statistical relevance of the experimental procedure.

Second three months. Install one or more test densimeters, depending on availability etc., and observe overall performance of density reference system with densimeters. Observe preliminary behavior of test densimeters.

1. Title. Liquefied Natural Gas Technology Transfer

   Principle Investigator. D. B. Mann

2. NBS Cost Center. 2750401

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

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

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

6. Background. The Merchant Marine Act of 1970 restructured federal maritime policies to make bulk carrier vessels, such as tankers and LNG ships, eligible for construction and operating subsidies. In December 1973 the keel was laid for a 926 foot long LNG vessel carrier at Quincy, Mass. The keel laying initiated the construction of the first LNG tanker to be built in the United States. American ship builders have orders for a total of 13 of these complicated ships. Various future projections indicate a total of from 25 to well over a 100 ships will be required to handle LNG importation within the next 10-15 years. LNG marine technology is presently foreign dominated. As a matter of fact, many of the ships being constructed in U.S. shipyards are using designs under license from foreign industrial groups or governments. LNG is a cryogenic fluid and the massive technology developed over the past 15-20 years in cryogenics as applied to industrial gases and the aerospace effort provides a resource which could be applied profitably to improving the U.S. competitive position in the construction and operation of LNG shipping. Because of its historical association with broad based cryogenic technology over a period of 20 years, the NBS Cryogenics Division was requested to provide support to the MarAd LNG ships program in order to aid in the transfer of cryogenic technology where it could enhance the effectiveness of maritime LNG shipping. Therefore, on April 17, 1973 we submitted a work statement which was confirmed by the establishment of a program in May.

7. Program and Results. (1 January to 30 June, 1974) In the initial phases of the LNG Cryogenic Technology Transfer program emphasis was placed on establishing the level and degree to which we could interface with MarAd, MarAd research centers (NMRC), and MarAd contractors. Progress therefore is measured as specific responses to MarAd and MarAd contract requests and NBS generated output felt necessary for the overall program.

7.1. Data and Information - LNG. On March 5, 1975, N. A. Olien, Acting Chief of the NBS Cryogenic Data Center visited the National Maritime Research Center at Galveston, Texas for the purpose of surveying the information and library needs of the center. It was his purpose to provide NMRC aid and assistance in establishing a reference library for subjects dealing with liquefied natural gas. Mr. Olien spent some time with Tom Burttschell, Superintendent of Documentation Services at NMRC discussing how best to accomplish the task. Discussions were productive and upon returning to Boulder, Mr. Olien sent the following items to Mr. Burttschell of NMRC:

1) Six bibliographies on the properties of construction materials.
2) A bibliography on LNG refrigeration utilization.
3) A bibliography on the properties of methane and one on methane mixtures.
4) Two copies of the LNG technology bibliography.
5) A list of books on cryogenic subjects.
6) A list of LNG related periodicals with ordering information for each.
7) A copy of Goodwin's NBSIR 73-242 "Thermophysical Properties of Methane".
8) Two copies of the quarterly Hydrogen - Future Fuel.

It is believed that the necessary contacts have been made between NBS Boulder and NMRC Galveston which should result in a continuing exchange of information on the general subject of LNG.

7.2. LNG Custody Transfer Systems. NBS has been requested to review a custody transfer system to be installed on one of the ships constructed in U. S. shipyards and dedicated to LNG service. The request for review came from the ship owner through the ship contractor. NBS notified the Maritime Administration of the request with the recommendation that the review be performed under this Maritime funded program. After several iterations, a work statement was submitted to the ship contractor outlining a two-phase work statement to accomplish the custody transfer review. The purpose of phase 1 - System Design Review - is twofold:

1) To estimate the total uncertainty of the shipboard measurement of LNG mass.
2) To suggest a possible testing program which would verify the design review.

The scope of work of phase 1 will entail the definition of technical areas which have direct bearing on the estimate of total uncertainty in the shipboard measurement of LNG mass. These areas will include, but not be limited to:

a) Physical dimension of system components
b) Changes in physical dimensions due to thermal contractions.
c) Tank strapping procedures.
d) Relationship between capacitance measurements, dielectric constant, liquid level and density.
e) Range of LNG mixture fractions.
f) Heat transfer and system thermodynamics.

It is expected that technical evaluations by the instrumentation subcontractor have already been performed in many of these areas, in these cases NBS will review the technical content of these valuations.

From the technical areas indicated above, it is expected that NBS will define a set of parameters which can be used to give a measure of the uncertainty in total mass. A mathematical relationship will then be derived for the total mass uncertainty in terms of these parameters. Limits on these parameters can then be set by NBS (or other users) giving the best information available. In this format, variations in system dimension from tank to tank can easily be incorporated in a total shipboard analysis.

Phase 2 - Physical Hardware Evaluation (Testing Program) - will not be initiated until the completion of phase 1.

Approval of the NBS work statement by General Dynamics was received on June 11 and authorization by MarAd to commit funds to the program was received on June 24. It is estimated that Phase 1 of the program will require 4 months for completion with the results being submitted to the sponsor in the form of an NBSIR.

7.3. Fourth International Conference on Liquefied Natural Gas. Dr. R. H. Kropschot and D. B. Mann of the Cryogenics Division of NBS attended the above conference held in Algiers, Algeria (23 June to 27 June 1974). LNG 4 is the fourth in a series of conferences sponsored by the International Gas Union (IGU), London; the International Insitute of Refrigeration (IIR), Paris; and the Institute for Gas Technology (IGT), Chicago. LNG 4 was held in Algeria by invitation of the Algerian Gas Union and the Algerian Government. All conference meetings were convened at the Palace of Nations, situated in the Club des Pins just outside the capitol of Algiers. Technical tours to industrial areas containing LNG liquefaction sites were also provided. Dr. Kropschot and Mr. Mann, in addition to attending all sessions of the conference, toured the Skikdka industrial zone which includes the 450 million cubic feet per day liquefaction plant and port facilities.

During the opening session an address "The Role of Liquefied Natural Gas in U. S. Energy Policy" by Mr. John N. Nassikas, Chairman of the Federal Power Commission, seemed at first to indicate an official aloofness on the part of the U. S. in respect to large LNG programs such as those involving Algeria and other Arab countries. A study of Mr. Nassikas' press release of his address does not confirm this impression. Although he does indicate energy self-sufficiency as the U. S. policy and outlines the methods to be used in accomplishing this goal, he nevertheless indicates imports of LNG are estimated to be 3 trillion cubic feet by 1985 with an estimated investment of $5 to 10 million in LNG. This is consistent with the AGA prediction of supplemental LNG import requirements of 2.7 trillion cubic feet by 1985 and 3.2 trillion cubic feet by 1990.

Mr. Louis A. Sarkes, Associate Director of the American Gas Assoc ation, Incorporated and Douglas Mann of the NBS Cryogenics Division co-authored a paper "A Survey of LNG Technological Needs in the U.S. - 1974 to 2000". Mr. Sarkes made the presentation which described the gas industry long range research plan and the current level of LNG research at NBS. The paper was well received and comments following the presentation indicated satisfaction on the part of delegates that the U. S. does have a structured plan for providing necessary research for continued U. S. participation in national and international LNG programs. (See Appendix O.)

Delegates (1900) from over 24 different countries, in addition to Algeria, were present at the conference with the U. S., France, Germany, Japan, and the United Kingdom representing the largest number of delegates in that order. This group of delegates assembled to attend a conference on a high technology industry that has matured over the past few years to a point where large expansion can and is taking place. They, the delegates, want assurance that fixed expansion will take place, they wish to be part of this expansion, they wish to identify who is responsible for the present program in Algeria, and to assess the political climate of this first of the Arab states to embark on a massive program of export of natural gas in liquid form.

The delegates found a demonstrated desire on the part of the government, both in policy and structure, to encourage input of foreign technology for expansion of their program in LNG and a demonstrated desire to show a stable political structure to accomplish this. The Algerian operating personnel had a pride in their workmanship and their progress and are working definitely towards technological self-sufficiency, independent of all foreign influences. It seems that their position is rather strong in that they feel that they can dedicate over 100 trillion cubic feet of natural gas reserves for possible LNG export projects. This should be compared with the north slope of Alaska estimated reserves of 26 trillion cubic feet which could possibly enter the LNG export trade.

Fifty-two papers were presented covering such subjects as world trade in LNG, large-scale transportation projects, liquefaction and processing, peak load plants and liquid handling, marine transportation, storage systems, new developments, and economic and legal aspects. Papers were printed and distributed in a bound proceedings. In spite of the tone of the subjects listed there did not seem to be a great deal of new technology, only improvements.

8. Problem Areas. Major problem areas under this program are the definition of scope and content. MarAd has a number of separate current advisory studies, the results of which are necessary for defining their position in LNG marine technology. Until these decisions by MarAd are made, NBS will continue to provide information and assistance of the type outlined above.

9. Funding. January 1 - June 30, 1974.

Labor		$67,000
Other Costs		3,000
	Total	$70,000
	Remaining	$42,000

The major portion of the remaining funding will be expended during the next 4 months on the custody transfer review. NBS will continue to provide consultation and advisory services in the transfer of LNG technology within the scope and present funding limitations.

1. Title. Federal Power Commission Consultation

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

2. Cost Center Number. 2750404

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

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

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

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

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

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

7. Funding.

Total Funding FY 74	$57,000
Expenses July 1 - June 30, 1974	$57,000
Man Years of Effort	1.0

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

FPC CONSULTATION - LNG FACILITY REVIEW

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

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* to be determined

** NBS visit not scheduled

1. Title. LNG - Dual Fuel Auto

   Principle Investigator. J. M. Arvidson

2. Cost Center Number. 2750590 (Reimbursable)

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

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

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

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

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

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

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

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

7. Program and Results. Review of the test reports is in progress by sponsor.

   A decision by GSA is expected by September on the future course of the program. Permission was requested of GSA and granted for NBS to start hydrogen gas venting studies.

8. Problem Areas. None

9. Funding. No expenditures this reporting period.

10. Future Plans. NBS submitted a preliminary work statement to GSA for further work designed to define the limits of venting capability of the sedan (by minor structural changes) and aquire venting data of this type of car body with hydrogen gas. In addition, a safety review of LNG distribution stations (gas stations) was proposed.

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APPENDIX A

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VISCOSITY OF SATURATED LIQUID METHANE[*]

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Received 27 June 1973

Synopsis

The results of absolute measurements of the viscosity of saturated liquid methane using a torsionally vibrating quartz crystal are reported for temperatures from 95 to 190 K. Comparisons are made with other data, all of which have been obtained with techniques different from that of the present work.

The viscosity of saturated liquid methane has been determined at temperatures from 95 to 190 K, and at densities from 0.2 to 0.45 g/cm^3 with a torsionally oscillating quartz cylinder. The precision and accuracy of these measurements are estimated to be better than 0.5 and 2%, respectively. Details of the apparatus and experimental techniques have been given in a previous publication^1).

The sample gas was obtained from commercial, research-grade methane. Mass-spectral analysis of a representative sample by the supplier resulted in a specified minimum purity of 99.97 mol percent. Its most probable impurities were nitrogen, carbon dioxide, and ethane. The sample gas was further purified by passing it through a silica-gel trap immersed in an ice bath.

Absolute measurements of the viscosity–density product were accomplished using a quartz crystal of approximately 5 cm length and 0.5 cm diameter. (Its exact dimensions and mass have been reported in an earlier paper^1).) Densities were obtained from measured temperatures and an equation developed by Goodwin and Prydz^2) to represent their liquid densities along the saturation curve. In general, the equation represented experimental density data within the 0.1% uncertainty of their measurements, except within a few degrees of the critical temperature. At 190 K the density may be in error by as much as 0.5%.

The present results are presented in table I as a function of temperature and density; in fig. 1 the experimental points are plotted as a function of temperature along with independent measurements$^{3-9}$) of other laboratories. The older and, generally, less consistent data$^{6-9}$) are included for the sake of completeness.

[*] Contribution of the National Bureau of Standards (USA), not subject to copyright.

[#] NRC-NBS Postdoctoral Research Associate, 1970–72.

TABLE I

Viscosity of saturated liquid methane

Temperature (K)	Density (g/cm^3)	Viscosity ($\mu g/cm\ s$)[‡]
95.000	0.44581	1784
100.000	0.43902	1569
105.000	0.43208	1383
110.000	0.42497	1225
115.000	0.41766	1090
120.000	0.41013	975
125.000	0.40235	883
130.000	0.39429	810
135.000	0.38591	733
140.000	0.37715	673
145.000	0.36793	612
150.000	0.35819	557
155.000	0.34779	514
160.000	0.33659	465
165.000	0.32437	419
170.000	0.31077	376
175.000	0.29523	343
180.000	0.27658	309
185.000	0.25174	261
190.000	0.20020	198

[‡] $1\ \mu g/cm\ s = 10^{-7}$ Pa s.

It is particularly satisfying that the discrepancies between the values obtained with four different techniques (this work; oscillating disk, ref. 3; capillary flow, ref. 4; falling cylinder, ref. 5) are generally within the estimated uncertainties of the independent measurements. It should be noted that the results of refs. 4 and 5 were acquired on viscometers calibrated with fluids of presumably known viscosity.

The agreement of the present saturated-liquid results for methane with those of refs. 3 and 4 is consistent with comparisons of saturated-liquid data for argon[1,3,4]) and oxygen[4,10,11]) obtained with the same apparatuses by the respective authors. However, it should be mentioned that, for compressed liquid argon and oxygen, the results obtained with the present apparatus[1,10]) showed a consistently larger pressure dependence than those obtained with the oscillating-disk viscometer of Hellemans *et al.*[3,11]). (The discrepancies are most significant at the higher liquid temperatures, *e.g.*, approximately 20% at 10 MN/m^2 at 140 K for argon[1]).) The above inconsistency is pointed out to illustrate that, although viscosity measurements by different experimenters on the same fluid may agree for the saturated liquid, it does not necessarily follow that this agreement would carry over to the compressed liquid or other fluid regions.

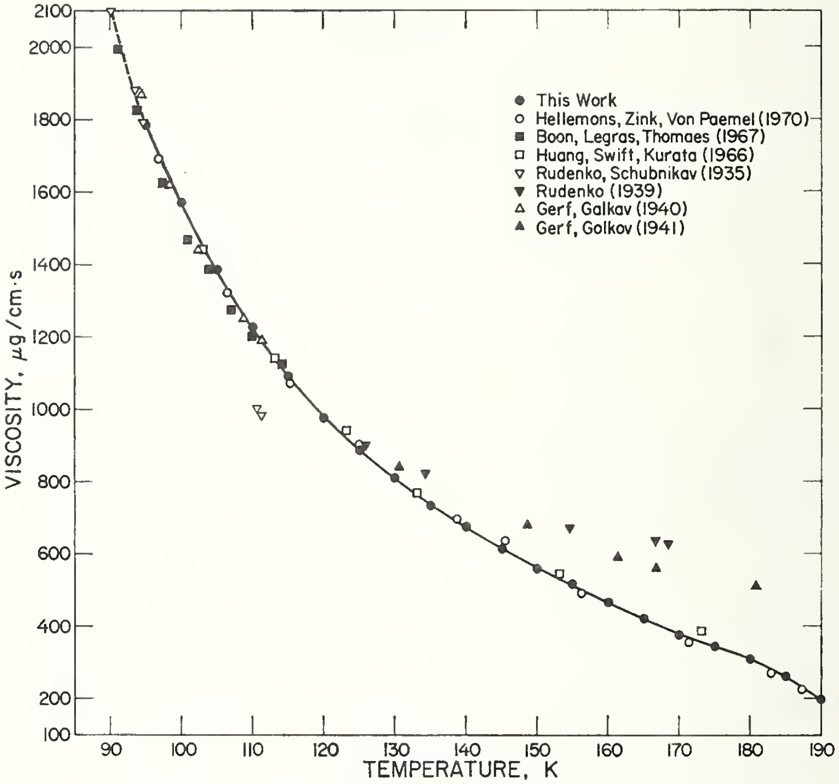

Fig. 1. Viscosity of saturated liquid methane; data from this work and refs. 3–9.

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APPENDIX B

This report gives accurate interpolation functions for the Clausius–Mossotti functions (molar polarizabilities) of pure compressed gaseous and liquid methane, ethane, propane, butanes and nitrogen; and suggests a method for calculating the dielectric constants or the densities of their mixtures. The accuracy of calculated Clausius–Mossotti functions for mixtures containing a high concentration of methane is expected to be better than 1% using only data for the pure components. Additional data for the dependence of the excess Clausius–Mossotti fuction on composition could reduce the uncertainty in Clausius–Mossotti functions for multicomponent mixtures to less than 0.2%.

The Clausius–Mossotti functions (molar polarizabilities) of pure compressed gaseous and liquid methane, ethane, propane, butanes, and nitrogen

D. E. Diller

Accurate thermophysical properties data for compressed and liquefied gases and their mixtures are needed to design liquefaction, storage, and transportation processes and to provide a basis for custody transfer agreements. For example, accurate Clausius–Mossotti function data for compressed and liquefied natural gas mixtures are useful for practical *densimetry applications;* the density of a multicomponent fluid mixture can be determined directly from a dielectric constant measurement (or vice versa). The compositions of technically important gas mixtures are so variable however that it is nearly impossible to obtain sufficiently comprehensive experimental data for many applications. Instead, accurate thermophysical properties data for multicomponent mixtures must usually be calculated from data for the pure components and selected binary mixtures.[1, 2] The purpose of this report is to give accurate interpolation functions for the dielectric constants and Clausius–Mossotti functions of pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen in a form useful for calculating the dielectric constants or densities of their mixtures.

Interpolation functions for the Clausius–Mossotti functions of pure compressed gaseous and liquid methane, ethane, propane, butanes, and nitrogen

The Clausius–Mossotti function (molar polarizability),

$$C\text{–}M \equiv \frac{\epsilon - 1}{\epsilon + 2} V \tag{1}$$

gives a relationship between the dielectric constant ϵ and the molar volume V of a non-polar fluid. For low density gases, the Clausius–Mossotti function is related to the molecular polarizability α by

$$C\text{–}M = \frac{4\pi}{3} N_0 \alpha \tag{2}$$

where N_0 is Avogadro's number; therefore $C\text{–}M$ depends mainly on a fixed molecular property of the fluid. The Clausius–Mossotti function for many non-polar gases and liquids has been found to be nearly independent of temperature, pressure, density, and state; varying less than 2% over large density and temperature ranges. The Clausius–Mossotti functions for compressed non-polar gases typically increase slightly with increasing density, reaching a maximum in the vicinity of the critical density, and then decreasing continually with further increasing density. The Clausius–Mossotti functions for most non-polar fluids decreases slightly with increasing temperature at fixed densities. Accurate empirical representation of the complete dependence of the Clausius–Mossotti functions of compressed gases and liquids on density and temperature is a difficult problem. An accurate 'equation of state' for the Clausius–Mossotti function is not available, even for the simplest pure gases. The dependence of $C\text{–}M$ on density (neglecting the dependence on temperature) is given to good approximation however by

$$C\text{–}M \simeq A_\epsilon + B_\epsilon \rho + C_\epsilon \rho^2 + D_\epsilon \rho^3 + \ldots \tag{3}$$

The coefficient B_ϵ is analogous to the second virial coefficient in the pressure virial expansion; the coefficients C_ϵ and D_ϵ are purely empirical. The coefficients for (3) have been obtained for pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen from available dielectric constant and density data. Further discussion of the data basis and the coefficients obtained for (3) is given for each fluid.

Methane. Accurate data for the dielectric constants and densities of pure compressed and liquefied methane are given in references 3 and 4. Data are available for temperatures between 91 and 373.4 K at pressures to 345 bars. The data for the low density limit A_ϵ and the liquid–vapour equilibrium curve have been fitted to (3). The coefficients obtained for (3) are given in Table 1. The uncertainty in the Clausius–Mossotti function for pure methane calculated with these coefficients is probably smaller than 0.2%.

Ethane. Accurate data for the dielectric constants and densities of pure gaseous and liquid ethane at temperatures

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The author is with the Cryogenics Division, Institute of Basic Standards, National Bureau of Standards, Boulder Laboratories, Boulder, Colorado 80302, USA. Received 29 November 1973.

Table 1 The Clausius–Mossotti functions for pure compressed and liquefied methane, ethane, propane, butanes, and nitrogen

	Coefficients for (3)			
	A_ϵ, cm^3 mole^{-1}	B_ϵ, (cm^3 mole^{-1})^2	C_ϵ, (cm^3 mole^{-1})^3	D_ϵ, (cm^3 mole^{-1})^4
Methane	6.541[4†]	8.52[3]	-4.26×10^{2} [3]	$+4.43 \times 10^{3}$ [3]
Ethane	11.22[5]	20.00[5]	-14.60×10^{2} [5]	
Propane	15.93[5]	76.00[5]	-58.40×10^{2} [5]	
n-butane	20.65[6]	141.00[*7]	-139.20×10^{2}[*] [7]	
i-butane	20.88[6]	143.00[*7]	-99.00×10^{2}[*] [7]	
Nitrogen	4.389[8]	2.20[8, 9]	-1.00×10^{2} [9, 10]	

[*] Obtained from refractive index measurements

[†] Reference numbers

between 283 and 305 K at densities up to twice the critical density are given in reference 5. The Clausius–Mossotti function for compressed fluid ethane changes less than 1% with density and temperature in this range. Coefficients for (3) are given in reference 5 and are reproduced in Table 1. It is expected that the Clausius–Mossotti function obtained by extrapolating (3) to densities up to $3\rho_c$ at temperatures down to 90 K will be accurate to about 0.5%.

Propane. Accurate data for the dielectric constants and densities of pure gaseous and liquid propane at temperatures between 293 and 369.5 K at densities to $2\rho_c$ are also given in reference 5. Coefficients obtained for (3) are given in reference 5 and reproduced in Table 1. If (3) is extrapolated to densities up to $3\rho_c$ and temperatures down to 90 K, the estimated uncertainty in C–M will be smaller than 1%.

Normal and isobutane. Accurate data for the dielectric constants and densities of pure gaseous normal and isobutane at temperatures above 400 K are given in reference 6. There are no dielectric constant data available for liquefied butanes at low temperatures, but accurate data for the refractive indices of gaseous and liquid normal and isobutane along the liquid–vapour equilibrium curve are given in reference 7. The coefficients B_n and C_n obtained for the dependence of Lorentz–Lorenz function, $(n^2 - 1/n^2 + 2) \times V$, on density are given in Table 1. The uncertainty in C–M obtained by using A_ϵ, B_n, and C_n in (3) is probably smaller than 1%.

Nitrogen. Accurate data for the dielectric constants and densities of compressed gaseous and liquid nitrogen at temperatures between 65 and 313 K are given in references 8, 9, 10. The Clausius–Mossotti function for gaseous and liquid nitrogen changes less than 1% with density and temperature in this range. Coefficients are given for (3) for nitrogen in Table 1. The uncertainty in C–M calculated for nitrogen using (3) with these coefficients is probably smaller than 0.5%.

Suggested method for calculating the Clausius–Mossotti functions (and dielectric constants or densities) for mixtures of compressed and liquefied gases

If the Clausius–Mossitti function,

$$C\text{–}M_{\text{mixture}} \equiv \frac{\epsilon_{\text{mixture}} - 1}{\epsilon_{\text{mixture}} + 2} \times V_{\text{mixture}} \qquad (4)$$

is known for a liquefied non-polar gas mixture, then the dielectric constant can be determined from a density measurement, or the density $\rho \equiv 1/V$ can be determined from a dielectric constant measurement. The Clausius–Mossotti function can be calculated for a multicomponent fluid mixture by using

$$C\text{–}M_{\text{mixture}} = \sum_i x_i\, C\text{–}M_i + C\text{–}M^E(x_i, T, P) \qquad (5)$$

where the x_i and C–M_i are the mole fractions and Clausius–Mossotti functions for the pure components and C–M^E is the excess Clausius–Mossotti function. The excess Clausius–Mossotti function is defined here as the change in C–M on mixing at fixed temperature and pressure. The excess Clausius–Mossotti function is zero for non-polar gas mixtures at low densities. There are no data available for the Clausius–Mossotti functions of liquefied gas mixtures. The excess Clausius–Mossotti function C–M^E is expected to be less than 1% of C–M_{mixture} for liquefied natural gas mixtures containing a high concentration of methane. Therefore calculations of C–M_{mixture} for liquefied natural gas mixtures are expected to be accurate to better than 1% using pure component data only. Accurate data for the dependence of C–M^E on composition could probably reduce the uncertainty in C–M_{mixture} to less than 0.2%.

I would like to thank G. C. Straty, R. D. Goodwin, and J. F. Ely for the use of their data before publication, and J. D. Olson for assistance with the calculations.

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APPENDIX C

A 33 term modified Benedict–Webb–Rubin equation of state is presented for methane. The adjustable parameters in the equation of state have been estimated using recent experimental data and least squares techniques which include the thermodynamic equilibrium conditions for the co-existing liquid and vapour phases. Comparisons of the new equation of state and an older modified Benedict–Webb–Rubin equation of state to experimental data are given.

A modified Benedict–Webb–Rubin equation of state for methane using recent experimental data

R. D. McCarty

There is currently an extensive worldwide interest in the properties of liquefied natural gas (LNG). This laboratory has recently completed an experimental programme on the thermodynamic properties of methane,[4, 7] the principal constituent of LNG. These new data are believed to be more accurate than those previously available and it therefore seemed worthwhile to use these new data to estimate the coefficients to a modified Benedict–Webb–Rubin (MBWR) type equation of state. The MBWR equation of state is especially appropriate for the study of the properties of mixtures for two reasons; first, the mathematical form of the equation allows the inclusion of the thermodynamic conditions for phase equilibria [1, 2] in the parameter estimation process, and second, the MBWR is widely used throughout the world for the calculation of the thermodynamic properties of other fluids. The particular form of the BWR modification used here was developed by Jacobsen [6] for nitrogen. The development of this equation by Jacobsen included a long and exhaustive study to determine an optimum functional form. The applicability of this form of the BWR to other fluids has since been demonstrated for oxygen by Stewart et al [9] and for hydrogen by this author.[8] The only other modification of the BWR considered was the form used by Bender[1] for a number of gases including nitrogen and methane. Both the equations of state for nitrogen (Jacobsen and Bender) were constructed using the thermo-dynamic conditions for phase equilibria. The comparisons given later in this paper show that the form used by Jacobsen reproduces the new experimental data better than the form used by Bender. This result is not surprising as the form used by Jacobsen has 33 adjustable constants while the form used by Bender has 20 adjustable constants.

Equation of state

The parameters N_1 N_{32} for the equation of state, (1), were estimated by least squares techniques using the data listed in Table 1. The parameter γ was chosen such that $\gamma\rho^2 \approx +1$ as suggested by Bender.[1]

Table 1 Summary of data

Reference	No of points	Temperature range, K	Saturation data	Density range, mole l^{-1}	Kind of data
4	555	92–300	No	3–28.5	*PVT*
10	274	92–300	No	8–28	C_v
4	200	91–190	Yes	0.016–28.12	Orthobaric densities
3	171	273–398	No	0.75–12.5	*PVT*
4	96	140–270	No	0.5–2.0	*PVT*
4	100	91–190	Yes	0.016–28.12	Gibbs function

The saturation data listed in Table 1 were calculated from equations given by Goodwin,[4] see appendix. The condition of equal Gibbs function for the saturated liquid and saturated vapour in isothermal co-existence was included as data points at the 100 saturation temperatures referred to in Table 1. The equation of state was also constrained at the critical point to $T = T_c = 190.555$ K, $\rho_c = 10.23$ mole l^{-1}, $P = P_c = 45.387$ atm, and $(\partial P/\partial\rho) \equiv (\partial^2 P/\partial\rho^2) \equiv 0$. For a more detailed description of the techniques of simultaneous data fitting, constraints, and weighting see Hust and McCarty [5] or McCarty.[7] The functional form of the equation of state is

$$\begin{aligned} P = {} & \rho RT + \rho^2\,(N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_5/T^2) \\ & + \rho^3\,(N_6 T + N_7 + N_8/T + N_9/T^2) \\ & + \rho^4\,(N_{10} T + N_{11} + N_{12}/T) + \rho^5\,(N_{13}) \\ & + \rho^6\,(N_{14}/T + N_{15}/T^2) + \rho^7\,(N_{16}/T) \\ & + \rho^8\,(N_{17}/T + N_{18}/T^2) + \rho^9\,(N_{19}/T^2) \\ & + \rho^3\,(N_{20}/T^2 + N_{21}/T^3)\exp(-\gamma\rho^2) \qquad (1) \\ & + \rho^5\,(N_{22}/T^2 + N_{23}/T^4)\exp(-\gamma\rho^2) \end{aligned}$$

The author is with the Cryogenics Division, National Bureau of Standards, Boulder, Colorado 80302, USA. Received 10 December 1973.

$$\begin{aligned}
&+\rho^7 (N_{24}/T^2 + N_{25}/T^3) \exp(-\gamma\rho^2)\\
&+\rho^9 (N_{26}/T^2 + N_{27}/T^4) \exp(-\gamma\rho^2)\\
&+\rho^{11} (N_{28}/T^2 + N_{29}/T^3) \exp(-\gamma\rho^2)\\
&+\rho^{13} (N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4) \exp(-\gamma\rho^2)
\end{aligned}$$

where P is in atmospheres, ρ is in mole l^{-1}, and T is in kelvins. The coefficients (N_i) are given in Table 2.

Comparisons

The equation,

$$\text{Gibbs}(\rho_l, T) - \text{Gibbs}(\rho_v, T) = 0 \qquad (2)$$

was formulated using the equation of state (1). Equation 2 was then solved for the co-existing saturated liquid and vapour densities (ρ_v and ρ_l) at various temperatures (T). The resulting $P-T$ locus is the vapour pressure curve given by the equation of state. Fig.1 compares the vapour pressures predicted by the equation of state to the vapour pressures given by Goodwin.[4]

Figs 2 and 3 show a comparison of the saturation densities using Goodwin's densities and values calculated by this equation of state and by Bender's equation of state, using the coefficients reported by Bender.

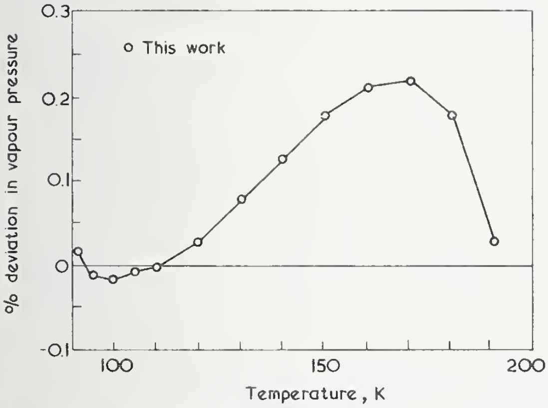

Fig.1 Comparison of vapour pressure predicted by the equation of state and those of Goodwin [4]

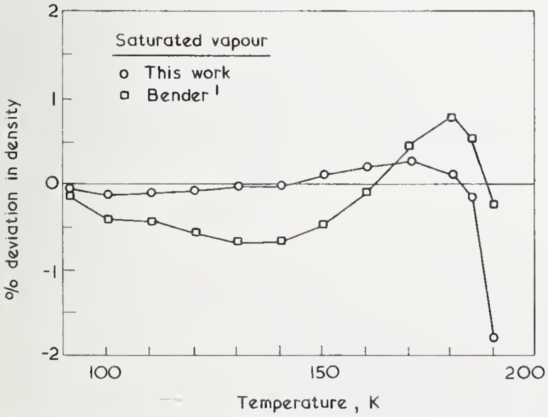

Fig.2 Comparison between saturated vapour densities of Goodwin [4] and those predicted by this equation of state and the equation of state by Bender [1]

Table 2 Coefficients to equation 1

N_1	$= -1.8439486666 \times 10^{-2}$
N_2	$= 1.0510162064$
N_3	$= -1.6057820303 \times 10$
N_4	$= 8.4844027562 \times 10^{2}$
N_5	$= -4.2738409106 \times 10^{4}$
N_6	$= 7.6565285254 \times 10^{-4}$
N_7	$= -4.8360724197 \times 10^{-1}$
N_8	$= 8.5195473835 \times 10$
N_9	$= -1.6607434721 \times 10^{4}$
N_{10}	$= -3.7521074532 \times 10^{-5}$
N_{11}	$= 2.8616309259 \times 10^{-2}$
N_{12}	$= -2.8685285973$
N_{13}	$= 1.1906973942 \times 10^{-4}$
N_{14}	$= -8.5315715699 \times 10^{-3}$
N_{15}	$= 3.8365063841$
N_{16}	$= 2.4986828379 \times 10^{-5}$
N_{17}	$= 5.7974531455 \times 10^{-6}$
N_{18}	$= -7.1648329297 \times 10^{-3}$
N_{19}	$= 1.2577853784 \times 10^{-4}$
N_{20}	$= 2.2240102466 \times 10^{4}$
N_{21}	$= -1.4800512328 \times 10^{6}$
N_{22}	$= 5.0498054887 \times 10$
N_{23}	$= 1.6428375992 \times 10^{6}$
N_{24}	$= 2.1325387196 \times 10^{-1}$
N_{25}	$= 3.7791273422 \times 10$
N_{26}	$= -1.1857016815 \times 10^{-5}$
N_{27}	$= -3.1630780767 \times 10$
N_{28}	$= -4.1006782941 \times 10^{-6}$
N_{29}	$= 1.4870043284 \times 10^{-3}$
N_{30}	$= 3.1512261532 \times 10^{-9}$
N_{31}	$= -2.1670774745 \times 10^{-6}$
N_{32}	$= 2.4000551079 \times 10^{-5}$
γ	$= +0.0096$
R	$= 0.08205616$ l atm mole^{-1} K^{-1}

The equation of state, (1), like other MBWR equations does not have the proper theoretical behaviour at the critical point, that is, the derivative $(\partial^2 P/\partial T^2)_\rho$ at the critical point does not become very large.

A comparison of experimental C_v with those calculated using (1) and those calculated by Bender's equation of state (coefficients from reference 1) is given in Fig.4. The large deviations between experimental C_v s and those calculated from Bender's equation were also noted in the case of O_2.

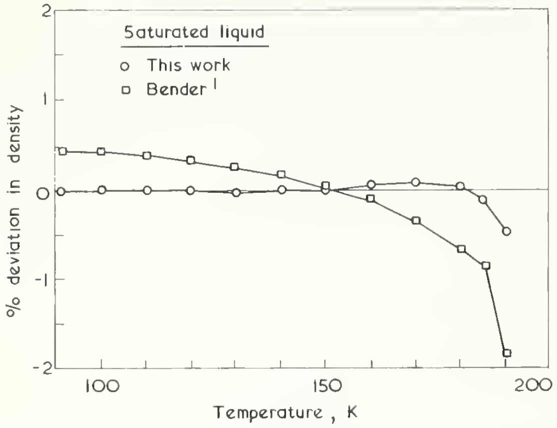

Fig.3 Comparison between saturated liquid densities of Goodwin [4] and the predictions of this equation of state and the equation of state by Bender [1]

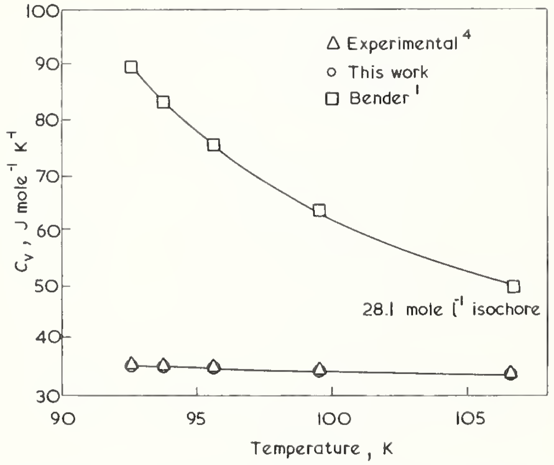

Fig.4 Comparison between experimental C_V data of Younglove [9] and predictions by this equation of state and the equation of state by Bender [1]

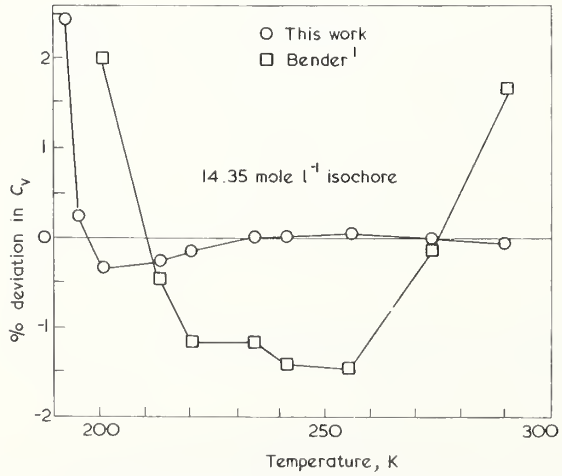

Fig.5 Comparison between experimental C_V data of Younglove [9] and predictions by this equation of state and the equation of state by Bender [1]

These large deviations between experimental C_V s and those calculated by Bender's equation of state occur only at low temperatures and high densities. Fig.5 gives a comparison of C_V s at moderate densities from the same three sources.

As is the case with all equations of state which cover a large range of pressure and temperature, the deviations between experimental and calculated densities become large in the region of the critical point. Fig.6 gives typical deviations between experimental and calculated densities from the same three sources.

The data points illustrated in the first six figures were chosen to show maximum deviations. A summary of the rms deviations is given in Table 3.

An attempt was made to use Bender's form of the modified BWR to represent the experimental data given in Table 1. Figs 7 and 8 compare the re-fitted Bender equation with (1) and experimental data. A comparison of Figs 4 and 6 with Figs 7 and 8 show a definite improvement in Bender's equation but also that it still does not represent the data as well as (1) does.

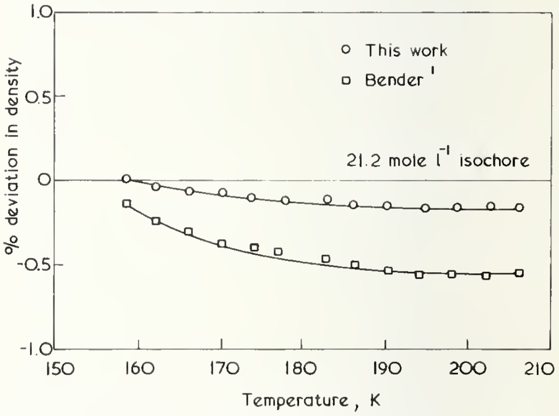

Fig.6 Comparison between experimental PVT data of Goodwin [4] and predictions by this equation of state and the equation of state by Bender [1]

Table 3 rms deviations between equation 1 and input data (Table 1)

Reference	No of points	rms in density, mole l^{-1}	rms in pressure, atm
4	555	0.024	0.91
9	274		0.211†
4	200	0.004	
3	171	0.012	0.40
4	96	0.0023	0.023
4	100		0.011*

* rms is in the Gibbs function difference of the saturated liquid and vapour in the units of J mole^{-1}

† rms is in C_V J mole^{-1} K^{-1}

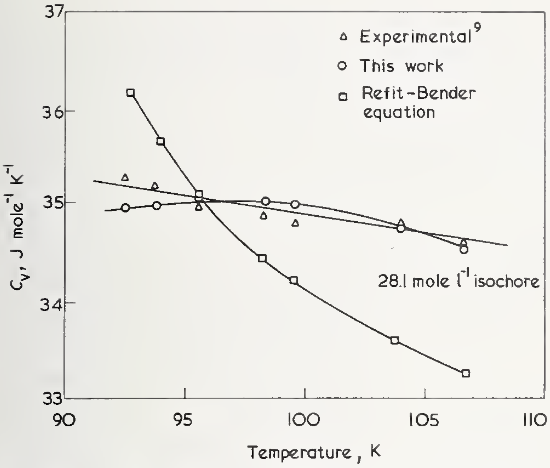

Fig.7 Comparison between experimental C_V data of Younglove [9] and predictions of this equation of state and a refit of Bender's equation of state

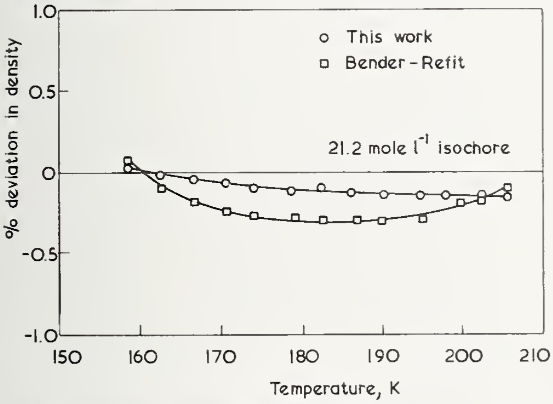

Fig.8 Comparison between experimental *PVT* data of Goodwin and predictions of this equation of state and a refit of Bender's equation of state

Conclusion

From experience of estimating the constants for (1) for methane, the region of greatest uncertainty for (1) was found to be the densities of the saturated vapour boundary. More experimental data are needed before the uncertainty can be reduced.

The 33 term equation of state given here will reproduce the experimental data with greater accuracy than the form suggested by Bender, however, the 33 term equation requires double precision arithmetic on most digital computers and a much greater exponent range than the twenty term equation.

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APPENDIX A

Supplemental equations

To provide a useful minimum set of equations which will be helpful to the reader who wishes to programme the equation of state for the calculation of thermodynamic properties, the following equations from Goodwin [4] are reprinted here.

Vapour pressure equation

$$\log_e \frac{P}{P_t} = a\,x + b\,x^2 + c\,x^3 + d\,x(1-x)^{3/2} \tag{A1}$$

Equation for the saturated liquid densities

$$\frac{(\rho - \rho_c)}{(\rho_t - \rho_c)} = w^E \exp\,[A(1 - w^{2/3}) + B(1 - w^{4/3}) + C(1 - w^2)] \tag{A2}$$

Equation for the saturated vapour densities

$$\log_e \frac{\rho}{\rho_c} = a_1\,w^{a_6} + a_2\,w + a_3\,w^{4/3} + a_4\,w^{5/3} + a_5\,Uw \tag{A3}$$

Equation for the ideal gas C_v^0

$$\frac{C_v^0}{R} = b_1 + \frac{4}{3}\,b_2\,Q^{1/3} + \frac{5}{3}\,b_3\,Q^{2/3} + 2\,b_4\,Q + b_5 \exp\left(\frac{b_6}{Q}\right)\left\{\frac{b_6}{Q[\exp(b_6/Q) - 1]}\right\}^2 \tag{A4}$$

See Appendix B for the coefficients to equations A1, A2, A3, and A4.

APPENDIX B

Coefficients to equations

Table 4 Critical and triple point parameters for equations (A1, A2, A3, and A4)*

$T_c = 190.55$ K	$\rho_c = 10.0$ mole l^{-1}
$T_t = 90.68$ K	$\rho_t = 28.147$ mole l^{-1}
$P_t = 0.117435675$ bar	

*The critical density for equations A1, A2, A3, and A4 is slightly lower than the one used for the equation of state. The lower ρ_c is preferred by Goodwin,[4] but did not work well as a constraint for (1)

Table 5 **Coefficients to equation A1**

$a = 4.77748580$ $c = -0.56788894$

$b = 1.76065363$ $d = 1.32786231$

$x = (1 - T_t/T)/(1 - T_t/T_c)$

Table 6 **Coefficients to equation A2**

$A = -0.178860165$ $C = -0.01848987$

$B = 0.04838475$ $E = 0.36$

$w = (T_c - T)/(T_c - T_t)$

Table 7 **Coefficients to equation A3**

$a_1 = -2.7036003$ $a_4 = 5.2640362$

$a_2 = 3.1661552$ $a_5 = -3.5269034$

$a_3 = -8.6573409$ $a_6 = 0.46$

$w = (T_c - T)/(T_c - T_t)$ $U = (T_c/T - 1)/(T_c/T_t - 1)$

Table 8 **Coefficients to equation A4**

$Q = T/400$ $b_5 = 4.7207907$

$b_1 = 2.5998981$ $b_6 = 5.02288$

$b_2 = 1.4449418$ $R = 8.3143$ J mole^{-1} K^{-1}

$b_3 = -1.8472716$ $T =$ in K

$b_4 = 0.8211218$

APPENDIX C

Sample calculations and table of symbols

Table 9 **Sample calculations from equations 1, A1, A2, A3, and A4**

For a temperature of 150 K and saturation pressure the equations 1 to A4 should give the following results.

	(1) Density, mole l^{-1}	(A1) Pressure, atm	(A2) Density, mole l^{-1}	(A3) Density, mole l^{-1}	(A4) C_v^0/R, dimensionless
Liquid phase	22.3223	10.278	22.325		3.0053
Vapour phase	1.0187	10.278		1.020	

Table 10 **List of symbols**

a, b, c, and d	parameters to vapour pressure equation
A, B, C, and D	parameters to equation for saturated liquid densities
$a_1, a_2 \ldots a_6$	parameters to equation for saturated vapour densities
$b_1, b_2 \ldots b_6$	parameters to equation for ideal gas C_v^0
P	pressure
P_c	critical pressure
P_t	triple point pressure
R	gas constant
T	temperature
T_c	critical temperature
T_t	triple point temperature
U	reduced temperature in (A3)
w	reduced temperature in (A1)
x	reduced temperature in (A2)
γ	parameter in (1)
ρ	density
ρ_c	critical density
ρ_t	triple point density

APPENDIX D

R-787

Properties Data for LNG

A.G.A.-supported research seeks data essential to transport and exchange of this new energy source

By D. E. DILLER
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Institute for Basic Standards
National Bureau of Standards
and
L. A. SARKES
Associate Director
Research and Engineering
American Gas Association

Imported natural gas is supplying an increasing percentage of the nation's energy requirements and new technology is being developed to support large importation projects. To take advantage of the large volume decrease, about 600 to 1, which occurs when natural gas is liquefied, ships and importation terminals with cryogenic tanks are being built for transporting, storing, and vaporizing large quantities of liquefied gas.

To support these projects, extremely accurate data on physical and thermodynamic properties for liquefied natural gas mixtures is needed. For example, accurate compressibility and enthalpy data is essential to the design and optimization of liquefaction processes. To provide an equitable basis for transfer of custody, accurate data is needed for heating value, which for liquefied natural gas mixtures depends on the total volume, the density, and the composition.

There is little accurate data available on thermodynamic properties of liquefied natural gas mixtures at low temperatures. (Typical natural gas mixtures liquefy at temperatures below −120 degrees F, boil at temperatures near −256 degrees F, and freeze at temperatures below −296 degrees F.)

Nor is there much accurate data available on thermodynamic properties of the liquefied pure components (methane, ethane, propane, etc.) in this temperature range. Moreover, the compositions of natural gas mixtures vary considerably from one source to another, and change continuously dur-

Thermophysical Properties of Pure Components of LNG Mixtures
Research Plan: 1970–1978

1970–1973	Thermodynamic Properties of Methane	
1973–1976	Thermodynamic Properties of Ethane (Densities, compressibilities, enthalpies, etc.)	Other Thermophysical Properties of Methane (Dielectric constants, sound velocities, viscosities)
1976–1978	Thermodynamic Properties of Propane	Other Thermophysical Properties of Ethane, Propane

Table 1

Thermophysical Properties of LNG (Pure Components)
Research Plan (April 1973–March 1976)

Task 1

Determine Densities, Compressibilities and Thermodynamic Properties of Ethane

- Analyze available data
- Measure vapor pressures and compressibilities (PVT)
- Measure specific heats, C_{sat}
- Calculate thermodynamic properties

Task 2

Determine Other Thermophysical Properties of Methane

- Measure dielectric constants
- Measure sound velocities
- Measure viscosities

Table 2

ing transport and storage due to selective vaporization.

The introduction of composition as an additional independent variable adds to the complexity of the task of providing an adequate data base.

Accurate data on thermodynamic properties of liquefied gases must be based on precise volumetric and calorimetric measurements. The dependence of the thermodynamic properties on pressure or density at fixed temperature is obtained from volumetric data. The dependence of these properties on temperature is determined by calorimetric measurements.

It is impossible to perform enough volumetric and calorimetric measurements directly on multicomponent mixtures to permit accurate interpolation in composition, temperature, and pressure. Instead, simple, accurate calculation methods are needed to predict thermophysical properties data for mixtures at arbitrary compositions, temperatures, and pressures from a minimum of measured input data (Note 1).

Several projects are underway currently at the Cryogenics Division of the National Bureau of Standards in Boulder, Colorado, to provide new input data for calculating the thermophysical properties of LNG mixtures.

One of these projects, supported directly by the American Gas Association, is obtaining accurate physical and thermodynamic properties data for the major pure components of LNG at temperatures down to −300 degrees F (90 K) and at pressures to 5000 psi. This range encompasses the combinations of temperatures and pressures most likely to be encountered in low temperature processes.

R. D. Goodwin and B. A. Younglove have developed accurate interpolation functions, computer programs, and data tables for all of the thermodynamic properties of gaseous and liquid methane at temperatures down to 296 degrees F. Methane is the most abundant major component of LNG with concentrations ranging from 80 to 99% in typical mixtures.

The NBS programs and data tables are based on precise measurements of the vapor pressures, densities, compressibilities, and specific heats performed at NBS and in other laboratories. Dr. Goodwin has developed an empirical equation of state for pure methane which is consistent with all of the available volumetric and calorimetric measurements at temperatures between −296 degrees F and 400 degrees F at pressures to 10,000 psi.

Extensive comparisons have been made between the NBS data and the volumetric and calorimetric data from other laboratories. The NBS data will soon be available in both the International System of Units and British engineering units for the convenience of a variety of users.

Note 1.

Several methods are available for calculating thermodynamic properties data for multicomponent liquid mixtures.[1] For liquid mixtures at temperatures well below the critical temperature, the "ideal mixture" is a useful concept. The molar volume and the molar enthalpy of an ideal liquid mixture are linear functions of the composition.

The only data required to calculate the properties of an ideal mixture are properties data for the pure components.

To calculate the properties of real liquid mixtures, one must add the small changes in the properties which occur in mixing. The following expressions give the recipe for calculating the volume and the enthalpy of a real liquid mixture:

$$V_{\substack{\text{real}\\ \text{mixture}}} = V_{\substack{\text{ideal}\\ \text{mixture}}} + V^E \qquad (1)$$

$$\text{where } V_{\substack{\text{ideal}\\ \text{mixture}}} = \sum_i x_i V_i$$

$$\text{and } H_{\substack{\text{real}\\ \text{mixture}}} = H_{\substack{\text{ideal}\\ \text{mixture}}} + H^E \qquad (2)$$

$$\text{where } H_{\substack{\text{ideal}\\ \text{mixture}}} = \sum_i x_i H_i$$

In these expressions the x_i, the V_i, and the H_i are the mole fractions, molar volumes, and molar enthalpies of each of the components. The V^E and H^E are the excess properties representing the property changes on mixing.

This calculation method separates the required input data into measurements of the physical properties of the pure components and measurements of the changes in the physical properties on mixing. Most of the information for the latter can be obtained from data on binary mixtures, i.e., pure components mixed two at a time.

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[1] J. S. Rowlinson, Liquids and Liquid Mixtures, New York Plenum Press, second edition (1969)

The other project, supported by a consortium of natural gas companies in cooperation with A.G.A., will obtain accurate input data for calculating the densities of LNG mixtures. Accurate density data is urgently needed to provide a basis for equitable custody transfer. W. M. Haynes and M. J. Hiza are developing a magnetic densitometer, applying Archimedes principle, for precise density measurement on liquid mixtures in equilibrium with their saturated vapor. Measurements will be performed at temperatures between −200 degrees F and −295 degrees F at pressures to 250 psi to include the conditions likely to be encountered in transporting and storing LNG.

The priorities for continuing systematic work on these projects through 1975 have been tentatively established. Objectives of the work on pure components of LNG mixtures will be to provide accurate data on dielectric constants, speed of sound and viscosity for compressed gaseous and liquid methane, and to provide accurate thermodynamic properties data for compressed liquid ethane and propane at low temperatures. The LNG density project will provide accurate density data for saturated liquid methane, ethane, propane, butanes and nitrogen, and for selected binary and multicomponent liquid mixtures. New phase equilibrium data and low precision estimates of the heats of mixing will also be obtained. The density data will be used to develop and test methods for calculating the change in volume on mixing. ■

APPENDIX E

Accurate measurements of the dielectric constant of methane have been made on the saturated liquid from near the triple point to 188 K and on the compressed fluid along selected isotherms from 100 K to 300 K and at pressures to 345 bar. The data are combined with accurate densities to obtain the molar polarizability and its dependence on density and temperature. The density range examined extends to nearly three times the critical density. The molar polarizability is found to increase initially with density and then decrease in qualitative agreement with theoretical predictions and the behaviour of other fluids.

Dielectric constant and polarizability of saturated and compressed fluid methane

G. C. Straty and R. D. Goodwin

In this paper, we present accurate, wide range measurements of the dielectric constant of saturated liquid methane from 91 K to 188 K and of compressed fluid methane along selected isotherms from 100 K to 300 K at pressures to 345 bar (1 bar = 10^5 N m^{-2}). The data have been combined with accurate densities [1] to determine the molar polarizability and its dependence on density and temperature. The density range examined extends to nearly three times the critical density.

In the low density limit, the molar polarizability θ is related to the dielectric constant ϵ and density ρ via the Clausius–Mossotti relation

$$\theta = \left(\frac{\epsilon - 1}{\epsilon - 2}\right)\rho^{-1} = \frac{4\pi N_0 \alpha}{3} \tag{1}$$

where N_0 is Avogadro's number and α is the average molecular polarizability. The molar polarizability has been found to be very nearly independent of density for most non-polar fluids, often varying only a fraction of a percent over wide density ranges.[2–5] A knowledge of the polarizability can therefore be of practical value since it can provide a simple and convenient method for density determination through a measurement of capacitance. With increasing transport and handling of natural gas in the liquid state (LNG) a knowledge of the molar polarizability of liquid methane, the principal constituent of LNG, can be of particular importance since it offers a potentially useful method of LNG density metering.

As with other fluids,[2–5] the molar polarizability of methane shows small but significant deviations from (1). These deviations are usually analysed by expressing the polarizability in a truncated virial type expansion, that is,

$$\theta \equiv \left(\frac{\epsilon - 1}{\epsilon + 2}\right)\rho^{-1} = A_\epsilon + B_\epsilon\rho + C_\epsilon\rho^2 \tag{2}$$

where $A_\epsilon = 4\pi N_0\alpha/3$ and B_ϵ and C_ϵ are the second and third dielectric virial coefficients. Existing theories [6] have yielded analytical expressions for these coefficients and wide range measurements of the dependence of the polarizability on density and temperature can be used to obtain information on molecular interactions.

Experimental

The dielectric constant was determined by measuring the capacitance C of a highly stable cylindrical capacitor [7] with fluid contained between the plates. A subsequent measurement of the capacitance C_0 of the evacuated capacitor then gives the dielectric constant directly as the ratio

$$\epsilon = \frac{C}{C_0}$$

The capacitances were measured using a commercial three terminal capacitance bridge capable of six figure resolution. Uncertainty in the measured dielectric constants is estimated at less than 0.005%. The methane used was 99.99% pure research grade and was passed through a molecular sieve to ensure no H_2O was present. Temperatures were measured on the IPTS 1968 using a platinum resistance thermometer calibrated by the National Bureau of Standards. Pressures were measured by reference to oil pressures derived from an oil dead weight gauge accurate to within 0.01% through differential pressure transducers.[8] The experimental apparatus and procedures were identical to those used previously for measurements on oxygen and fluorine and have already been described in detail.[4,5]

Results and discussion

The dielectric constants obtained for the saturated liquid are shown plotted against temperature in Fig. 1 and are tabulated along with the calculated polarizabilities in Table 1. Also shown for comparison are dielectric constants at the melting and boiling points obtained by Amey and Cole.[9] The dielectric constant for the critical point was calculated from an extrapolated value of the

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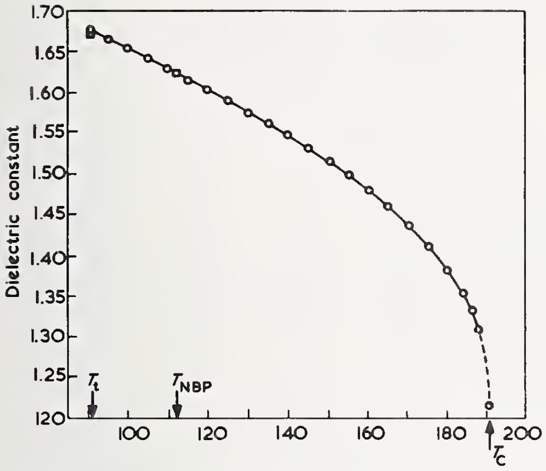

Fig.1 Dielectric constant as a function of temperature for saturated liquid methane
○ this work; □ reference 9
Arrows indicate triple point, normal boiling point and critical point temperatures

polarizability of the saturated liquid from Fig.2. The polarizability at the critical density of 10.10 ± 0.1 mole l^{-1} was taken as 6.585 ± 0.005 cm^3 $mole^{-1}$ resulting in a calculated dielectric constant of 1.2137 ± 0.0025 at the critical point.

The polarizabilities for the saturated and compressed liquid are shown plotted against density in Fig.2. The polarizability increases initially with density and then decreases in qualitative agreement with the behaviour of other fluids [3,5] and with theoretical prediction.[6] Data for the compressed fluid are tabulated in Table 2. The densities were calculated from the measured temperatures and pressures and the $P\rho T$ data of Goodwin and Prydz [1]

Table 1. Dielectric constant and polarizability of saturated liquid methane

T, K	ρ, mole l^{-1}	ϵ	θ, cm^3 $mole^{-1}$
91.000	28.121	1.67619	6.5410
95.000	27.789	1.66668	6.5428
100.000	27.367	1.65456	6.5448
105.000	26.934	1.64225	6.5468
110.000	26.491	1.62970	6.5488
115.000	26.035	1.61688	6.5509
120.000	25.566	1.60372	6.5527
125.000	25.081	1.59024	6.5549
130.000	24.578	1.57640	6.5574
135.000	24.055	1.56204	6.5595
130.000	24.578	1.57638	6.5572
135.000	24.055	1.56204	6.5594
140.000	23.508	1.54719	6.5621
145.000	22.933	1.53167	6.5645
150.000	22.326	1.51539	6.5669
155.000	21.678	1.49819	6.5695
160.000	20.980	1.47979	6.5718
165.000	20.219	1.45992	6.5744
170.000	19.372	1.43800	6.5766
175.000	18.401	1.41319	6.5789
180.000	17.232	1.38377	6.5816
184.000	16.036	1.35418	6.5846
186.000	15.269	1.33543	6.5864
188.000	14.260	1.31117	6.5903
150.000	22.326	1.51546	6.5677
175.000	18.401	1.41329	6.5804
180.000	17.232	1.38391	6.5838
184.000	16.036	1.35430	6.5867
190.53*	10.10	1.2137	6.585†

*Critical point; the dielectric constant is calculated from an extrapolated value of θ
†Extrapolated value of θ, see Fig.2

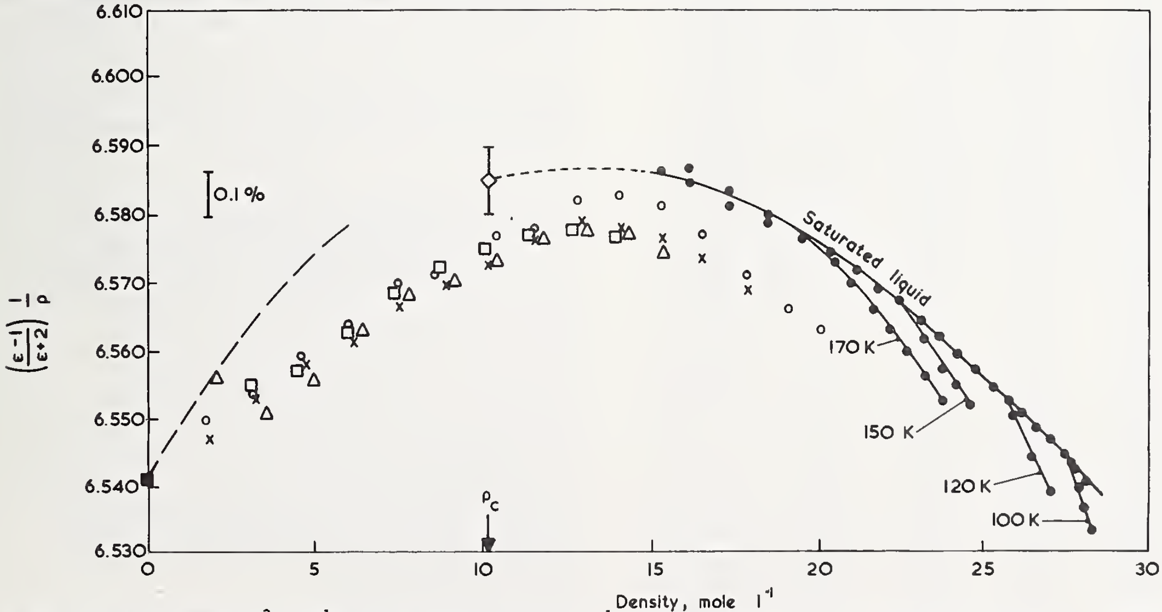

Fig.2 Molar polarizability (cm^3 $mole^{-1}$) as a function of density (mole l^{-1}) for saturated and compressed fluid methane ○ 220 K; X 250 K; Δ 280 K; □ 300 K; ● saturated and compressed liquid as indicated. The broken line and its intercept ■ are from reference 9 (see text).
◆ Extrapolated value of θ at critical density

Table 2. Dielectric constant and polarizability of compressed fluid methane

T, K	Pressure, bar (1 bar = 10^5 N m^{-2})	ρ, mole l^{-1}	ϵ	θ, cm^3 $mole^{-1}$
100.000	228.079	28.314	1.68094	6.5336
100.000	153.203	28.031	1.67300	6.5366
100.000	97.110	27.801	1.66663	6.5396
100.000	51.839	27.598	1.66117	6.5436
120.000	266.417	27.022	1.64387	6.5390
120.000	147.997	26.448	1.62795	6.5443
120.000	50.442	25.884	1.61252	6.5506
150.000	348.259	25.286	1.59475	6.5431
150.000	234.488	24.553	1.57517	6.5522
150.000	167.521	24.046	1.56140	6.5555
150.000	117.544	23.608	1.54951	6.5576
150.000	64.940	23.053	1.53473	6.5622
150.000	23.946	22.492	1.52074	6.5759
170.000	322.417	23.642	1.54996	6.5527
170.000	261.170	23.138	1.53653	6.5567
170.000	200.661	22.555	1.52099	6.5603
170.000	154.135	22.019	1.50678	6.5632
170.000	116.695	21.501	1.49316	6.5662
170.000	81.608	20.903	1.47759	6.5701
170.000	54.927	20.328	1.46270	6.5735
220.000	343.100	20.000	1.45331	6.5634
220.000	274.601	18.982	1.42716	6.5664
220.000	213.396	17.725	1.39549	6.5713
220.000	171.259	16.473	1.36454	6.5772
220.000	142.848	15.249	1.33469	6.5819
220.000	122.996	14.014	1.30494	6.5838
220.000	108.846	12.760	1.27507	6.5820
220.000	98.454	11.494	1.24537	6.5782
220.000	90.162	10.192	1.21544	6.5737
220.000	82.842	8.853	1.18534	6.5720
220.000	75.722	7.512	1.15576	6.5703
220.000	67.738	6.133	1.12584	6.5644
220.000	58.009	4.728	1.09602	6.5595
220.000	45.581	3.301	1.06634	6.5541
220.000	28.747	1.842	1.03663	6.5500
250.000	345.558	17.729	1.39544	6.5692
250.000	284.251	16.512	1.36527	6.5735
250.000	238.340	15.295	1.33551	6.5764
250.000	203.208	14.059	1.30573	6.5783
250.000	176.512	12.831	1.27660	6.5790
250.000	154.248	11.523	1.24600	6.5770
250.000	136.108	10.211	1.21585	6.5736
250.000	120.569	8.906	1.18643	6.5698
250.000	105.714	7.550	1.15650	6.5668
250.000	90.896	6.181	1.12682	6.5618
250.000	74.891	4.780	1.09709	6.5580
250.000	56.522	3.343	1.06719	6.5534
250.000	34.727	1.884	1.03746	6.5472
280.000	333.164	15.299	1.33549	6.5743
280.000	290.178	14.249	1.31025	6.5775
280.000	250.396	13.053	1.28177	6.5777
280.000	215.396	11.749	1.25122	6.5767
280.000	186.296	10.430	1.22083	6.5735
280.000	161.737	9.130	1.19144	6.5704
280.000	139.635	7.827	1.16259	6.5688
280.000	117.974	6.474	1.13312	6.5634
280.000	95.475	5.057	1.10287	6.5561
280.000	71.641	3.616	1.07278	6.5511
280.000	45.150	2.143	1.04275	6.5567
300.000	330.057	13.911	1.30214	6.5773
300.000	280.913	12.604	1.27122	6.5781
300.000	242.818	11.370	1.24249	6.5774
300.000	209.259	10.082	1.21299	6.5752
300.000	179.506	8.766	1.18342	6.5724
300.000	151.916	7.414	1.15359	6.5688
300.000	124.943	6.011	1.12321	6.5631
300.000	98.027	4.590	1.09310	6.5576
300.000	71.072	3.205	1.06438	6.5551

(see Appendix). The uncertainty in the calculated polarizabilities is estimated to be better than ±0.15% at low densities where $\epsilon - 1$ is small, decreasing to about ±0.1% at higher densities and is limited by the accuracy of the densities, estimated by Goodwin and Prydz [1] as ±0.1%. The overall precision is better as reflected by the scatter of the data.

Our experimental apparatus and procedures were designed for making measurements over a wide pressure and density range and are not particularly suitable for making high precision measurements at low density where $\epsilon - 1$ becomes very small. As a result, attempts to extract dielectric virial coefficients from these data must be approached with some caution. Bose et al [10] have recently published the results of high precision measurements of the dielectric constant of methane at pressures below about 100 bar. They use an expansion technique to obtain relative densities. The polarizability for their 279.8 K isotherm calculated using their virial coefficients is shown in Fig.2 for comparison with our 280 K data. The value of A_ϵ, the zero density intercept, is the most directly and accurately determined quantity in their experiments. They obtained a slightly temperature dependent value for A_ϵ but select $A_\epsilon = 6.541$ cm^3 $mole^{-1}$ as a best value which is consistent with our data. Their value for B_ϵ however appears to be somewhat large when compared to our higher density data.

Attempts to simply fit the polarizability data to (2) were unsatisfactory. For those isotherms which exhibit a maximum in the polarizability however, an additional constraint can be imposed, that is, $C_\epsilon = -B_\epsilon/2\rho_{max}$ where ρ_{max} is the density at the maximum in the polarizability. Using the temperature dependent values of A_ϵ from reference 9, a large number of one parameter (B_ϵ) fits with ρ_{max} constrained to the limits 12.0 mole $l^{-1} \leqslant \rho_{max} \leqslant 16.0$ mole l^{-1} resulted in a best fit with the parameters in Table 3. These curves are shown together with the experimental data in Fig.3. Note that the curves do not fit the data well at low densities. The vertical bars, however, indicate the variation in the polarizability which could result from ±0.1% variation in density. The slight oscillatory behaviour of the isothermal data is believed to be the result of the polynomials used to represent the $P\rho T$ data [1] (see Appendix).

The scatter in our low density data for the various isotherms does not permit us to resolve the temperature dependence of B_ϵ although the data do suggest that it is small. This is to be expected since the $1/T$ dependence of B_ϵ arises from dipole moments induced in one molecule by multipole moments in the other. The first non-vanishing multipole is the octopole in methane because of its tetrahedral symmetry and octupole effects should be small.

APPENDIX

We discuss briefly the method of obtaining densities from the $P\rho T$ data of Goodwin and Prydz.[1] They have measured the density of methane from the triple point to 300 K at pressures up to about 340 bar. They chose to represent their data by a unique, non-analytic equation of state capable of reproducing the experimental data to reasonable accuracy over the complete region of the state surface investigated. Because of the importance of density in the calculation of the polarizability from dielectric constant measurements, severe demands are made on the representation of the $P\rho T$ data and it was found that the equation of state was not adequate for our analysis. The somewhat sparse experimental $P\rho T$ data along isotherms were therefore fitted to polynomials of the form

$$P = \rho R T + \sum_n A_n \rho^n$$

and an iterative procedure was then used to calculate the density from the measured temperature and pressure.

Experimental saturated liquid densities were represented by an equation, derived by Goodwin,[1] of the form

$$\frac{(\rho - \rho_c)}{(\rho_t - \rho_c)} = \omega^a \exp\,[b(1 - \omega^{2/3}) + c(1 - \omega^{4/3}) + d(1 - \omega^2)]$$

where $\omega = (T_c - T)/(T_c - T_t)$, $a = 0.36$ consistent with scaling theory, and the subscripts c and t refer to the values at the critical and triple points respectively. This equation reproduced the experimental saturated liquid densities to within the accuracy of the data.

The authors wish to express their appreciation to Dr J. F. Ely and Dr J. D. Olson for helpful discussions and assistance with the calculations.

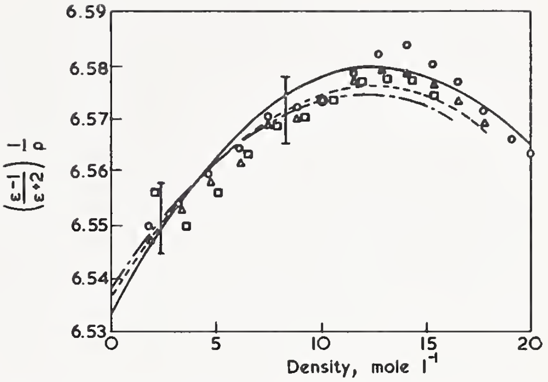

Fig.3 Fit of the molar polarizability data (cm^3 mole^{-1}) as a function of density (mole l^{-1}) for
○ 220 K; △ 250 K; □ 280 K; —— 220 K; – – – 250 K; —·— 280 K (see text)
The vertical bars indicate the possible effect of the ±0.1% uncertainty in the densities of reference 1

Table 3. Dielectric virial coefficients of methane

T, K	A_ϵ,* cm^3 mole^{-1}	B_ϵ, (cm^3 mole^{-1})^2	C_ϵ, (cm^3 mole^{-1})^3	ρ_{max}, mole l^{-1}
220	6.534	7.10	−278.4	12.75
250	6.536	6.53	−266.5	12.25
280	6.538	6.07	−252.7	12.00

*Values of A_ϵ calculated from reference 9

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APPENDIX F

Measurements of the velocity of sound in saturated and compressed fluid methane are reported. Measurements were made on the saturated liquid from 91 K to 186 K and on the compressed fluid along selected isotherms from 100 K to 300 K at pressures to about 35 MN m^{-2}. Data were combined with newly available PρT data to obtain the isentropic compressibility and the ratio of the specific heats. Measurements along the higher temperature isotherm were limited to densities greater than about 10 mole l^{-1} at 300 K increasing to about 14 mole l^{-1} at 210 K due to the large low pressure sound attenuation in methane.

Velocity of sound in dense fluid methane

G. C. Straty

The increased handling, storage, and transportation of fuel gases in the liquid state has created a need for wide range thermodynamic and transport properties data on these fluids in engineering and development applications. The properties of methane are particularly important since it is the principal constituent of liquefied natural gas (LNG). Sound velocity measurements, when combined with newly available pressure, density, temperature ($P\rho T$) data [1,2] offer a convenient and more accurate method of obtaining certain thermodynamic quantities which cannot easily be determined by other means, as well as providing a sensitive check on the $P\rho T$ surface and its derivatives.

The well-known equations

$$W^2 = (\rho\kappa_S)^{-1} = \gamma \left(\frac{\partial P}{\partial \rho}\right)_T$$

relate the sound velocity W to the density ρ, the isentropic compressibility κ_S, and the ratio of specific heats, γ. This relation has been used together with $P\rho T$ data [1,2] to determine κ_S and γ from the measured sound velocities for saturated and compressed fluid methane.

Measurements of the sound velocity for saturated liquid methane have been made from near the triple point to 186 K and on compressed fluid methane along several isotherms from 100 K to 300 K at pressures to about 35 MN m^{-2}. Measurements, in our apparatus, on the compressed fluid were limited however to minimum pressures corresponding to densities ranging from about 10 mole l^{-1} at 300 K to about 14 mole l^{-1} at 210 K because of the large sound attenuation in low pressure gaseous methane.

Experimental

The pulse echo technique was used for the sound velocity measurements. The apparatus was identical to that used previously in this laboratory for measurements on hydrogen,[3] oxygen,[4] and fluorine [5] and has been described in detail. Uncertainty in the measured velocities is estimated at about 0.05% at the higher densities increasing somewhat in the regions of high attenuation. Measurements were made at frequencies of 1 MHz and 10 MHz with no observable dispersion. Temperatures were measured using a platinum resistance thermometer calibrated by the National Bureau of Standards on the IPTS 1968. Uncertainty in temperature is estimated at 0.005 K at the lower temperatures increasing to 0.030 K at 300 K.[6] Pressures were measured by referencing to oil pressures derived from an oil dead weight gauge, accurate to within 0.01%, through differential pressure transducers.[7] The methane used was a commercially available, ultra high purity (99.97%) grade.

Results

The measured sound velocities for the saturated liquid are tabulated along with the density and the calculated compressibility and specific heat ratio in Table 1. Also shown in Table 1, for comparison, are the sound velocities interpolated from the data of Blagoi et al [8] and Van Dael et al [9] and the sound velocities calculated by Goodwin [2] directly from $P\rho T$ and specific heat data.

Sound velocities for the compressed fluid along several isotherms and for the saturated liquid are shown as a function of density in Fig.1 and are tabulated along with the measured pressures and temperatures and the derived values of compressibility and specific heat ratio in Table 2. Van Itterbeek et al [10] have also made measurements on the compressed liquid at 190 K and below but their data are not directly comparable with the present data without multiple interpolations. Their compressed liquid data however were obtained on the same apparatus as the saturated liquid data of Van Dael et al [8] and our agreement with these saturated liquid values is indicative of the overall agreement. No ultrasonic data are available for comparison at temperatures above 190 K.

Densities for the saturated liquid were obtained from the measured temperatures and a correlation for the saturated liquid densities due to Goodwin.[2] Densities for the compressed fluid and the derivatives necessary for the calculations were obtained from the measured temperatures and pressures and an equation of state for methane also due to Goodwin.[2]

The uncertainty in the derived isentropic compressibilities is estimated at about ± 0.2% due to the combined uncertainty

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Table 1 Velocity of sound W and derived values of the isentropic compressibility κ_S and ratio γ of the heat capacities in saturated liquid methane at temperature T and density ρ

T, K	W, m s^{-1}				ρ, mole l^{-1}	κ_S, (G N m^{-2})$^{-1}$	γ
	Expt	Reference 9	Reference 8	Calc Reference 2			
91.0	1538.1		1530.2		28.121	0.9369	1.525
92.0	1528.7		1522.0	1564	28.038	0.9514	1.530
96.0	1490.6	1491.5	1487.3	1523	27.703	1.013	1.551
100.0	1452.2	1451.4	1442.8	1480	27.364	1.080	1.575
104.0	1413.4	1413.2	1401.5	1437	27.020	1.155	1.601
108.0	1373.8	1374.6	1364.6	1393	26.669	1.238	1.629
112.0	1334.1	1334.7	1352.2	1351	26.310	1.331	1.660
116.0	1294.0	1294.1	1208.7	1308	25.943	1.435	1.693
120.0	1252.9	1253.6	1245.3	1266	25.567	1.553	1.726
124.0	1211.3	1212.6	1207.6	1224	25.181	1.687	1.763
128.0	1169.1	1170.0	1165.2	1181	24.783	1.840	1.801
132.0	1126.0	1227.0	1120.4	1138	24.372	2.017	1.842
136.0	1082.2	1083.0	1079.2	1093	23.947	2.222	1.886
140.0	1037.4	1038.0	1034.7	1047	23.507	2.464	1.933
144.0	991.7	992.4	987.2	999	23.050	2.750	1.986
148.0	944.8	945.3	946.5	951	22.572	3.094	2.045
150.0	921.0	921.4	921.4	927	22.324	3.292	2.079
152.0	896.6	897.2	896.3	902	22.071	3.513	2.114
156.0	846.9	847.6	850.2	852	21.524	4.034	2.195
160.0	795.5	796.0	796.4	802	20.981	4.695	2.295
164.0	742.2	742.5	746.0	749	20.379	5.552	2.423
168.0	686.3	686.7	684.6	695	19.724	6.709	2.590
170.0	657.5	657.5	657.5	667	19.373	7.444	2.698
172.0	627.5	628.2	632.2	637	19.001	8.331	2.824
176.0	564.1	564.8	568.0	570	18.183	10.77	3.168
178.0	530.5	530.8		536	17.725	12.50	3.413
180.0	495.0	495.5		500	17.222	14.77	3.736
182.0	457.7	458.0		462	16.662	17.86	4.195
184.0	417.2	415.8		421	16.022	22.35	4.882
186.0	370.9	371.7		377	15.263	29.68	6.012

Columns 3, 4 and 5 give values of W from references 9 and 8 and those calculated from $P\rho T$ data in reference 2

in the experimental densities of ± 0.1% [1,2] and the equation of state correlation.[2] The uncertainty in γ is difficult to assess, depending almost entirely on the accuracy of the derivative $(\partial P/\partial\rho)_T$ used to obtain γ from the sound velocity. Goodwin,[2] however, has shown that his equation of state can be used successfully for the calculation of wide range self-consistent thermodynamic functions involving extensive use of both first and second derivatives of the $P\rho T$ surface, which adds confidence to the accuracy of values of $(\partial P/\partial\rho)_T$ used here. Comparison of the measured sound velocities with those calculated from the equation of state suggests [11] that the uncertainty in γ is probably less than 1.0% at the higher temperatures increasing somewhat for the low temperature, high density liquid where $(\partial P/\partial\rho)_T$ is very large and most difficult to determine accurately from $P\rho T$ data.

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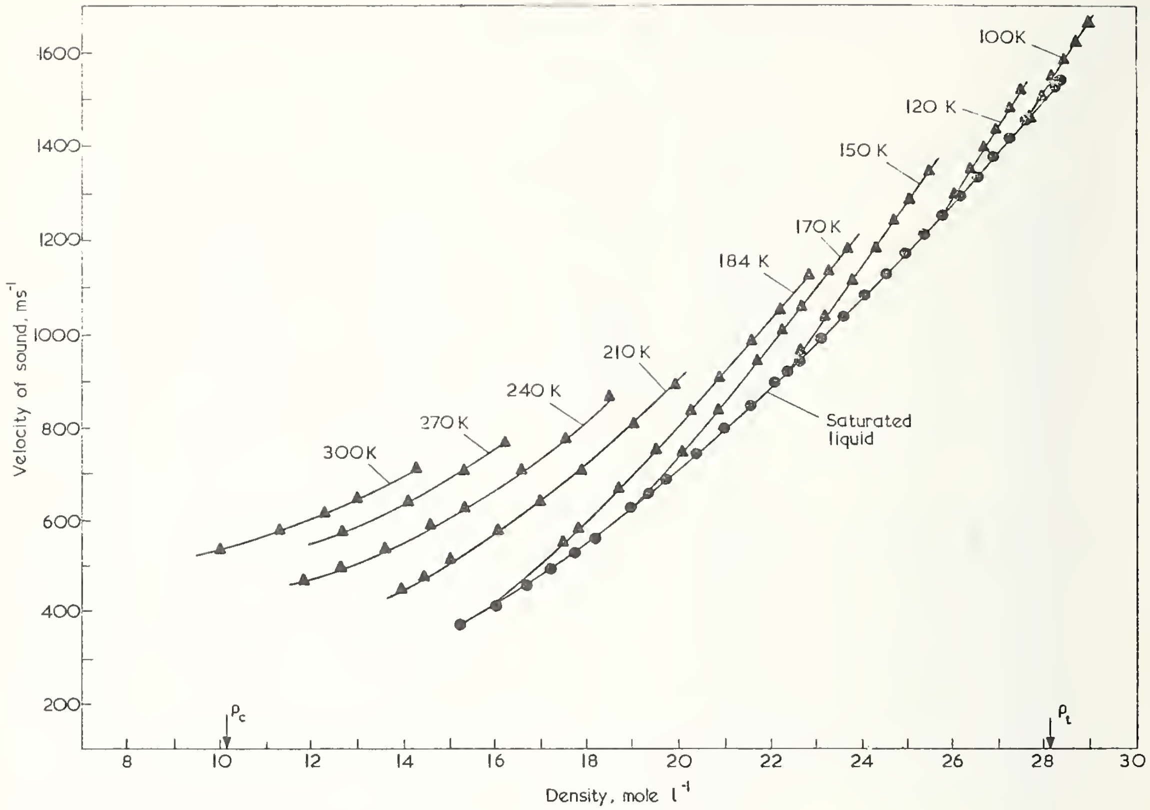

Fig.1 Velocity of sound plotted against density for saturated and compressed fluid methane

Table 2 Velocity of sound *W* and derived values of the isentropic compressibility κ_S and ratio γ of heat capacities in compressed fluid methane at temperature *T* and density ρ

P, M N m^{-2}	W, m s^{-1} Expt	Calc Reference 2	ρ, mole l^{-1}	κ_S, (G N m^{-2})$^{-1}$	γ
		T = 100.0 K			
33.385	1672.6	1610.3	28.692	0.7766	1.576
26.077	1630.7	1589.5	28.430	0.8245	1.566
19.123	1588.1	1566.0	28.169	0.8774	1.561
13.088	1548.5	1542.4	27.930	0.9307	1.561
7.244	1507.4	1516.5	27.686	0.9908	1.565
1.661	1465.1	1488.9	27.439	1.058	1.572
		T = 120.0 K			
31.161	1517.2	1475.3	27.225	0.9947	1.611
26.233	1482.8	1449.5	27.004	1.050	1.620
19.980	1436.0	1413.4	26.707	1.132	1.635
15.149	1397.0	1382.7	26.460	1.207	1.651
9.258	1345.2	1341.3	26.136	1.318	1.675
4.367	1290.5	1302.8	25.841	1.448	1.681
		T = 150.0 K			
34.530	1339.6	1303.6	25.275	1.374	1.700
28.845	1290.0	1260.0	24.923	1.503	1.727
23.669	1240.3	1216.1	24.572	1.649	1.758
18.433	1184.6	1166.4	24.178	1.837	1.797

P, MN m^{-2}	W, m s^{-1} Expt	Calc Reference 2	ρ, mole l^{-1}	κ_S, (G N m^{-2})$^{-1}$	γ
12.667	1114.5	1103.3	23.682	2.119	1.855
7.263	1036.6	1032.5	23.132	2.508	1.931
3.020	962.1	964.4	22.609	2.979	2.021
		T = 170.0 K			
31.457	1183.8	1169.0	23.584	1.886	1.778
26.994	1135.5	1124.7	23.213	2.082	1.813
20.773	1059.2	1053.8	22.619	2.456	1.877
17.538	1013.9	1011.2	22.263	2.724	1.922
13.012	940.7	941.9	21.684	3.249	2.009
7.774	833.5	838.6	20.819	4.309	2.183
4.528	742.9	750.5	20.078	5.624	2.397
		T = 184.0 K			
34.254	1129.0	1119.8	22.751	2.150	1.794
27.883	1055.1	1050.5	22.145	2.528	1.850
22.511	982.8	981.6	21.538	2.996	1.919
17.863	909.0	910.3	20.903	3.609	2.007
13.839	831.9	834.9	20.221	4.454	2.126
10.436	751.2	754.2	19.475	5.672	2.301
7.722	666.6	669.4	18.661	7.517	2.561
5.770	579.9	584.5	17.809	10.41	2.934
5.301	552.8	558.2	17.535	11.63	3.091
		T = 210.0 K			
34.074	987.0	988.0	20.741	3.085	1.843
27.598	898.0	901.2	19.885	3.887	1.929
22.264	809.8	813.7	18.981	5.007	2.045
17.486	711.5	714.8	17.885	6.884	2.228
14.832	643.9	646.2	17.053	8.817	2.405
12.703	577.5	579.5	16.159	11.56	2.635
10.944	511.5	512.1	15.124	15.76	2.988
10.173	477.0	477.4	14.512	18.88	3.239
9.646	451.2	451.3	14.001	21.86	3.481
		T = 240.0 K			
34.638	863.5	870.2	18.505	4.517	1.871
29.111	782.7	789.0	17.531	5.803	1.964
24.656	707.0	712.4	16.520	7.549	2.076
20.885	632.6	636.8	15.395	10.12	2.221
18.890	588.8	591.9	14.637	12.28	2.330
16.841	540.2	541.7	13.673	15.62	2.478
15.186	498.4	498.8	12.697	19.77	2.617
14.071	469.8	470.0	11.907	23.72	2.698
		T = 270.0 K			
34.769	771.5	775.8	16.311	6.420	1.867
30.486	711.2	714.6	15.387	8.010	1.935
25.972	641.6	643.6	14.167	10.69	2.029
21.837	572.8	573.3	12.708	14.95	2.131
		T = 300.0 K			
34.838	713.9	713.7	14.331	8.534	1.818
29.732	649.5	648.5	13.065	11.31	1.873
27.295	618.0	616.7	12.352	13.21	1.896
24.427	580.4	580.1	11.404	16.23	1.904
20.983	537.3	537.9	10.094	21.39	1.896

Column 3 gives the value of W calculated from $P\rho T$ data

APPENDIX G

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The Specific Heats, C_σ, and C_V, of Compressed and Liquefied Methane*

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The specific heats, C_σ, of saturated liquid methane have been measured at 66 temperatures in the temperature range 95–187 K. The specific heats at constant volume, C_V, have been measured at 20 densities ranging from 0.8 to 2.8 times the critical density, at temperatures between 91 and 300 K, and at pressures to 330 bar (at 280 PVT states in all). The uncertainty of most of the measurements is estimated to be less than 0.5 percent, except near the critical point. These measurements were performed primarily to provide input data for accurate thermodynamic properties data calculations for liquid methane. They are believed to be the most comprehensive specific heat measurements available for pure compressed gaseous and liquid methane.

Key words: Constant volume; heat capacity; liquid; saturated liquid; specific heat; methane.

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1. Introduction

For the calculation of fluid thermodynamic properties such as internal energy, enthalpy, entropy, and velocity of sound, at temperatures less than the critical point, one needs either the latent heat of vaporization or specific heat along a path traversing the temperatures of interest. Heat capacity measurements are much easier than latent heat measurements and the specific heat measurements are not restricted to the liquid-vapor curve but can be made covering temperatures and densities in the single phase fluid region as well.

For methane, specific heat of the saturated liquid, C_σ, was measured from 95 to 187 K, and specific heat at constant volume, C_V, was measured on 20 isochores with densities ranging from 8 mol/l to 28 mol/l, temperatures from 90 to 300 K, and pressures to 330 bar [1].[1]

2. Apparatus

The specific heats were obtained using a constant volume adiabatic calorimeter, as described previously by Goodwin [2]. Basically, it consists of a thin spherical stainless-steel sample holder bearing a heater and platinum resistance thermometer and enclosed in an adiabatic shield. The calorimeter and cryostat are shown in figure 1. The refrigerant was liquid nitrogen.

The versatility of this instrument is demonstrated in that it has been used with very minor modifications for the C_V and C_σ measurements of hydrogen [3, 4], oxygen [5, 6], fluorine [7, 8], and in this work on methane. These measurements cover temperatures from 14 to 300 K and pressures to 330 bar.

The thermometer was calibrated by the NBS Temperature Section. Temperatures are on the IPTS–68 scale. The temperature of the adiabatic shield and guard ring are controlled to the sample temperature with difference thermocouples and automatic power regulation. Heat exchange to the sample holder is considered negligible.

The sample used was 99.99 percent methane. Impurities as analyzed by the supplier in ppm were $CO_2 < 10$; O_2, 4; N_2, 12. A molecular sieve in an ice bath served to ensure removal of water vapor present in the sample.

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[1] Figures in brackets indicate the literature references at the end of this paper.

3. Procedure

In essence, the specific heat C_V is calculated from the measured parameters as follows. The total heat capacity is determined as the ratio of the heat input ΔQ to the temperature increase ΔT brought about by applying a very stable power source to a resistor attached to the calorimeter sample holder, for an elapsed time Δt. The heat capacity of the empty sample holder Co is then subtracted off. It, of course, was previously measured in exactly the same way except with the sample space pumped to a vacuum. The difference of these two quantities is the heat capacity of the methane sample. The specific heat is obtained by dividing the heat capacity by the amount of methane, N.

Actually, several corrections are made to the above. Since the sample holder is a thin stainless steel sphere ($\sim$ 0.16 mm wall thickness and 5 cm diam), it stretches as the pressure increases. This allows work to be done by the methane due to the increase of the sample volume. This correction [4, 5, 6], developed by Walker [9], ranges from 0.5 to 5 percent of the resulting C_V value. However, it can be made accurately.

Of the three variables, pressure, temperature, and density, only temperature is measured during the measurement of an isochore. The pressure and temperature are measured at filling and the density calculated from the *PVT* surface [10]. The amount of methane, N, is calculated from the volume $V(T, P)$ as previously determined [3, 5]. The density for each C_V measurement is calculated from the filling density after correcting for sample holder expansion and the amount compressed into the filling capillary [6].

In the case of the C_σ measurement, the two phase heat capacity (liquid and gas) is first determined as the difference of the total heat capacity (*DQ/DT*, column 6 of table 1) and the empty heat capacity (CO, column 7) and the result divided by the total amount of sample (C_2, column 8). Then the effects of the latent heat of vaporization and heat absorbed by the vapor are subtracted [3, 5, 7] to give C_σ (column 10). This type of correction is derived by Hoge [11].

The temperature increment, resulting from a constant power input over a time Δt, is evaluated at the middle of the heating interval by extrapolating the temperature drift rates evaluated just before heating and after an equilibrating time has elapsed (about 20 min). Care was taken to reduce the effects of noise on drift rate by taking many (10 to 20) measurements of time and temperature.

TABLE 1. *Specific heat of saturated liquid methane,* C_{σ} *or* C_{SAT}*; specific heat at constant volume of saturated liquid calculated,* C_V*; specific heat of the two phase (liquid-vapor) system,* C_2*; heat capacity of the calorimeter (empty)* C_0*, and heat capacity of the calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT*, with temperature, pressure, density, and temperature increment,* DT

ID	Temp K	Press bar	Dens mol/l	Delt K	*DQ/DT* J/K	C_0 J/K	C_2 J/mol · K	C_V J/mol · K	C_{sat} J/mol · K
201	95.402	0.209	27.755	3.657	133.482	46.671	54.418	34.274	54.240
401	95.846	.219	27.718	5.799	139.159	46.881	54.252	34.103	54.131
202	99.021	.311	27.450	3.574	135.870	48.348	54.864	34.169	54.647
302	101.651	.409	27.224	6.638	141.300	49.520	55.058	34.016	54.877
402	101.961	.422	27.198	6.420	143.111	49.656	54.943	33.883	54.790
203	102.574	.448	27.145	3.524	137.905	49.923	55.152	33.898	54.896
204	106.891	.673	26.767	5.110	140.924	51.750	55.899	33.941	55.602
303	108.219	.758	26.649	6.495	145.302	52.293	55.794	33.710	55.583
403	108.800	.797	26.597	7.236	146.902	52.528	55.483	33.349	55.315
205	112.604	1.097	26.254	6.273	144.013	54.022	56.410	33.478	56.075
304	115.165	1.343	26.019	7.386	149.404	54.988	56.638	33.391	56.434
206	119.117	1.802	25.649	6.702	147.576	56.412	57.144	33.041	56.310
305	122.474	2.278	25.327	7.194	153.257	57.561	57.404	32.862	57.287
405	123.367	2.419	25.240	7.498	154.829	57.858	57.008	32.389	56.996
207	125.766	2.830	25.005	6.568	151.006	58.636	57.899	32.534	57.645
406	130.765	3.852	24.500	7.297	158.819	60.171	57.992	32.000	58.245
208	132.274	4.209	24.343	6.430	154.477	60.612	58.834	32.162	58.774
1001	132.751	4.326	24.293	5.117	122.552	60.750	62.894	32.148	58.879
902	135.455	5.038	24.007	4.538	137.072	61.512	60.813	31.499	58.930
1002	137.805	5.723	23.752	4.973	125.195	62.151	64.157	31.650	59.729
903	139.970	6.412	23.513	4.476	139.223	62.720	61.570	30.986	59.698
801	144.305	7.971	23.017	4.019	141.250	63.808	62.323	30.460	60.560
904	144.401	8.009	23.005	4.386	141.728	63.831	62.689	30.797	60.929
802	148.500	9.725	22.514	4.371	143.789	64.800	63.565	30.407	62.033
905	148.881	9.896	22.467	4.316	143.807	64.888	63.509	30.230	62.005
1003	150.824	10.807	22.224	4.332	133.134	65.326	68.994	31.449	64.014
803	152.809	11.798	21.969	4.247	146.566	65.763	65.022	30.468	63.898
906	153.157	11.978	21.924	4.229	146.775	65.838	65.129	30.459	64.048
1004	155.542	13.267	21.606	4.941	135.238	66.345	70.092	30.518	65.246
804	157.043	14.128	21.401	4.180	148.588	66.657	65.926	29.932	65.435
907	157.355	14.312	21.358	4.167	148.747	66.721	66.001	29.899	65.569
1005	159.127	15.388	21.107	4.035	137.307	67.080	71.446	30.244	66.905
805	161.181	16.707	20.808	4.095	151.123	67.486	67.294	29.823	67.733
908	161.483	16.908	20.763	4.088	151.284	67.545	67.375	29.793	67.898
1006	163.136	18.036	20.512	3.982	138.917	67.864	72.280	29.161	68.379
1402	163.782	18.492	20.412	5.441	153.354	67.987	68.702	30.257	69.936
806	165.249	19.556	20.179	4.036	153.713	68.263	68.749	29.716	70.534
1407	165.128	19.467	20.199	5.131	154.144	68.240	69.132	30.171	70.865
909	165.548	19.779	20.131	4.043	153.880	68.318	68.838	29.719	70.745
1007	166.549	20.536	19.967	2.738	141.994	68.503	74.756	29.907	71.756
807	169.253	22.687	19.505	3.963	156.273	68.991	70.216	29.609	73.960
910	169.565	22.945	19.450	3.949	156.656	69.047	70.480	29.743	74.411
1220	170.157	23.440	19.344	7.335	138.896	69.151	79.614	29.404	74.696
1008	170.197	23.474	19.336	4.297	144.726	69.159	76.862	30.033	75.369
1408	170.251	23.520	19.327	5.020	157.666	69.168	71.213	30.181	75.575
1403	171.097	24.243	19.172	5.271	158.018	69.316	71.376	29.980	76.320
808	173.180	26.094	18.773	3.890	159.054	69.675	71.898	29.577	78.540
911	173.480	26.369	18.714	3.873	159.572	69.727	72.273	29.813	79.194
701	173.505	26.392	18.709	5.002	141.928	69.731	81.284	29.262	78.678
1216	174.032	26.880	18.603	7.180	141.932	69.820	82.310	29.445	79.623
1009	174.429	27.252	18.522	4.167	148.478	69.887	79.930	30.556	81.334
1409	175.228	28.012	18.355	4.900	161.213	70.021	73.374	30.069	82.128
1404	176.295	29.051	18.125	5.118	162.367	70.198	74.158	30.312	84.253
809	177.029	29.782	17.961	3.811	162.720	70.318	74.323	30.097	85.466
1221	177.420	30.177	17.872	6.968	146.364	70.382	86.720	31.201	87.382
702	177.902	30.670	17.760	3.799	145.938	70.461	84.967	29.552	86.790
1010	178.557	31.349	17.603	4.090	151.355	70.567	82.156	29.861	88.641
1200	180.613	33.553	17.078	5.694	148.814	70.895	88.923	30.420	95.067
1217	181.034	34.018	16.963	6.825	149.125	70.961	89.202	30.254	96.349
703	181.645	34.702	16.790	3.688	150.564	71.057	89.496	30.451	98.844
1011	182.572	35.759	16.516	3.940	156.745	71.201	86.983	31.025	103.442
1222	184.222	37.703	15.976	6.616	154.219	71.454	94.445	31.451	113.330
704	185.271	38.982	15.588	3.549	156.464	71.613	95.503	31.421	121.769
1201	186.127	40.050	15.236	5.329	158.456	71.742	98.948	32.509	132.153
1012	187.577	41.915	14.530	6.026	151.278	71.957	80.630	16.306	141.359
1218	187.633	41.988	14.499	6.358	160.079	71.965	100.540	30.050	156.489

4. Results

The specific heat of the saturated liquid was measured for 66 temperatures. The lowest was 95 K (triple point, 90.68 K) and the highest 187 K (see fig. 2 and table 1). The estimated uncertainty in the measured value of C_σ is about 0.5 percent generally but increasing to about 5 percent within a few Kelvin of the critical point. The data of Weibe and Breevort [12] are shown for comparison as the closed circles. Their measurements agree remarkably well with the new data, considering the state of the art at that time.

Figure 3 and table 2 show C_V as a function of temperature for the various isochores. The dashed line is the locus of C_V for saturated liquid as extrapolated from the C_V measurements. The uncertainties in C_V are the same as for C_σ. Densities Q, R, S, and T have uncertainties as large as 5 percent near critical temperature, indicated as T_c on figure 3. Density T is 22 percent less than critical density.

Figure 4 shows C_V at saturation. The circles are values extrapolated from the C_V data and the triangles are computed from C_σ data by adding the term $T\left(\frac{\partial P}{\partial T}\right)_v \frac{dV}{dT}$. These derivatives, evaluated analytically from a representation of the PVT surface [2], introduce the scatter and the lowering of the values from the extrapolated values which have essentially the same accuracy as the measured C_V values.

Comparison was made with the C_p data of Jones et al. [17] on their 2000 lb/in^2 (136.7 bar) by interpolation of the C_V data and adding the PVT contribution. Figure 5 shows the close agreement of the two sets of data. The other curve is calculated from spectroscopic heat capacities together with the PVT term above critical temperature, (T_c). Below the critical temperature, latent heats must also be used. The discontinuity is, of course, at T_c.

TABLE 2. *Specific heat at constant volume,* C_v, *of methane; heat correction for calorimeter expansion* CI, *heat capacity of empty calorimeter,* CO, *total heat capacity of calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT, *with temperature, pressure, density, and temperature increment,* DT

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	CO J/K	CI J/mol · *K*	C_v J/mol · K
2209	200.342	56.917	7.991	7.542	94.477	73.734	0.166	35.351
2203	201.339	58.027	7.991	5.459	94.406	73.865	.167	35.004
2210	207.854	65.217	7.988	7.559	94.152	74.691	.170	33.153
2204	208.168	65.562	7.988	7.419	94.184	74.729	.170	33.141
2211	215.402	73.451	7.984	7.554	94.227	75.593	.175	31.732
2212	222.937	81.598	7.980	7.511	94.677	76.439	.182	31.046
2205	222.993	81.658	7.980	7.361	94.691	76.445	.182	31.059
2206	230.373	89.583	7.977	7.387	95.264	77.226	.189	30.698
2213	230.453	89.668	7.977	7.484	95.130	77.234	.189	30.455
2207	237.534	97.229	7.973	7.324	95.819	77.940	.195	30.419
2214	238.128	97.862	7.973	7.382	95.748	77.998	.196	30.198
2208	244.733	104.881	7.970	7.292	96.283	78.619	.202	30.045
2215	245.476	105.669	7.969	7.369	96.374	78.687	.203	30.084
2216	252.815	113.433	7.966	7.332	97.017	79.335	.210	30.067
2218	266.349	127.671	7.959	7.246	97.960	80.436	.222	29.785
1505	195.780	53.853	10.176	6.728	102.498	73.123	.185	39.325
1523	198.095	57.310	10.175	5.257	101.084	73.436	.189	36.999
1521	198.426	57.804	10.174	5.284	101.071	73.480	.189	36.921
1506	202.601	64.048	10.171	6.923	100.060	74.028	.194	34.818
1502	203.142	64.857	10.171	6.470	106.980	74.098	.195	44.032
1524	203.375	65.206	10.171	5.301	100.142	74.128	.196	34.793
1522	203.731	65.739	10.171	5.320	99.881	74.173	.197	34.382
1525	208.704	73.193	10.167	5.334	99.538	74.795	.203	33.078
1523	209.057	73.722	10.167	5.326	99.856	74.838	.204	33.447
1507	209.526	74.426	10.166	6.942	99.491	74.895	.203	32.879
1503	209.853	74.915	10.166	6.955	99.636	74.935	.204	33.020
1526	214.044	81.206	10.164	5.346	99.736	75.434	.211	32.476
1508	216.467	84.845	10.161	6.956	99.479	75.715	.213	31.750
1504	216.813	85.365	10.161	6.945	99.842	75.755	.214	32.185
1509	223.396	95.256	10.157	6.923	99.937	76.489	.223	31.318
1510	230.790	106.373	10.151	6.920	100.066	77.268	.233	30.432
1511	237.756	116.844	10.147	6.901	100.143	77.962	.242	29.998
1512	244.636	127.181	10.142	6.864	100.993	78.610	.251	29.857
1513	251.488	137.466	10.137	6.819	101.457	79.221	.261	29.650
1514	259.403	149.331	10.131	6.782	102.116	79.886	.271	29.632
1515	266.154	159.433	10.126	6.725	102.604	80.421	.280	29.560
1517	282.516	183.843	10.114	6.617	104.067	81.599	.301	29.922
1518	289.146	193.696	10.110	6.625	104.538	82.032	.310	29.964
1519	295.822	203.596	10.105	6.556	105.109	82.444	.319	30.170
219	195.627	55.318	11.838	9.621	105.430	73.102	.204	37.165
223	196.581	57.055	11.839	7.285	104.709	73.232	.209	36.177
224	203.924	70.601	11.832	7.393	103.134	74.198	.226	33.223
225	211.370	84.550	11.826	7.394	102.930	75.118	.242	31.908
205	215.626	92.584	11.822	8.023	102.779	75.618	.250	31.148
226	218.787	98.572	11.819	7.411	102.950	75.979	.256	30.922
206	223.653	107.819	11.815	8.022	103.224	76.517	.265	30.609
227	226.191	112.653	11.813	7.374	103.274	76.789	.270	30.347

TABLE 2. *Specific heat at constant volume,* C_V, *of methane; heat correction for calorimeter expansion* C1, *heat capacity of empty calorimeter,* C0, *total heat capacity of calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT, *with temperature, pressure, density, and temperature increment,* DT—*Continued*

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	C0 J/K	C1 J/mol · K	C_V J/mol · K
207	231.675	123.117	11.808	7.947	103.685	77.359	0.279	30.155
228	233.566	126.729	11.806	7.338	103.858	77.549	.283	30.130
208	239.625	138.319	11.801	7.906	104.383	78.141	.293	30.043
229	204.923	140.803	11.800	7.311	104.171	78.264	.296	29.653
209	248.734	155.761	11.792	7.882	104.855	78.979	.309	29.604
210	257.453	172.459	11.784	9.556	105.552	79.726	.323	29.534
211	266.957	190.643	11.775	9.438	106.408	80.482	.339	29.632
212	276.534	208.934	11.766	9.341	107.186	81.187	.355	29.702
214	296.364	246.647	11.748	9.271	108.845	82.476	.388	30.098
301	204.751	77.746	13.088	7.244	105.556	74.303	.264	32.393
302	212.016	93.924	13.080	7.229	105.596	75.195	.282	31.485
303	219.265	110.242	13.073	7.214	105.859	76.033	.299	30.868
304	226.524	126.697	13.065	7.179	106.293	76.824	.315	30.478
305	234.072	143.881	13.057	7.166	106.784	77.600	.331	30.165
306	241.245	160.256	13.050	7.146	107.321	78.295	.347	29.985
307	248.387	176.580	13.042	7.078	107.969	78.948	.362	29.965
309	262.566	208.987	13.026	7.007	109.144	80.140	.391	29.918
310	276.780	241.398	13.011	6.874	110.608	81.204	.419	30.309
313	276.944	241.772	13.010	6.908	110.434	81.216	.419	30.114
314	283.783	257.318	13.003	6.854	110.947	81.684	.433	30.147
311	290.591	272.756	12.995	6.847	111.617	82.124	.446	30.375
312	297.427	288.216	12.987	6.788	112.344	82.540	.460	30.687
501	191.539	52.228	14.388	7.056	108.595	72.531	.268	34.042
528	195.039	61.226	14.383	8.352	107.756	73.021	.281	32.765
502	198.638	70.602	14.379	7.127	107.453	73.509	.295	32.000
520	200.323	75.028	14.377	8.432	107.534	73.732	.299	31.860
503	205.816	89.577	14.371	7.131	107.532	74.437	.315	31.171
521	208.733	97.366	14.366	8.358	107.655	74.799	.321	30.940
504	212.954	108.696	14.362	7.102	107.804	75.306	.334	30.585
522	217.103	119.884	14.356	8.319	107.990	75.788	.347	30.292
505	220.066	127.901	14.353	7.075	108.187	76.123	.356	30.152
523	225.394	142.360	14.346	8.245	108.656	76.704	.369	30.032
506	227.167	147.180	14.344	7.039	108.887	76.892	.375	30.067
524	234.287	166.574	14.334	8.234	109.380	77.621	.392	29.826
507	234.417	166.928	14.335	6.969	109.372	77.634	.393	29.805
508	241.372	185.902	14.326	6.927	109.898	78.307	.411	29.647
525	242.493	188.962	14.324	8.159	109.939	78.412	.412	29.585
509	248.293	204.791	14.317	6.910	110.378	78.940	.428	29.485
510	255.197	223.622	14.308	6.870	111.009	79.538	.445	29.500
511	262.143	242.543	14.299	6.820	111.759	80.107	.461	29.656
514	265.537	251.779	14.294	7.970	112.059	80.373	.468	29.631
512	269.538	262.650	14.289	7.971	112.383	80.678	.478	29.689
515	273.495	273.386	14.284	7.928	112.890	80.969	.487	29.885
513	277.494	284.223	14.278	7.914	113.176	81.255	.497	29.877
516	281.439	294.892	14.273	7.875	113.651	81.527	.506	30.061
517	289.349	316.229	14.262	7.793	114.710	82.045	.524	30.557

TABLE 2. *Specific heat at constant volume*, C_v, *of methane; heat correction for calorimeter expansion* C1, *heat capacity of empty calorimeter*, C0, *total heat capacity of calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT, *with temperature, pressure, density, and temperature increment*, DT—*Continued*

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	C0 J/K	C1 J/mol · K	C_v J/mol · K
701	187.947	51.088	16.104	7.172	110.110	72.012	0.350	32.038
707	188.669	53.498	16.103	6.957	110.164	72.118	.353	31.990
721	191.577	63.245	16.098	6.895	110.072	72.537	.367	31.543
702	195.118	75.188	16.093	7.178	110.019	73.032	.378	31.066
708	195.637	76.943	16.092	6.947	110.062	73.103	.380	31.040
720	199.140	88.833	16.087	6.859	110.111	73.576	.390	30.670
703	202.277	99.525	16.082	7.135	110.530	73.987	.397	30.670
709	202.632	100.738	16.082	6.943	110.308	74.032	.399	30.441
704	209.408	123.943	16.071	7.112	110.909	74.881	.426	30.204
710	209.569	124.495	16.071	6.933	110.994	74.901	.427	30.258
711	216.494	148.306	16.060	6.873	111.429	75.718	.450	29.911
705	216.509	148.360	16.060	7.078	111.388	75.720	.450	29.875
712	223.352	171.937	16.049	6.816	112.095	76.484	.472	29.805
706	223.900	173.825	16.048	7.007	112.128	76.544	.473	29.780
713	230.437	196.359	16.038	6.824	112.675	77.232	.494	29.639
714	237.251	219.833	16.027	6.791	113.485	77.913	.515	29.729
715	244.048	243.213	16.016	6.758	113.994	78.556	.536	29.594
716	250.777	266.302	16.005	6.660	114.660	79.159	.557	29.627
717	257.424	289.044	15.994	6.627	115.322	79.724	.577	29.689
718	264.035	311.587	15.983	6.571	116.177	80.256	.597	29.944
719	270.623	333.970	15.972	6.544	116.590	80.759	.616	29.849
1601	185.501	42.477	16.038	2.172	110.226	71.648	.337	32.608
1602	187.587	49.323	16.035	2.006	110.069	71.959	.348	32.198
1603	189.591	55.934	16.032	2.009	109.944	72.252	.358	31.832
1604	191.595	62.582	16.029	2.004	110.119	72.539	.361	31.732
1618	192.871	66.824	16.024	6.135	109.928	72.719	.367	31.410
1605	193.605	69.272	16.026	2.010	109.753	72.822	.377	31.163
1606	195.615	75.989	16.023	2.012	109.895	73.100	.383	31.041
1607	197.622	82.719	16.020	2.003	110.311	73.373	.389	31.157
1608	199.628	89.464	16.017	2.005	110.203	73.640	.396	30.831
1619	200.031	90.821	16.011	8.252	110.152	73.693	.391	30.746
1620	209.230	121.946	15.996	10.164	110.765	74.859	.419	30.246
1609	217.884	151.399	15.986	6.097	111.290	75.877	.452	29.793
1611	223.224	169.616	15.977	6.069	111.946	76.470	.469	29.830
1610	223.903	171.930	15.976	6.052	112.026	76.544	.471	29.834
1622	229.421	190.764	15.964	10.032	112.633	77.128	.484	29.842
1612	229.453	190.871	15.967	6.063	112.588	77.131	.488	29.795
1623	239.424	224.878	15.948	9.937	113.475	78.122	.515	29.681
1613	241.503	231.959	15.948	5.956	113.763	78.319	.525	29.748
1614	247.521	252.433	15.939	5.898	114.298	78.871	.544	29.715
1615	253.443	272.535	15.929	5.912	114.868	79.389	.562	29.742
1616	259.333	292.473	15.919	5.842	115.529	79.880	.579	29.869
1617	265.198	312.270	15.910	5.849	116.001	80.347	.597	29.856

TABLE 2. *Specific heat at constant volume*, C_v, *of methane; heat correction for calorimeter expansion* C1, *heat capacity of empty calorimeter*, C0, *total heat capacity of calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT, *with temperature, pressure, density, and temperature increment*, DT—*Continued*

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	C0 J/K	C1 J/mol · K	C_v J/mol · K
1309	184.764	45.449	16.723	5.354	110.741	71.537	0.381	31.721
1301	187.826	56.698	16.717	6.932	110.769	71.994	.394	31.357
1310	190.103	65.099	16.714	5.347	110.862	72.326	.406	31.150
1302	194.733	82.255	16.706	6.892	110.968	72.979	.423	30.685
1311	195.445	84.904	16.706	5.344	111.063	73.077	.427	30.679
1303	201.094	105.956	16.696	5.855	111.252	73.833	.446	30.196
1323	202.937	112.841	16.693	6.031	111.551	74.072	.453	30.239
1312	206.062	124.532	16.688	5.287	111.919	74.468	.465	30.204
1304	206.122	124.756	16.689	4.249	111.707	74.475	.466	30.023
1324	208.680	134.336	16.683	5.477	112.228	74.792	.473	30.184
1305	210.401	140.788	16.681	4.330	112.079	75.001	.481	29.882
1313	211.348	144.339	16.679	5.286	112.322	75.115	.483	29.987
1325	214.143	154.818	16.674	5.464	112.494	75.446	.492	29.847
1306	215.024	158.123	16.673	4.934	112.592	75.549	.496	29.840
1314	216.658	164.252	16.670	5.219	112.889	75.737	.501	29.924
1326	219.582	175.218	16.665	5.433	112.992	76.069	.511	29.727
1327	225.003	195.545	16.655	5.423	113.635	76.662	.530	29.749
1317	232.337	223.009	16.643	5.178	114.228	77.426	.555	29.585
1318	237.657	242.891	16.633	5.448	114.856	77.952	.572	29.651
1319	243.097	263.174	16.624	5.401	115.579	78.468	.590	29.802
1320	248.519	283.339	16.614	5.387	115.951	78.960	.608	29.686
1321	253.921	303.370	16.604	5.359	116.619	79.430	.626	29.831
1322	259.304	323.264	16.595	5.339	117.189	79.878	.644	29.913
411	187.325	58.469	17.007	8.019	111.229	71.920	.416	31.221
401	193.924	83.993	16.997	6.900	111.328	72.867	.443	30.513
406	196.587	94.337	16.992	7.437	111.563	73.233	.452	30.399
413	203.953	123.025	16.978	7.970	112.216	74.202	.478	30.119
414	211.983	154.390	16.964	7.898	113.134	75.192	.507	30.033
415	219.901	185.282	16.950	7.850	113.769	76.104	.535	29.782
416	227.768	215.952	16.936	7.807	114.550	76.955	.562	29.698
417	235.598	246.397	16.922	7.735	115.435	77.751	.590	29.743
418	245.293	283.931	16.904	7.650	116.261	78.670	.623	29.635
419	252.926	313.338	16.890	7.598	117.007	79.345	.649	29.667
1801	178.581	37.972	18.086	3.069	112.484	70.571	.469	31.280
1802	181.649	51.836	18.080	3.085	112.625	71.057	.495	30.991
1803	186.224	72.545	18.068	6.089	112.813	71.756	.503	30.598
1804	192.299	100.083	18.056	6.060	113.438	72.639	.530	30.377
1805	198.354	127.540	18.044	6.039	113.922	73.471	.554	30.090
1806	204.379	154.828	18.032	6.010	114.564	74.256	.578	29.958
1807	210.370	181.915	18.019	5.964	115.132	74.998	.602	29.803
1808	216.641	210.187	18.006	5.923	115.821	75.735	.627	29.741
1809	222.620	237.053	17.994	5.886	116.615	76.404	.651	29.812
1810	228.488	263.318	17.982	5.854	117.179	77.031	.674	29.742
1811	234.304	289.242	17.970	5.825	117.723	77.623	.697	29.683
1812	240.990	318.901	17.955	5.797	118.614	78.271	.723	29.841

TABLE 2. *Specific heat at constant volume,* C_V*, of methane; heat correction for calorimeter expansion* C1, *heat capacity of empty calorimeter,* C0, *total heat capacity of calorimeter (full)* ΔQ/ΔT *or* DQ/DT, *with temperature, pressure, density, and temperature increment,* DT — *Continued*

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	C0 J/K	C1 J/mol · K	C_V J/mol · K
1709	172.603	40.302	19.500	6.087	114.035	69.577	0.596	30.637
1710	178.550	73.409	19.486	6.101	114.965	70.566	.608	30.586
1701	181.613	90.419	19.479	6.082	115.092	71.052	.636	30.306
1711	184.637	107.182	19.472	6.065	115.515	71.517	.650	30.262
1702	187.628	123.725	19.465	6.054	115.740	71.965	.663	30.094
1712	190.680	140.564	19.457	6.039	116.187	72.408	.676	30.082
1703	193.640	156.857	19.450	6.008	116.537	72.827	.690	30.021
1713	196.693	173.622	19.443	5.997	116.917	73.247	.704	29.980
1704	199.616	189.630	19.435	5.980	117.239	73.639	.717	29.918
1714	202.661	206.260	19.428	5.946	117.740	74.036	.731	29.976
1705	205.568	222.086	19.421	5.941	117.875	74.406	.745	29.798
1715	208.615	238.633	19.413	5.927	118.353	74.784	.759	29.854
1706	211.480	254.140	19.406	5.895	118.705	75.131	.772	29.844
1716	214.522	270.555	19.398	5.886	118.998	75.490	.787	29.783
1707	217.573	286.970	19.391	5.857	119.326	75.842	.801	29.752
1717	220.387	302.058	19.384	5.842	119.782	76.158	.814	29.837
1708	223.411	318.216	19.376	5.818	120.066	76.491	.829	29.789
807	161.140	39.441	21.313	5.723	116.134	67.478	.746	30.544
801	165.189	68.515	21.299	6.791	116.981	68.251	.772	30.565
808	166.828	80.226	21.296	5.647	117.232	68.554	.798	30.507
802	171.921	116.429	21.279	6.676	118.171	69.459	.833	30.495
809	172.488	120.439	21.279	5.633	118.018	69.557	.831	30.336
810	178.091	159.906	21.262	5.566	118.950	70.491	.859	30.307
803	178.582	163.345	21.258	6.640	118.980	70.571	.859	39.275
811	183.640	198.640	21.244	5.532	119.742	71.365	.890	30.224
804	185.182	209.346	21.238	6.587	119.938	71.600	.896	30.193
812	189.153	236.787	21.227	5.487	120.631	72.188	.921	30.236
805	191.734	254.532	21.218	6.521	120.927	72.559	.933	30.175
813	194.626	274.322	21.210	5.456	121.445	72.964	.953	30.229
806	198.229	298.849	21.197	6.467	121.824	73.454	.971	30.139
814	200.078	311.376	21.193	5.439	122.044	73.700	.985	30.109
2109	153.984	30.846	22.126	4.385	117.420	66.016	.818	31.040
2101	157.876	62.103	22.113	4.327	118.099	66.827	.845	30.931
2102	162.200	96.526	22.098	4.314	118.875	67.684	.927	30.800
2103	166.497	130.432	22.083	4.273	119.755	68.493	.940	30.832
2104	170.767	163.847	22.069	4.251	120.349	69.259	.951	30.716
2105	175.011	196.789	22.054	4.233	120.874	69.985	.976	30.567
2106	179.314	229.914	22.040	4.211	121.698	70.688	1.003	30.615
2107	183.514	261.982	22.025	4.186	122.103	71.346	1.029	30.432
2108	187.701	293.689	22.011	4.164	122.834	71.976	1.056	30.468
1406	148.828	44.459	22.933	6.789	118.758	64.875	0.899	31.314
1407	155.536	104.131	22.907	6.633	120.057	66.344	1.015	31.098
1402	155.969	107.942	22.906	6.629	120.154	66.435	1.017	31.100
1401	156.936	116.449	22.900	7.882	120.264	66.635	1.020	31.042
1408	162.130	161.805	22.883	6.560	121.193	67.671	1.042	30.958
1403	162.555	165.498	22.881	6.564	121.222	67.753	1.043	30.925
1409	168.648	217.963	22.858	6.496	122.400	68.883	1.075	30.923
1404	169.076	221.618	22.856	6.499	122.320	68.960	1.078	30.826
1410	175.122	272.905	22.834	6.453	123.385	70.003	1.120	39.798
1405	175.530	276.347	22.832	6.440	123.626	70.071	1.123	30.898

TABLE 2. *Specific heat at constant volume,* C_v*, of methane; heat correction for calorimeter expansion* C1*, heat capacity of empty calorimeter,* C0*, total heat capacity of calorimeter (full)* $\Delta Q/\Delta T$ *or* DQ/DT*, with temperature, pressure, density, and temperature increment,* DT – *Continued*

ID	Temp K	Press bar	Den mol/l	*DT* K	*DQ/DT* J/K	C0 J/K	C1 J/mol · K	C_v J/mol · K
2001	139.073	45.399	24.008	4.195	119.866	62.486	0.988	31.796
2002	143.270	88.569	23.990	4.184	120.961	63.554	1.146	31.655
2003	147.448	130.924	23.972	4.155	121.919	64.557	1.165	31.612
2004	151.599	172.491	23.954	4.133	122.597	65.498	1.191	31.437
2005	155.908	215.104	23.935	4.091	123.742	66.422	1.205	31.550
2006	160.011	255.209	23.917	4.084	124.120	67.256	1.236	31.258
2007	164.072	294.445	23.900	4.052	124.977	68.042	1.268	31.267
901	130.508	34.766	24.785	2.255	121.056	60.095	1.097	32.662
909	131.693	48.379	24.772	5.484	121.045	60.443	1.106	32.454
904	132.694	59.842	24.767	5.557	121.433	60.734	1.136	32.479
902	134.136	76.278	24.761	4.991	121.346	61.144	1.174	32.166
910	137.159	110.410	24.746	5.421	122.150	61.977	1.245	32.080
903	139.337	134.756	24.735	5.473	122.514	62.555	1.258	31.949
911	142.547	170.300	24.720	5.356	123.309	63.375	1.283	31.911
906	143.713	183.112	24.715	5.439	123.701	63.663	1.287	31.964
912	147.886	228.554	24.695	5.336	124.401	64.659	1.303	31.785
907	149.124	241.915	24.689	5.389	124.607	64.943	1.313	31.732
913	153.185	285.371	24.670	5.287	125.563	65.844	1.348	31.728
908	154.473	299.029	24.664	5.310	126.059	66.120	1.359	31.839
1201	121.160	64.484	25.872	3.070	122.005	57.118	1.274	33.145
1202	124.223	104.694	25.855	3.048	122.909	58.138	1.400	32.958
1203	127.262	144.001	25.838	3.035	123.532	59.107	1.420	32.757
1204	130.274	182,414	25.822	3.013	124.390	60.025	1.455	32.691
1101	110.867	44.963	26.655	5.194	121.731	53.349	1.309	33.910
1106	111.917	60.514	26.649	5.165	121.991	53.758	1.354	33.789
1103	111.855	59.603	26.649	5.215	121.835	53.734	1.351	33.724
1102	116.030	120.523	26.624	5.136	123.377	55.306	1.503	33.557
1107	117.051	135.181	26.618	5.109	123.607	55.677	1.510	33.478
1104	122.089	206.386	26.588	5.057	125.308	57.432	1.546	33.415
1108	122.094	206.453	26.588	5.051	125.107	57.434	1.546	33.311
1109	127.100	275.451	26.559	4.981	126.527	59.056	1.574	33.180
1105	127.123	275.769	26.558	5.028	126.592	59.064	1.574	33.210
1004	102.424	48.414	27.388	5.069	121.472	49.858	1.475	34.428
1001	105.029	90.948	27.371	5.078	122.552	50.974	1.619	34.267
1005	107.466	129.912	27.355	5.035	123.275	51.986	1.613	34.129
1002	110.058	170.735	27.338	4.981	124.205	53.030	1.637	34.049
1006	112.446	207.806	27.322	4.941	125.126	53.962	1.646	34.035
1003	115.142	249.013	27.305	4.914	126.082	54.979	1.652	33.999
1007	117.361	282.491	27.290	4.903	126.695	55.789	1.673	33.879
1912	92.592	40.274	28.164	3.061	120.491	45.311	1.351	35.326
1901	92.609	40.540	28.164	2.871	120.603	45.319	1.313	35.415
1907	93.793	62.384	28.155	2.873	121.008	45.899	1.458	35.186
1902	95.465	92.859	28.143	2.842	122.072	46.701	1.769	35.003
1913	95.634	95.885	28.141	3.022	122.178	46.780	1.765	35.020
1908	96.675	114.525	28.134	2.824	122.424	47.269	1.769	34.898
1903	98.301	143.313	28.122	2.807	123.144	48.020	1.740	34.913
1909	99.505	164.435	28.114	2.821	123.531	48.566	1.745	34.830
1904	101.123	192.506	28.102	2.793	124.316	49.288	1.768	34.839
1910	102.319	213.085	28.093	2.791	124.573	49.812	1.767	34.710
1905	103.902	240.032	28.082	2.749	125.401	50.495	1.755	34.793
1911	105.104	260.314	28.074	2.766	125.538	51.005	1.766	34.600
1906	106.655	286.252	28.063	2.751	126.307	51.653	1.781	34.644

for in

Comparison of C_v methane, extrapolated to saturation, to several other liquids: F_2 [8], O_2 [6], KR [13], Ar [14], and Ne [15] is shown if figure 6. The density is reduced by the critical density. The spectroscopic heat capacity, C_v^0 is subtracted in each case. Molar specific heats are independent of reducing parameters [16]. All of the data except that for Ne correlate quite well. Presumably this departure of Ne is a result of its being more of a quantum fluid. H_2 and He also depart markedly from this grouping as shown by Diller [16].

I would like to acknowledge the support of the American Gas Association. R. D. Goodwin's data of the PVT of methane were essential and his computer programs calculating the various functions and derivatives were of great help. I thank D. E. Diller for his numerous contributions. ~~The data shown in figure 6 are from his work~~.

5. References

[1] The S. I. (international system) unit of pressure is the Pascal (1 Pa $\equiv$ 1 N/m^2). The bar is 10^5 Pa, also 1 atm = 1.01325×10^5 Pa, 1 lb/in^2 = 6894.757 Pa, 1 dyne/cm^2 = 10^{-1} Pa. Also one mole methane = 16.0430 g, based on the ^{12}C scale and the natural isotopic abundance averages: see Remy, H., Chem. Berichte **101**, I (1968).
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54A

FIGURE 1. *Calorimeter and cryostat.*

55A

FIGURE 2. *Specific heat of the saturated liquid for methane, this work,* ○, *the measurements of Wiebe and Breevort* ● [12].

56A

FIGURE 3. *Specific heat at constant volume of methane on isochores versus temperature.*

Open and closed circles on altercate isochores are for clarity.

A−28.0 mol/l, B−27.4 mol/l C−26.7 mol/l
D−25.8 E−24.7 F−24.0
G−23.0 H−22.1 I−21.3
J−19.5 K−18.0 L−17.0
M−16.7 N−16.0 P−14.4
Q−13.1 R−13.1 S−11.8
T−7.9

57A

FIGURE 4. C_v *of liquid methane evaluated at the liquid-gas boundary.*

Extrapolation of C_v(○). calculation from C_σ using *PVT* surface (△).

58A

FIGURE 5. *Comparison of methane* C_p *from Jones, et al.* (-○-): *to* C_p *calculated from* C_v *data, this work* (△), *and to* C_p *calculated from* PVT *data* (—).

57A

FIGURE 6. *Reduced specific heats versus reduced density for* CH_4 (●), F_2 (◊), O_2 (△), Kr (□), Ar (○), *and* Ne (▽).

APPENDIX H

This survey provides a convenient summary of available data on liquid–vapour equilibria for systems of interest in cryogenics. An annotated bibliography of 392 references has been compiled, current to January 1973. These references have been scanned individually with few exceptions, and cross-indexed by system with notation of extent of data and other significant features. The systems included are those made up of the possible combinations of $H_2(D_2, HD)$, N_2, O_2, F_2, CO, H_2S, He (He^3), Ne, Ar, Kr, Xe, and the saturated and unsaturated hydrocarbons through the C_4s.

R-789

Liquid–vapour equilibria research on systems of interest in cryogenics – A survey

A. J. Kidnay, M. J. Hiza, and R. C. Miller

This paper is intended as a survey of the available experimental data for the equilibria between the liquid and vapour phases of fluid mixture systems of interest in cryogenics. These data are described in a number of different ways in the scientific literature, that is, dew- and bubble-points, total vapour pressures of solutions, *K*-values or equilibrium distribution coefficients, solubility of gases in liquids, Henry's constants, liquid–gas equilibria, liquid–vapour, etc. Such terms are simply related to the type of data and method of representation or are intended to clarify the relationship between critical temperatures of the included components. In this paper, the term 'liquid–vapour equilibria' is used collectively for all of the various descriptors.

This survey on liquid–vapour equilibria is only one part of an extensive compilation and evaluation effort on the important equilibrium and thermodynamic properties of low temperature mixtures. These include solid–liquid, solid–vapour, solid–liquid–vapour, liquid–liquid, liquid–vapour, and gas–gas phase equilibria, liquid densities, gas or vapour densities, enthalpies, and Joule–Thomson coefficients. A complete annotated bibliography of these properties will be published as a special NBS-Office of Standard Reference Data publication. However, there is an immediate interest in liquid–vapour equilibria data for a number of low temperature systems, such as those related to liquefied natural gas technology. Thus, it seems warranted to make this section available prior to publication of the complete bibliography.

In an earlier paper,[1] a review of research associated with low temperature solid–vapour equilibria was given with emphasis on the fundamental value of such studies. The present survey of low temperature liquid–vapour equilibria is a logical sequel, and many of the fundamental aspects presented in the earlier paper apply here as well. The same molecular species were considered in this survey of liquid–vapour equilibria data; however, the number was expanded to include isotopes of helium and hydrogen, additional hydrocarbon species, and hydrogen sulphide. Thus, the information included here would be valuable to the low temperature physicist as well as to the cryogenic engineer, whose current interest may be in liquefied natural gas technology.

Literature search

In the early phases of the fluid mixtures research programme in the NBS Cryogenics Division, an indexed bibliography of 681 references was prepared current to October 1959.[2] Included were references to experimental and theoretical work on phenomena and properties of selected pure components and mixtures containing these species. The components of primary interest were: hydrogen, helium, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, and propane. Oxygen, the remaining noble gas species, and other hydrocarbons were considered only when included in the primary systems. From experience in using this early bibliography, it was apparent that the scope was too broad and the number of primary components was too limited. The scope of the present effort was reduced to experimental properties of fluid mixtures only, but for an increased number of primary components. The components included here are: $H_2(D_2, HD)$, N_2, O_2, F_2, CO, CO_2, H_2S, He(He–3), Ne, Ar, Kr, Xe, and the saturated and unsaturated hydrocarbons through the C_4s. In addition, systems containing components other than those of primary interest (for example, the methane–benzene system) were not included. References in the 1959 bibliography which met these new criteria contributed significantly to the present effort.

A search of the NBS-Cryogenic Data Center computer listing for citations on properties of mixtures containing the subject molecular species resulted in approximately 1 400 citations. These were also screened in accordance with the criteria described above. Though the Cryogenic Data Center personnel expend considerable effort to attain comprehensive coverage of the literature,[3] all of the fluid species of interest here were not consistently subjects in their search of the literature. Specifically, the hydrocarbon species other than methane were not adequately covered. On the other hand, since the Cryogenic Data Center operation was begun just before Tech Note 56 [2] was completed, the two sources provide comprehensive coverage for some

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of the systems of interest. The deficient areas were the primary objects of the present search.

The following sources of references were used as cross-checks and to remedy the deficiency of coverage discussed above.

a The monograph of Hala, et al [4]

b The handbook of Katz, et al [5]

c The bibliography of Ruhemann and Harmens [6]

d The bibliography of Gunn and Mainkar [7]

e The bibliography of Mendelssohn et al [8]

f Extensive bibliographies found in several dissertations and papers scanned

g The files of the NBS Cryogenics Division fluids mixtures project, which have been maintained for the past 14 years

h Lists of publications of our colleagues who have been actively engaged in fluid mixtures research for a number of years

The resulting list of references was finally updated by searching Chemical Abstracts, section 68 – Phase equilibriums, chemical equilibriums, and solutions, and section 69 – Thermodynamics, and thermal properties, all of 1971 and 1972, and with an issue by issue search of the following periodicals for 1972.

a *AIChE J*
b *Can J Chem Eng*
c *Ind Eng Chem Fundam*
d *J Chem Eng Data*
e *J Chem Thermodyn*

Finally, more current papers, of which we were aware, were included for the sake of completeness.

	H_2	He^3	He	O_2	Ne	CO	N_2	O_2	H_2S	F_2	Ar	CO_2	Kr	Xe	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	n-C_4H_{10}
HD	5																				
He^3	2																				
He	9	20																			
O_2	6	1	1																		
Ne	3		2	3																	
CO	6		1																		
N_2	15		14	1	6	7															
O_2			5		3		13														
H_2S																					
F_2			2																		
Ar	2		7	1	7	1	10	11													
CO_2	8		3			4	10	6	3		1										
Kr			1		1			3			2										
Xe													1								
CH_4	8		9		1	4	16	1	2		6	7	2								
C_2H_2																					
C_2H_4	3		3		1		1					1			4						
C_2H_6	5		4		1	1	5		1		2				12		4				
C_3H_6	1		1			1	1		1		2	5	2	1		1	1	2			
C_3H_8	3		2			3	5		4			4			10	1		4	5		
n-C_4H_{10}	2		1				6		1			3			7			1		3	
iso-C_4H_{10}	1						2								2			1	1	3	2

Liquid-vapour equilibria for binary systems

Fig.1 Summary of the number of references which report original liquid–vapour equilibria data for each binary system

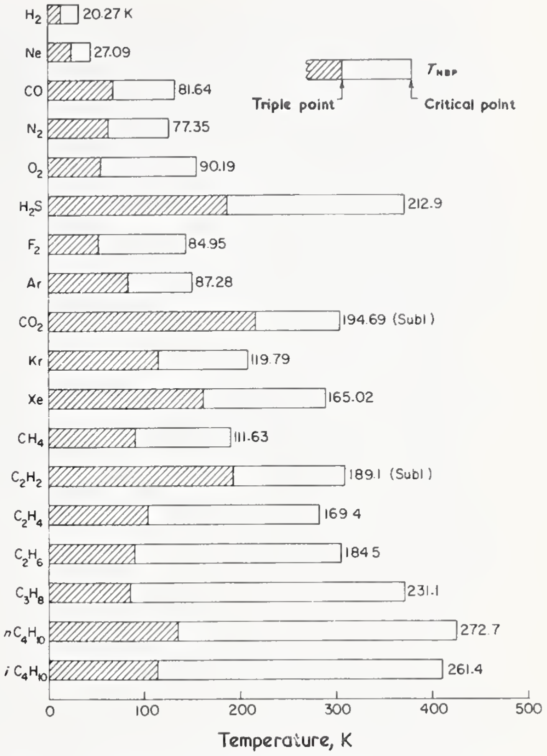

Fig.2 The saturated liquid phase temperature range of representative pure component species included in this survey

Availability of liquid–vapour equilibria data

The bibliography of references on liquid–vapour equilibria data and the tables in which the references are indexed by system are the results of this effort.

The references are indexed in the tables by system with separate tables for binary systems, ternary systems, and systems containing four or more components. For binary systems, the lowest molecular weight component is listed first. The systems are arranged in order of increasing molecular weight of the light component, with systems having non-hydrocarbon light components preceding those having hydrocarbon light components. For ternary and higher systems, components within the mixture are listed in order of increasing molecular weight. The arrangement of the systems follows the same pattern as for binary systems. The bibliography of 392 references is arranged in alphabetical order by author.

Fig.1 provides a superficial summary of the available data for the binary systems. The numbers in the spaces indicate the number of papers reporting data for each system. Dissertations were not included in these totals if the included data were subsequently published in the periodical literature. The one reference for the carbon dioxide–cyclopropane system is included in the total for C_3H_6 under CO_2. Two references not included are those for the propene–1–butene and propane–isobutene systems.

Fig.2, which portrays the normal liquid range of representative pure component species, is included as an aid to indicate the temperature regions in which liquid–vapour equilibria can exist for given combinations.

Discussion

It is important to emphasize that this survey is intended to include all references containing experimental data without judgement as to the reliability of the results given. Selection of best values for a given system is a complicated process at best, but must begin with a common method of data reduction which is most sensitive to discrepancies in the available data sets. A cursory discussion of the fundamental relationships is given here only to indicate the basis of data reduction or presentation methods. Examples of two such methods of liquid phase data reduction are given which serve to indicate the potential ease or difficulty in best value selection.

The equilibria represented here fall into two distinct categories: (1) equilibria of close-boiling systems in which the included components would be subcritical at the temperature of solution, and (2) equilibria of systems in which both subcritical and supercritical components are included. In either case, the equation of equilibrium is

$$\bar{f}_i(\text{vapour}) = \bar{f}_i(\text{liquid}) \qquad (1)$$

where $\bar{f}_i$ is the fugacity of component i in the mixture. The fugacity of i in the vapour is related to its mole fraction y_i and the pressure of solution π by

$$\bar{f}_i(\text{vapour}) = \bar{\varphi}_i y_i \pi \qquad (2)$$

where $\bar{\varphi}_i$ is the fugacity coefficient of i in the vapour mixture. The fugacity of i in the liquid is related to its mole fraction x_i and a standard state fugacity term S_i° by

$$\bar{f}_i(\text{liquid}) = \gamma_i x_i S_i^\circ \qquad (3)$$

where γ_i is the activity coefficient of i in the liquid mixture. The differences in the two categories of liquid–vapour equilibria are manifested in (3) in the method of normalization of γ and in the choice of the standard state term.

For close-boiling systems, γ for each component is conventionally normalized in the sense of Raoult's law (symmetric convention) such that

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \qquad (4)$$

The standard state term is taken as the fugacity for the pure fluid at the temperature and pressure of solution. Thus (3) becomes

$$\bar{f}_i(\text{liquid}) = \gamma_i x_i f_i^\circ \qquad (5)$$

where

$$f_i^\circ = p_i \varphi_i \exp \int_{p_i}^{\pi} \frac{v_i \mathrm{d}\pi}{RT} \qquad (6)$$

The terms p_i and φ_i are the pure component vapour pressure and fugacity coefficient, respectively.

It is also common practice to correct activity coefficients at the conditions of the solution to a reference state pressure $\pi^{(R)}$ by the following relationship

$$\gamma_i = \gamma_i^{(R)} \exp \int_{\pi^{(R)}}^{\pi} \frac{\bar{v}_i \mathrm{d}\pi}{RT} \qquad (7)$$

The excess Gibbs energy, directly related to the activity coefficients by

$$g^E = \Sigma x_i RT \ln \gamma_i^{(R)} \qquad (8)$$

is often reported in experimental papers, and in a number of cases appears to have been the primary purpose of the investigation.

For systems containing both subcritical and supercritical components, the activity coefficient of the subcritical component is still normalized in the sense of Raoult's law, but it is more convenient to normalize the activity coefficient of the supercritical component in the sense of Henry's law (unsymmetric convention) such that

$$\gamma_j^* \rightarrow 1 \text{ as } x_j \rightarrow 0 \qquad (9)$$

The standard state term is taken as the infinite dilution Henry's law coefficient. Equation 3 then becomes

$$f_j(\text{liquid}) = \gamma_j^* x_j H_{j,i} \qquad (10)$$

where

$$H_{j,i} = \lim_{x_j \rightarrow 0} \frac{\bar{f}_j}{x_j} \qquad (11)$$

Full details of these relations and their uses are given by Prausnitz.[9] The brief discussion given here, however, is adequate for an understanding of the data reduction that is encountered in the literature on liquid–vapour equilibria of mixtures, and to some extent the significance of the general relationships which apply. Typical examples of reduced liquid phase data for the two categories of equilibria, taken from the bibliography of references are given in Figs 3 and 4.

Fig.3 is an example of the excess Gibbs energy for a close-boiling system, nH_2–Ne, derived from the data of two different investigations. Since this system also exhibits liquid phase separation, the data were taken from the region of complete liquid phase miscibility. This is also an example of excellent agreement between two different sets of data, which unfortunately is not the general case. Fig.4 is an example of a Henry's law reduction of data from two different investigations for a system, nH_2–Ar, containing a supercritical component. This is also an example of discordant results for which critical selection becomes extremely difficult without additional information on this particular mixture. In this case pressure has been used rather than fugacity, which is quite common. Though the data have not been reduced in the true sense of Henry's law, the infinite dilution intercepts are for practical purposes the same as the Henry's constant.

Critical evaluation of the data for a given system also will require knowledge of the best available pure fluid properties which are an inherent part of the fundamental relations discussed above. The importance of thermodynamically consistent vapour pressure data was specifically emphasized

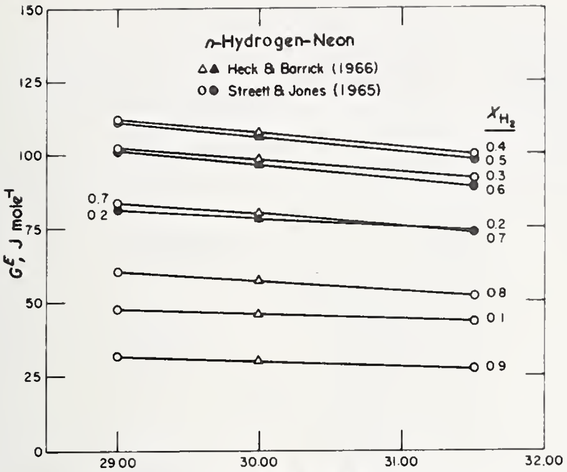

Fig.3 Excess Gibbs energy for the nH_2–Ne system as determined by Duncan and Hiza (1972) from the data of the two investigations indicated

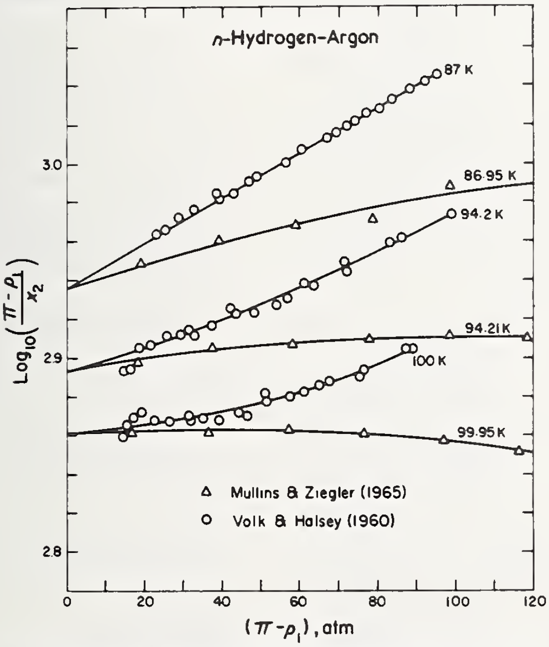

Fig.4 Gas solubility data from two investigations for the nH_2–Ar system as reduced in the sense of Henry's law by Mullins and Ziegler (1965)

in the review of solid–vapour equilibria research,[1] and selected references were included.

A similar list of vapour pressure references for the entire liquid region of each fluid has not been included as part of this liquid–vapour equilibria survey. However, it is worth noting several non-periodical sources of vapour pressure values and citations which are quite useful. The references to the work of W. T. Ziegler et al given in reference 1 include calculated values of vapour pressure up to the normal boiling point for most of the fluids of interest here, as well as providing a review of the available properties of the substance considered. A brief survey of vapour pressure data for the hydrocarbons not included in those references are given in an earlier NBS Technical Note of Ziegler.[10] Also, the bibliography of Olien and Hall [11] is a valuable source of vapour pressure references for methane and the non-hydrocarbon fluids. These may still be the best available sources of vapour pressure values and citations for most of the fluids in the regions covered, but some have been definitely out-dated in part by new precise experimental measurements. Notably, the new vapour pressure measurements of Prydz and Goodwin [12] on methane cover the entire liquid range, and are considered by the present authors to be the best values currently available for this fluid. Nevertheless, in addition to the above sources, an examination of the literature from 1964 to the present would provide a fairly complete list of vapour pressure data references.

It is hoped that this survey of experimental liquid–vapour equilibria data for fluid mixtures of cryogenic interest includes all of the significant experimental research done prior to January 1972 and most of that done between January 1972 and January 1973. Literature searches, however, seem to approach the intended objective asymptotically. Therefore, we would welcome correspondence from those who are aware of appropriate research papers which do not appear in this survey.

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Liquid—vapour equilibria for binary systems

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Hydrogen—helium 3	22—28	1—16	Hiza (1972)	
Hydrogen—helium 3	17—24	0—9	Matyash, Mank, Starkov (1966)	Pressures given as He^3 pressure
Hydrogen—hydrogen deuteride	17—18	<1	Hoge, Arnold (1951)	
Hydrogen—hydrogen deuteride	20	1	Karwat (1960)	
Hydrogen—hydrogen deuteride	19—27	0—4	Newman (1954)	Graphs only
Hydrogen—hydrogen deuteride	18—28	1—4	Newman, Jackson (1958)	
Hydrogen—hydrogen deuteride	18—32	0.1—11	Trevino (1956)	Graphs only
Hydrogen—helium 4	14—16	1—16	Greene (1966)	Normal and para hydrogen, bubble-point
Hydrogen—helium 4	14—16	1—16	Greene, Sonntag (1968)	Normal and para hydrogen, bubble-point, graphs only
Hydrogen—helium 4	20—28	1—20	Hiza (1972)	
Hydrogen—helium 4	16—29	2—8	Roellig, Giese (1962)	Pressures given are partial
Hydrogen—helium 4	17, 20, 22	2—58	Smith (1952)	
Hydrogen—helium 4	15—30	26—102	Sneed (1966), Sneed, Sonntag, Van Wylen (1968)	Both normal and para hydrogen, barotropic and critical locus
Hydrogen—helium 4	15—33	2—34	Sonntag, Crain, Streett (1964)	Both normal and para hydrogen, barotropic and critical locus
Hydrogen—helium 4	20—32	2—34	Sonntag, Van Wylen, Crain (1964)	Equilibrium hydrogen
Hydrogen—helium 4	16—33	2—34	Streett (1963), Streett, Sonntag, Van Wylen (1964)	Normal hydrogen
Hydrogen—deuterium	4	—	Bulatova, Kogan, Lazarev (1960)	Qualitative data from x-ray measurements
Hydrogen—deuterium	19—20	<1	Hoge, Arnold (1951)	
Hydrogen—deuterium	19	<1	Lewis, Hanson (1934)	Limited qualitative data graphs only
Hydrogen—deuterium	20—28	0—5	Newman (1954)	Graphs only
Hydrogen—deuterium	18—28	1—4	Newman, Jackson (1958)	
Hydrogen—deuterium	18—30	0.1—8	Trevino (1956)	Graphs only
Hydrogen—neon	26—43	0—26	Heck, Barrick (1966)	Normal hydrogen
Hydrogen—neon	25	<1	Simon (1963b)	Para hydrogen, graphs only
Hydrogen—neon	25—34	0—14	Streett, Jones (1965)	Normal hydrogen
Hydrogen—carbon monoxide	83, 100, 122	21—238	Akers, Eubanks (1960)	Graphs only
Hydrogen—carbon monoxide	32—70	1—50	Dokoupil, Van Soest, Swenker (1955)	Isobaric data, gas phase only
Hydrogen—carbon monoxide	83, 100, 122	21—238	Eubanks (1956)	Graphs only
Hydrogen—carbon monoxide	78, 83, 90	7—50	Ruhemann, Tsin (1937)	Graphs only
Hydrogen—carbon monoxide	68—88	17—225	Verschoyle (1931)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Hydrogen—carbon monoxide	77—123	10—150	Yorizane, Yoshimura, Masuoka, Toyama (1968)	
Hydrogen—nitrogen	83—122	0—170	Akers, Eubanks (1960)	Graphs only
Hydrogen—nitrogen	63—113	0—200	Charlseworth, Ruhemann (1965)	Graphs only
Hydrogen—nitrogen	25—70	1—50	Dokoupil, Van Soest, Swenker (1955)	Isobaric data, gas phase only
Hydrogen—nitrogen	83, 100, 122	21—157	Eubanks (1956)	
Hydrogen—nitrogen	79—109	13—175	Gonikberg, Fastovskii, Gurvitsch (1939)	
Hydrogen—nitrogen	90, 95	3—45	Maimoni (1956) (1961)	
Hydrogen—nitrogen	77	0—8	Matyash, Mank, Starkov (1966)	Graphs only
Hydrogen—nitrogen	63—75	5—45	Omar, Dokoupil (1962)	Isobaric data, gas phase only
Hydrogen—nitrogen	78, 83, 90	11—50	Ruhemann, Tsin (1937)	Graphs only
Hydrogen—nitrogen	79—91	<1	Sister, Sokolov (1940)	
Hydrogen—nitrogen	88, 90, 108, 113	0—110	Stekkel, Tsin (1939a)	Graphs only
Hydrogen—nitrogen	88, 90, 108, 113	0—110	Stekkel, Tsin (1939b)	Graphs only
Hydrogen—nitrogen	58—88	0—225	Verschoyle (1931)	
Hydrogen—nitrogen	77, 88	<188	Yorizane (1971)	
Hydrogen—nitrogen	77	5—150	Yorizane, Yoshimura, Masuoka, Toyama (1968)	
Hydrogen—argon	68—105	20—120	Mullins (1965), Mullins, Ziegler (1965)	
Hydrogen—argon	87—140	10—100	Volk, Halsey (1960)	
Hydrogen—carbon dioxide	273—298	—	Abdulayev (1939a)	
Hydrogen—carbon dioxide	298	78—195	Abdulayev (1939b)	Graphs only
Hydrogen—carbon dioxide	222, 273	39—242	Greco, Casale, Negri (1954)	
Hydrogen—carbon dioxide	233—298	50—197	Kaminishi, Toriumi (1966)	
Hydrogen—carbon dioxide	281, 288	56—106	Mills, Miller (1945)	
Hydrogen—carbon dioxide	220—290	11—200	Spano, Heck, Barrick (1968)	
Hydrogen—carbon dioxide	273	<370	Yorizane (1971)	
Hydrogen—carbon dioxide	273	60—370	Yorizane, Yoshimura, Masuoka (1970)	
Hydrogen—methane	117, 144, 172	34—272	Benham (1956), Benham, Katz (1957)	
Hydrogen—methane	90—127	31—227	Fastovsky, Gonikberg (1940a, 1940b)	
Hydrogen—methane	91	17—205	Freeth, Verschoyle (1931)	
Hydrogen—methane	67—117	10—125	Kirk (1964), Kirk, Ziegler (1965)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Hydrogen–methane	158–178	31–78	Levitskaya (1941)	
Hydrogen–methane	158–188	28–83	Likhter, Tikhovovich (1940)	
Hydrogen–methane	107	4–90	Steckel, Tsin (1939a, 1939b)	Graphs only
Hydrogen–methane	103–163	10–150	Yorizane, Yoshimura, Masuoka, Toyama (1968)	
Hydrogen–ethene	80–170	2–150	Hiza, Heck, Kidnay (1968a)	
Hydrogen–ethene	158–188	1–80	Likhter, Tikhonovich (1939)	
Hydrogen–ethene	117–255	17–544	Williams, Katz (1954)	
Hydrogen–ethane	144–200	7–136	Cohen, Hipkin, Koppany (1967)	
Hydrogen–ethane	80–190	3–154	Hiza, Heck, Kidnay (1968b)	
Hydrogen–ethane	158–188	31–78	Levitskaya (1941)	
Hydrogen–ethane	139–149	1	Uehara (1932)	
Hydrogen–ethane	103–283	17–544	Williams, Katz (1954)	
Hydrogen–propene	117–297	17–544	Williams, Katz (1954)	
Hydrogen–propane	278–361	27–497	Burriss, Hsu, Reamer, Sage (1953)	
Hydrogen–propane	88–348	10–204	Trust (1968), Trust, Kurata (1971)	
Hydrogen–propane	89–297	17–544	Williams, Katz (1954)	
Hydrogen–*n*–butane	144–297	20–544	Aroyan, Katz (1951)	
Hydrogen–*n*–butane	297–389	22–106	Nelson, Bonnell (1943)	
Hydrogen–isobutane	311–394	34–204	Dean, Tooke (1946)	
Helium 3–helium 4	1–2	–	Abraham, Weinstock, Osbourne (1949)	He^3–He^4 liquid λ temperature only
Helium 3–helium 4	1–3	–	Daunt, Heer (1952)	
Helium 3–helium 4	1.5–2.5	<1	Daunt, Tseng (1955)	Graphs only
Helium 3–helium 4	1–3	–	Eselson (1954)	Graphs only
Helium 3–helium 4	1–3	<1	Eselson, Berezryak (1954)	Dew-point measurement
Helium 3–helium 4	1–3	<1	Eselson, Berezryak (1956)	Extensive tabular data
Helium 3–helium 4	1–3	<1	Eselson, Berezryak (1955)	Graphs only
Helium 3–helium 4	1–2	–	Eselson, Kaganov, Lifshits (1957)	2nd order phase transition in He I–He II
Helium 3–helium 4	1	–	Eselson, Lazarev, Alekseevskii (1950)	
Helium 3–helium 4	2–5	–	Fairbank, Lane, Aldrich, Nier (1947)	
Helium 3–helium 4	2–5	–	Fairbank, Lane, Aldrich, Nier (1948)	
Helium 3–helium 4	1–4	–	Fairbank et al (1948)	Graphs only

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Helium 3–helium 4	1–2	<1	Grigorev, Eselson, Masimov et al (1968)	Data obtained by NMR
Helium 3–helium 4	1–2	<1	Nelson, Band (1952)	Graphs only
Helium 3–helium 4	1–2	<1	Peshkov, Kachinskii (1957)	Dew-point measurement
Helium 3–helium 4	1–3	<1	Sreedhar, Daunt (1960)	
Helium 3–helium 4	0–2	<1	Sydoriak, Roberts (1960)	
Helium 3–helium 4	1–2	<1	Taconis, Bennakker, Nier, Aldrich (1949)	
Helium 3–helium 4	1–2	<1	Wansink, Taconis, Staas (1956)	
Helium 3–helium 4	1–3	<1	Weinstock, Osborne, Abraham (1950)	Graphs only
Helium 3–deuterium	20–30	1–16	Hiza (1972)	
Helium 4–deuterium	20–30	1–20	Hiza (1972)	
Helium–neon	27–42	3–200	Heck (1968), Heck, Barrick (1967)	
Helium–neon	25–27	6–51	Knorn (1967)	
Helium–carbon monoxide	77–128	17–136	Sinor, Kurata (1966)	
Helium–nitrogen	83, 113	5–50	Burch (1964)	
Helium–nitrogen	78–122	12–68	Buzyna, Macriss, Ellington (1963)	
Helium–nitrogen	77	14–68	Davis, Rodewald, Kurata (1963)	
Helium–nitrogen	77–126	15–98	Davydov, Budnevich (1971)	
Helium–nitrogen	77–120	14–136	Devaney, Dalton, Meeks (1963)	
Helium–nitrogen	65–125	10–100	Forg, Wirtz (1970)	Graphs only
Helium–nitrogen	78, 90, 109	1–295	Gonikberg, Fastovsky (1940a)	
Helium–nitrogen	68–112	1–215	Kharakhorin (1940)	
Helium–nitrogen	65, 69, 77	14–68	Rodewald (1963), Rodewald, Davis, Kurata (1964)	
Helium–nitrogen	64–108	5–150	Ruhemann, Fedoritenko (1937)	Graphs only
Helium–nitrogen	67–90	6–26	Skripka, Dykhno (1964)	
Helium–nitrogen	78–122	66–816	Streett (1967)	
Helium–nitrogen	112–162	1 000–10 000	Streett, Erickson (1972)	
Helium–nitrogen	122–126	34–211	Tully, Devaney, Rhodes (1971)	
Helium–oxygen	78–122	20, 48	Cannon, Robson, English (1968)	Liquid phase only
Helium–oxygen	70–150	10–200	Herring (1964), Herring, Barrick (1965)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Helium—oxygen	77—143	17—136	Sinor, Kurata (1966)	
Helium—oxygen	67—90	6—26	Skripka, Dykhno (1964)	
Helium—oxygen	65—116	<216	Skripka, Lobanova (1971)	
Helium—fluorine	77, 120	0—35	Cannon, Crane (1968)	
Helium—fluorine	78—111	20, 48	Cannon, Robson, English (1968)	Liquid phase only
Helium—argon	84—87	<1	Karasz (1958), Karasz, Halsey (1958)	Graphs only
Helium—argon	68—108	20—120	Mullins (1965), Mullins, Ziegler (1965)	
Helium—argon	93—148	17—136	Sinor, Kurata (1966)	
Helium—argon	91	6—26	Skripka, Dykhno (1964)	
Helium—argon	90—115	196—235	Skripka, Lobanova (1971)	
Helium—argon	91—148	14—680	Streett (1969)	
Helium—argon	98—160	218—4 080	Streett, Hill (1971a)	
Helium—carbon dioxide	253, 273, 293	20—139	Burfield, Richardson, Guereca (1970)	
Helium—carbon dioxide	200, 220	80—144	Liu (1969)	Gas phase only
Helium—carbon dioxide	220—290	10—200	MacKendrick, Heck, Barrick (1968)	
Helium—krypton	100—150	3—121	Kidney, Miller, Hiza (1971)	
Helium—methane	124—191	3—68	Devaney, Rhodes, Tully (1971)	
Helium—methane	90, 106	30—160	Gonikberg, Fastovsky (1940b)	
Helium—methane	95—185	5—203	Heck, Hiza (1967)	
Helium—methane	91	13—102	Hiza, Kidnay (1966)	Gas phase only
Helium—methane	91—150	5—170	Kharakhorin (1959a)	
Helium—methane	94—192	68—259	Rhodes, Devaney, Tully (1971)	
Helium—methane	93—188	0—136	Sinor (1965), Sinor, Schindler, Kurata (1966)	
Helium—methane	95—290	136—10 000	Streett, Erickson, Hill (1972)	
Helium—methane	91—124	0—67	Tully, Devaney, Rhodes (1971)	
Helium—ethene	144—228	20—48	Cannon, Robson, English (1968)	Liquid phase only
Helium—ethene	<260	<120	Garber (1971)	
Helium—ethene	91—150	4—130	Hiza, Duncan (1969)	Gas phase only
Helium—ethane	144—228	20—48	Cannon, Robson, English (1968)	Liquid phase only
Helium—ethane	170—290	9—200	Heck (1968)	
Helium—ethane	95—150	4—130	Hiza, Duncan (1969)	Gas phase only

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Helium–ethane	113–273	5–120	Nikitina, Skripka, Gubkina (1970)	
Helium–propene	<260	<120	Garber (1971)	
Helium–propane	172–255	20–48	Cannon, Robson, English (1968)	Liquid phase only
Helium–propane	123–348	0–204	Schindler, Swift, Kurata (1966)	
Helium–*n*–butane	330–426	10–71	Jones, Kay (1967)	Graphs only
Deuterium–neon	25	<1	Simon (1962)	Graphs only
Deuterium–neon	25	<1	Simon (1963a)	
Deuterium–neon	25–40	1–21	Streett (1968b)	
Deuterium–nitrogen	90, 95	8–67	Maimoni (1961)	
Deuterium–argon	87–120	10–100	Volk, Halsey (1960)	
Neon–nitrogen	83, 113	5–50	Burch (1964)	
Neon–nitrogen	90	8–30	Skripka (1965)	Liquid phase only
Neon–nitrogen	67–90	6–26	Skripka, Dykhno (1964)	
Neon–nitrogen	65–101	85–123	Skripka, Lobanova (1971)	
Neon–nitrogen	66–121	4–70	Streett (1965)	
Neon–nitrogen	66–114	73–217	Streett (1968a)	
Neon–oxygen	67–90	6–26	Skripka, Dykhno (1964)	
Neon–oxygen	64–118	176–206	Skripka, Lobanova (1971)	
Neon–oxygen	63–152	2–340	Streett, Jones (1966)	
Neon–argon	80–104	0–10	Browning (1964)	Phase boundary measurements, graphs only
Neon–argon	84–88	<1	Karasz (1958), Karasz, Halsey (1958)	Graphs only
Neon–argon	91	6–26	Skripka, Dykhno (1964)	
Neon–argon	90–120	176–206	Skripka, Lobanova (1971)	
Neon–argon	84–130	4–71	Streett (1965)	
Neon–argon	96–130	74–613	Streett (1967)	
Neon–argon	87–94	63–1 020	Streett, Hill (1971b)	
Neon–krypton	100–150	3–106	Miller, Kidnay, Hiza (1972)	
Neon–methane	95–181	20–4 300	Streett, Hill (1971c)	
Neon–ethene	102, 122	7–45	Hiza, Duncan (1969)	Gas phase only
Neon–ethane	112, 130	15–33	Hiza, Duncan (1969)	Gas phase only
Carbon monoxide–nitrogen	68	0.1–0.3	Duncan (1966), Duncan, Staveley (1966)	Liquid phase only
Carbon monoxide–nitrogen	84	1–2	Pool, Saville, Herrington, Shields, Staveley (1962)	Liquid phase only
Carbon monoxide–nitrogen	84	1–2	Sprow, Prausnitz (1966a)	
Carbon monoxide–nitrogen	83–114	2–17	Steckel (1935)	
Carbon monoxide–nitrogen	70–122	0–28	Torocheshnikov (1937)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Carbon monoxide—nitrogen	70—79	0—1	Verschoyle (1931)	
Carbon monoxide	70—122	0—28	Yushkevich, Torocheshnikov (1936)	
Carbon monoxide—argon	84	0.7—1.3	Duncan (1966), Duncan, Staveley (1966)	Liquid phase only
Carbon monoxide—carbon dioxide	273—298	—	Abdulayev (1939a)	
Carbon monoxide—carbon dioxide	273	200	Abdulayev (1939b)	Graphs only
Carbon monoxide—carbon dioxide	223—283	24—129	Kaminishi, Arai, Saito, Maeda (1968)	
Carbon monoxide—carbon dioxide	223—283	10—130	Kaminishi, Toriumi (1968)	Graphs only
Carbon monoxide—methane	91—124	0—5	Cheung, Wang (1964)	
Carbon monoxide—methane	91	0—2	Mathot, Staveley, Young, Parsonage (1956)	Liquid phase only
Carbon monoxide—methane	91	1—2	Sprow, Prausnitz (1966a)	
Carbon monoxide—methane	114—186	7—48	Toyama, Chappelear, Leland, Kobayashi (1962)	
Carbon monoxide—ethane	173—273	8—116	Trust (1967), Trust, Kurata (1971)	
Carbon monoxide—propene	311	17—41	Widdoes, Katz (1948)	
Carbon monoxide—propane	86—128	0—6	Cheung, Wang (1964)	
Carbon monoxide—propane	148—323	7—136	Trust (1967), Trust, Kurata (1971)	
Carbon monoxide—propane	252—361	10—177	Widdoes, Katz (1948)	
Nitrogen—oxygen	65, 70, 78	0—1	Armstrong, Goldstein, Roberts (1955)	
Nitrogen—oxygen	77—91	1	Baly (1900)	
Nitrogen—oxygen	81—91	1	Cockett (1957)	
Nitrogen—oxygen	79—115	1—10	Din (1960)	
Nitrogen—oxygen	77—125	0—30	Dodge, Dunbar (1927)	
Nitrogen—oxygen	63	0.01—0.12	Duncan (1966), Duncan, Staveley (1966)	Liquid phase compositions only
Nitrogen—oxygen	75, 79	0—1	Inglis (1906)	
Nitrogen—oxygen	132—153	28—56	Kuenen, Verschoyle, Van Urk (1923)	Condensation measurements on two mixtures
Nitrogen—oxygen	84	1—2	Pool, Saville, Herrington, Shields, Staveley (1962)	Liquid phase only
Nitrogen—oxygen	77—90	1—2	Sagenkahn, Fink (1944)	
Nitrogen—oxygen	88—90	1	Thorogood, Haselden (1963)	
Nitrogen—oxygen	78	—	Wilhelm, Schneider (1961)	Graph of excess Gibbs free energy, graphs only
Nitrogen—oxygen	78—134	1—26	Wilson, Silverberg, Zellner (1965)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Nitrogen–argon	66–75	<1	Browning (1964)	Phase boundary determinations, graphs only
Nitrogen–argon	78–103	1–4	Fastovsky, Petrovsky (1956b)	
Nitrogen–argon	74–95	0–2	Holst, Hamburger (1916a)	
Nitrogen–argon	74–95	0–2	Holst, Hamburger (1916b)	
Nitrogen–argon	112	8–15	Miller, Kidnay, Hiza (1973)	
Nitrogen–argon	90–120	1–24	Narinskii (1966)	
Nitrogen–argon	84	1–2	Pool, Saville, Herrington, Shields, Staveley (1962)	Liquid phase only
Nitrogen–argon	84	1–2	Sprow, Prausnitz (1966a)	
Nitrogen–argon	80–115	1–11	Thorpe (1968)	Graphs only
Nitrogen–argon	72–134	1–26	Wilson, Silverberg, Zellner (1965)	
Nitrogen–carbon dioxide	273–298	–	Abdulayev (1939a)	
Nitrogen–carbon dioxide	273	0–181	Abdulayev (1939b)	Graphs only
Nitrogen–carbon dioxide	233–298	50–125	Kaminishi, Toriumi (1966)	
Nitrogen–carbon dioxide	223, 243, 273	7–100	Kulikov (1969)	Graphs only
Nitrogen–carbon dioxide	273	48–116	Muirbrook (1964), Muirbrook, Prausnitz (1965)	Graphs only
Nitrogen–carbon dioxide	222, 273	41–155	Pollitzer, Strebel (1924)	
Nitrogen–carbon dioxide	140–190	5–200	Smith (1963)	
Nitrogen–carbon dioxide	273	34–117	Yorizane, Yoshimura, Masuoka (1970)	
Nitrogen–carbon dioxide	273	<117	Yorizane (1971)	
Nitrogen–carbon dioxide	218–273	12–137	Zenner, Dana (1963)	
Nitrogen–methane	100–187	7–48	Bloomer, Eakin, Ellington, Gami (1955)	Graphs only
Nitrogen–methane	91–191	1–48	Bloomer, Parent (1952), (1953)	
Nitrogen–methane	129–179	34	Brandt, Stroud (1958)	
Nitrogen–methane	122, 171	3–49	Chang, Lu (1967)	
Nitrogen–methane	92–124	0–4	Cheung, Wang (1964)	
Nitrogen–methane	100–172	1–44	Cines, Roach, Hogan, Roland (1953)	
Nitrogen–methane	79–187	1–48	Ellington, Eakin, Parent et al (1959)	
Nitrogen–methane	90–150	1–16	Fastovsky, Petrovsky (1957)	
Nitrogen–methane	80–180	1–103	Forg, Wirtz (1970)	Graphs only
Nitrogen–methane	84–89	0.9–2.4	Fuks, Bellemans (1967)	Liquid phase only
Nitrogen–methane	77–109	1	McTaggart, Edwards (1919)	
Nitrogen–methane	112	2–13	Miller, Kidnay, Hiza (1973)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Nitrogen–methane	113	–	Skripka et al (1970)	
Nitrogen–methane	91	0–4	Sprow, Prausnitz (1966a)	
Nitrogen–methane	89–133	0–24	Torochesnikov, Levius (1939)	Graphs only
Nitrogen–methane	90	0–1	Vellinger, Pons (1943)	Graphs only
Nitrogen–ethene	144–228	20–48	Cannon, Robson, English (1968)	Liquid phase only
Nitrogen–ethane	144–228	20–48	Cannon, Robson, English (1968)	Liquid phase only
Nitrogen–ethane	122, 171	3–34	Chang, Lu (1967)	
Nitrogen–ethane	93	<1	Cheung, Wang (1964)	
Nitrogen–ethane	101–302	7–126	Ellington, Eaking, Parent et al (1959)	
Nitrogen–ethane	114–133	18–40	Yu, Elshayal, Lu (1969)	
Nitrogen–propene	78–91	0–3	Blagoi, Orobinskii (1965)	
Nitrogen–propane	172–255	20–48	Cannon, Robson, English (1968)	Liquid phase only
Nitrogen–propane	92–128	1–6	Cheung, Wang (1964)	
Nitrogen–propane	312–365	41–149	Roof, Baron (1967)	Critical locus measurements
Nitrogen–propane	103–353	0–136	Schindler, Swift, Kurata (1966)	
Nitrogen–propane	90	0–1	Vellinger, Pons (1943)	Graphs only
Nitrogen–*n*–butane	311–422	35–287	Akers, Atwell, Robinson (1954)	
Nitrogen–*n*–butane	311	137–284	Lehigh, McKetta (1966)	
Nitrogen–*n*–butane	311–411	16–231	Roberts, McKetta (1961)	
Nitrogen–*n*–butane	294–394	17–131	Sage, Budenholzer, Lacey (1940)	
Nitrogen–*n*–butane	153–273	5–200	Skripka et al (1969)	
Nitrogen–*n*–butane	273, 283, 293	4, 6, 9, 11	Steinbach, Steinbrecher (1966)	
Nitrogen–isobutane	248–323	0–100	Ryabtsev, Khuchua (1970)	
Nitrogen–isobutane	273, 283, 293	4, 6, 9, 11	Steinbach, Steinbrecher (1966)	
Oxygen–argon	87, 90, 95	1–2	Burbo, Ischkin (1936)	
Oxygen–argon	85–118	1–10	Burn, Din (1962)	
Oxygen–argon	90–110	1–3	Clark, Din, Robb (1953)	
Oxygen–argon	87–110	1–7	Din (1953)	
Oxygen–argon	89–96	1–2	Fastovsky, Petrovsky (1955)	
Oxygen–argon	82	<1	Inglis (1906)	
Oxygen–argon	90–120	1–12	Narinskii (1957)	
Oxygen–argon	84, 90	0–1	Pool, Saville, Herrington, Shields, Staveley (1962)	Liquid phase only

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Oxygen–argon	87–97	1–2	Sagenkahn, Fink (1944)	
Oxygen–argon	91, 95	1–2	Wang (1960)	
Oxygen–argon	87–139	1–26	Wilson, Silverberg, Zellner (1965)	
Oxygen–carbon dioxide	224	7–142	Fredenslund, Mollerup, Persson (1972)	
Oxygen–carbon dioxide	223–283	10–130	Fredenslund, Sather (1970)	
Oxygen–carbon dioxide	233–298	50–125	Kaminishi, Toriumi (1966)	
Oxygen–carbon dioxide	282–298	1–2	Keesom (1903)	
Oxygen–carbon dioxide	273	41–116	Muirbrook (1964), Muirbrook, Prausnitz (1965)	
Oxygen–carbon dioxide	218–273	22–147	Zenner, Dana (1963)	
Oxygen–krypton	94–107	1–4	Burch (1966)	
Oxygen–krypton	90–100	1–3	Fastovsky, Gurvich (1939a, b)	
Oxygen–krypton	94–151	0–6	Fastovsky, Petrovsky (1956a)	
Oxygen–methane	93–107	1–4	Hodges, Burch (1967)	
Hydrogen sulphide–carbon dioxide	254–366	20–80	Bierlein, Kay (1953)	
Hydrogen sulphide–carbon dioxide	225–364	7–82	Sobocinski, Kurata (1959)	
Hydrogen sulphide–carbon dioxide	221, 246, 273	–	Steckel (1945)	
Hydrogen sulphide–methane	167–344	0–136	Kohn, Kurata (1958)	
Hydrogen sulphide–methane	278–344	11–133	Reamer, Sage, Lacey (1951)	
Hydrogen sulphide–ethane	267–355	17–82	Kay, Brice (1953)	
Hydrogen sulphide–propene	243, 273, 288	–	Steckel (1945)	
Hydrogen sulphide–propane	217–344	1–27	Brewer, Rodewald, Kurata (1961)	
Hydrogen sulphide–propane	324–367	27, 34, 41	Gilliland, Scheeline (1940)	
Hydrogen sulphide–propane	272–370	1–79	Kay, Rambosek (1953)	
Hydrogen sulphide–propane	243, 237, 288	–	Steckel (1945)	
Hydrogen sulphide–*n*–butane	311–408	3–79	Robinson, Hughes, Sondercock (1964)	
Argon–carbon dioxide	233–273	25–131	Kaminishi, Arai, Saito, Maeda (1968)	
Argon–krypton	104, 116	1–9	Davies, Duncan, Saville, Staveley (1967), Duncan (1966)	Liquid phase only
Argon–krypton	88	1	Schmidt (1960)	
Argon–methane	116	1–9	Calado, Staveley (1972)	Liquid phase only
Argon–methane	92–124	0–4	Cheung, Wang (1964)	
Argon–methane	105–126	2–16	Duncan, Hiza (1972)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Methane—*n*—butane	252—316	10—30	Nederbragt (1938)	
Methane—*n*—butane	311	65—130	Rigas, Mason, Thodos (1958)	
Methane—*n*—butane	211—411	2—119	Roberts, Wang, Azarnoosh, McKetta (1962)	
Methane—*n*—butane	294—394	2—131	Sage, Hicks, Lacey (1940)	
Methane—*n*—butane	177	5—31	Wang, McKetta (1964)	
Methane—isobutane	198—293	5 to critical values	Barsuk, Skripka, Benyaminovich (1970)	
Methane—isobutane	311—378	5—114	Olds, Sage, Lacey (1942)	
Ethyne—propene	295—357	15—62	McCurdy, Katz (1954)	
Ethyne—propane	283—365	15—63	McCurdy, Katz (1945)	
Ethene—ethane	200, 233, 255	1—26	Hanson, Hogan, Ruchlen, Cines (1953)	
Ethene—ethane	169—273	0—40	Kharakhorin (1941)	
Ethene—ethane	169—273	0—41	Kharakhorin (1959b)	
Ethene—ethane	149—196	0—2	Moran (1959)	
Ethene—propene	303, 323	<40	Rozhnov, Dorochinskaya (1969)	
Ethane—propene	243—343	2—50	Lu, Newitt, Ruhemann (1941)	
Ethane—propene	261—344	4—49	McKay, Reamer, Sage, Lacey (1951)	
Ethane—propane	128—256	0—15	Djordjevich (1968), Djordjevich, Budenholzer (1970)	
Ethane—propane	311—367	13—51	Matschke, Thodos (1962)	
Ethane—propane	255—283	7—27	Price (1957), Price, Kobayashi (1959)	
Ethane—propane	203—273	—	Skripka et al (1970)	
Ethane—*n*—butane	338, 367, 394	32—55	Mehra, Thodos (1965)	
Ethane—isobutane	203—273	—	Skripka et al (1970)	
Propene—propane	270, 298, 330	4—23	Hanson, Nelson, Hogan, Cines (1952)	
Propene—propane	—	—	Hirata, Hakuta, Onoda (1967)	
Propene—propane	—	—	Hirata, Hakuta (1968)	
Propene—propane	—	22	Mann, Pardee, Smyth (1963)	Isobaric measurement, temperature not measured
Propene—propane	261—361	3—41	Reamer, Sage (1951)	
Propene—I—butene	278—411	1—46	Goff, Farrington, Sage (1950)	
Propene—isobutane	315—397	13—41	Gilliland, Scheeline (1940)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Propane—isobutene	338—402	13—41	Scheeline, Gilliland (1939)	
Propane—*n*—butane	333—419	15—42	Kay (1940)	
Propane—*n*—butane	311—411	5—42	Nysewander et al (1940)	
Propane—*n*—butane	253, 263, 273	—	Skripka et al (1970)	
Propane—isobutane	267—394	1—39	Hipkin (1966)	
Propane—isobutane	340	10—24	Hirata, Suda, Miyashita, Hoshino (1970)	
Propane—isobutane	253, 263, 273	—	Skripka et al (1970)	
n—Butane—isobutane	—	—	Hirata, Suda (1968)	
n—Butane—isobutane	353, 373	11	Yokoyama, Ohe (1971)	
Hydrogen—hydrogen deuteride—deuterium	18—20	<1	Arnold, Hoge (1950)	Measurement of dew-point pressures
Hydrogen—carbon monoxide—nitrogen	83, 100, 122	21—136	Akers, Eubanks (1960)	
Hydrogen—carbon monoxide—nitrogen	35—66	5—15	Dokoupil, Van Soest, Swenker (1955)	
Hydrogen—carbon monoxide—nitrogen	83, 100, 122	21—136	Eubanks (1956)	
Hydrogen—carbon monoxide—nitrogen	68—88	30—150	Fischer (1938)	Graphs only
Hydrogen—carbon monoxide—nitrogen	78, 83, 90	12—50	Ruhemann, Tsin (1937)	Graphs only
Hydrogen—carbon monoxide—nitrogen	68—88	30—150	Verschoyle (1931)	Graphs only
Hydrogen—carbon monoxide—carbon dioxide	233—283	50—200	Kaminishi, Arai, Saito, Maeda (1968)	
Hydrogen—carbon monoxide—carbon dioxide	233—283	50—200	Kaminishi, Toriumi (1968)	Graphs only
Hydrogen—nitrogen—carbon dioxide	273—293	51—203	Abdulayev (1941)	
Hydrogen—carbon monoxide—propane	87	32	Stein, Claitor, Geist (1962)	Graphs only
Hydrogen—carbon monoxide—propane	88—348	to 204	Trust (1967)	
Hydrogen—carbon monoxide—propane	88—348	to 204	Trust, Kurata (1971)	
Hydrogen—nitrogen—methane	144	34, 68	Cosway (1958)	
Hydrogen—nitrogen—methane	144, 200	34, 68	Cosway, Katz (1959)	
Hydrogen—nitrogen—methane	90, 108	10—100	Steckel, Tsin (1939a)	
Hydrogen—nitrogen—methane	90, 108	10—100	Steckel, Tsin (1939b)	
Hydrogen—methane—ethene	158—188	30—80	Likhter, Tikhonovich (1940)	Graphs only
Hydrogen—methane—ethane	115—255	2—136	Cohen, Hipkin, Koppany (1967)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Hydrogen–methane–ethane	144, 200	34, 68	Cosway (1958)	
Hydrogen–methane–ethane	144, 200	34, 68	Cosway, Katz (1959)	
Hydrogen–methane–ethane	158–188	30, 40, 80	Levitskaya (1941)	
Hydrogen–methane–propene	200	34	Benham, Katz (1957)	
Hydrogen–methane–propane	144–255	34, 68	Benham, Katz (1957)	
Helium–neon–nitrogen	83, 113	5–50	Burch (1964)	
Helium–neon–nitrogen	68–78	7–48	Tompkins, Geist (1963)	Graphs only
Helium–nitrogen–methane	76–130	14–136	Boone, Devaney, Stroud (1963)	
Helium–nitrogen–methane	77–164	7–82	Rhodes, Stroud, Tully (1972)	
Helium–nitrogen–propane	273	34–204	Schindler, Swift, Kurata (1966)	
Nitrogen–oxygen–argon	81–88	1	Fastovskii, Petrovskii (1957)	
Nitrogen–oxygen–argon	90–120	1–23	Narinskii (1969)	
Nitrogen–oxygen–argon	81–96	1–2	Sagenkahn, Fink (1944)	
Nitrogen–oxygen–argon	–	–	Weishaupt (1948)	Graphs only
Nitrogen–oxygen–argon	78–137	1–26	Wilson, Silverberg, Zellner (1965)	Graphs only
Nitrogen–oxygen–carbon dioxide	273	51–104	Muirbrook (1964), Muirbrook, Prausnitz (1965)	
Nitrogen–oxygen–carbon dioxide	218–273	52–129	Zenner, Dana (1963)	
Nitrogen–argon–methane	112	3–13	Miller, Kidnay, Hiza (1973)	
Nitrogen–argon–methane	91	1–4	Sprow, Prausnitz (1966b)	
Nitrogen–methane–ethane	122, 171	2–28	Chang, Lu (1967)	
Nitrogen–methane–ethane	144, 200	34, 68	Cosway (1958)	
Nitrogen–methane–ethane	144, 200	34, 68	Cosway, Katz (1959)	
Nitrogen–methane–ethane	112	14	Lu, Yu, Poon (1969)	Liquid–liquid–vapour
Nitrogen–methane–ethane	114–129	15–35	Yu, Elshayal, Lu (1969)	
Nitrogen–methane–*n*–butane	311–411	34–204	Roberts (1963)	
Nitrogen–methane–*n*–butane	311–411	34–204	Roberts, McKetta (1963)	
Nitrogen–ethane–propane	87	0–1	Cheung, Wang (1964)	
Nitrogen–ethane–*n*–butane	311–411	34–272	Lehigh (1965), Lehigh, McKetta (1966)	
Nitrogen–propene–propane	77	0–1	Cheung, Wang (1964)	
Hydrogen sulphide–carbon dioxide–methane	222, 239	20–48	Hensel, Massoth (1964)	
Hydrogen sulphide–carbon dioxide–methane	311	41, 82, 103	Robinson, Bailey (1957)	
Hydrogen sulphide–carbon dioxide–methane	278, 344	27–109	Robinson, Lorenzo, Macrygeorgos (1959)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Hydrogen sulphide—methane—*n*—butane	244, 269, 311	27—82	Robinson, Saxena (1966)	Graphs only
Hydrogen sulphide—methane—*n*—butane	244, 278, 311	27, 54, 82	Saxena, Robinson (1969)	
Argon—methane—ethane	116	4—7	Elshayal, Lu (1971)	
Carbon dioxide—methane—*n*—butane	244, 269, 311	27—82	Robinson, Saxena (1966)	Graphs only
Carbon dioxide—methane—*n*—butane	244, 278, 311	27, 54, 82	Saxena, Robinson (1969)	
Carbon dioxide—methane—*n*—butane	177—311	27—116	Wang, McKetta (1964)	
Carbon dioxide—ethene—propane	—	—	Shearn (1955)	
Carbon dioxide—propene—propane	273, 293, 313	10—65	Toyoshima, Yoshimura, Masuoka (1971)	
Methane—ethene—ethane	169—273	5—50	Guter, Newitt, Ruhemann (1940)	
Methane—ethene—ethane	159	⩽22	Hsi, Lu (1971)	
Methane—ethene—isobutane	311, 344	34, 68	Benedict, Solomon, Ruben (1945)	
Methane—ethane—propane	144—283	7—88	Price (1957)	
Methane—ethane—propane	144—283	7—88	Price, Kobayashi (1959)	
Methane—ethane—propane	158—213	2—60	Wichterle, Kobayashi (1972c)	
Methane—ethane—propane	115—143	1	Watanabe, Kuroki, Oguro Saito (1969)	Graphs only
Methane—ethane—*n*—butane	—	—	Cota, Thodos (1962)	Measurement of critical temperature and pressure
Methane—propane—*n*—butane	311	48—117	Rigas, Mason, Thodos (1959)	
Methane—propane—*n*—butane	278—378	0—100	Wiese, Jacobs, Sage (1970)	
Ethyne—ethene—ethane	236, 255, 278	10—32	Hogan, Nelson, Hanson, Cines (1955)	
Ethyne—ethene—ethane	278, 289	32—52	McCurdy, Katz (1944)	
Hydrogen—carbon monoxide—nitrogen—oxygen—methane	78, 90	6—78	Torochesnikov, Gurevich (1941)	
Hydrogen—carbon monoxide—nitrogen—methane	—	—	Torochesnikov, Serenova (1954)	
Hydrogen—carbon monoxide—carbon dioxide—propane	273	8—45	Yorizane, Yoshimura, Masuoka (1972)	
Hydrogen—carbon monoxide—carbon dioxide—*n*—butane	273	8—45	Yorizane, Yoshimura, Masuoka (1972)	
Hydrogen—nitrogen—methane—ethane	144, 200	34, 68	Cosway (1958), Cosway, Katz (1949)	
Hydrogen—methane—ethene—ethane—propene—propane	200, 255	34, 68	Benham (1956), Benham, Katz (1957)	

System	Temperature range, K	Pressure range, atm	Reference	Remarks
Helium–nitrogen–methane–ethane–propane–butane	123–183	7	Stutzman, Brown (1949)	
Nitrogen–methane–ethane–propane–*n*–butane	153–253	28–38	Banks, Haselden (1969)	
Methane–ethane–propane–*n*–butane	222	14–20	De Priester (1953)	
Methane–ethane–propane–isobutane	244	14	De Priester (1953)	
Natural gas system	102–255	7–34	Brandt, Stroud, Miller (1961)	
Natural gas system	229–300	34, 68, 101	Buckley, Lightfoot (1941)	
Natural gas system	311–411	34–204	Roberts (1963)	
Natural gas system	311–378	34–204	Roberts, McKetta (1963)	
Natural gas system	102–200	7–34	Stroud, Miller, Brandt (1959)	
Natural gas system	339–394	7–136	Stuckey (1966)	Graphs only

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ERRATA

LIQUID-VAPOUR EQUILIBRIA RESEARCH ON SYSTEMS OF INTEREST IN CRYOGENICS -- A SURVEY

by

A. J. Kidnay, M. J. Hiza, and R. C. Miller

in Cryogenics Vol. 13, No. 10, 575-99 (Oct. 1973)

- page 575: Last sentence of Abstract --- add CO_2 after CO.

- page 577: Change equations (7) and (10) as follows

$$\gamma_i = \gamma_i^{(R)} \frac{f_i^{o(R)}}{f_i^{o}} \exp \int_{\pi^{(R)}}^{\pi} \frac{\bar{v}_i \, d\pi}{RT} \qquad (7)$$

$$\bar{f}_j(\text{liquid}) = \gamma_j^{*} \; x_j \; H_{j,i} \qquad (10)$$

- page 578: Ref. 4. Hala et al; change date to 1967.

- page 579: (a) - 4th entry under Hydrogen-helium 4; Roellig, Giese (1962); change remark to "Pressures given are partial pressures of helium"

  (b) - 7th entry under Hydrogen-helium 4; Sonntag, Crain, Streett (1964); delete remark.

- page 581: 2nd entry under Hydrogen-methane; change Tikhovovich to Tikhonovich.

- page 583: Entry under Helium-krypton; change Kidney to Kidnay.

- page 586: 5th entry under Nitrogen-carbon dioxide; Muirbrook (1964), etc.; delete remark.

- page 588: 4th entry under Hydrogen sulphide-propane; Steckel (1945); change temperature from 237 to 273.

- page 591: Entry under Ethyne-propene; change reference date to (1945).

- page 592: After n-Butane-isobutane entries, insert new table title: "Liquid-vapour equilibria for ternary systems."

- page 594: After Ethyne-ethene-ethane entries, insert new table title: "Liquid-vapour equilibria for systems of four or more components."

- page 595: BIBLIOGRAPHY
    - (a) Abdulayev (1941); change Priki to Prikl
    - (b) Aerov et al. (1968); change Zalayaletoinova to Zalyaletoinova.
    - (c) Benham, Katz, Williams (1957); change AICHe J to AIChE J.
    - (d) Burn, Din (1962); change the page no. 1241 to 1341.

- page 596:
    - (a) Cines et al. (1953); add the page no. 1 after (1953).
    - (b) Greene, Sonntag (1968); change)Plenum (Plenum.
    - (c) Hirata, Hakuta (1968); change the page no. 594 to 1594.

- page 597:
    - (a) Kulikov (1969); change the page no. 8 to 18.
    - (b) Morlet (1963); change the page no. 27 to 127.
    - (c) Newman, Jackson (1958); change the page no. 481 to 1481.

- page 598:
  - (a) Rodewald (1963); change An Arbor to Ann Arbor.
  - (b) Scheeline, Gilliland; change year and page no. from (1969) 69 to (1939) 1050.
- page 599:
  - (a) Watanabe et al. (1969); change the page no. 293 to 292.
  - (b) Yokoyama, Ohe (1971); add the page no. 4 after (1971).

APPENDIX I

LIQUID-VAPOR EQUILIBRIA IN THE NITROGEN-METHANE SYSTEM BETWEEN 95 and 120 K

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LIQUID-VAPOR EQUILIBRIA IN THE NITROGEN-METHANE SYSTEM BETWEEN 95 and 120 K*

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ABSTRACT

A study was undertaken to obtain liquid-vapor equilibria data for the nitrogen-methane system at uniform temperature increments between the triple point of methane and the critical point of nitrogen. The measured liquid and vapor phase equilibria compositions and the derived excess Gibbs energy values for six isotherms from 95 to 120 K are compared with the corresponding values taken from other investigations. The excess Gibbs energy for the equimolar mixture exhibits a zero to slightly positive temperature dependence, in qualitative agreement with calculations based on the Snider-Herrington hard sphere model. This temperature dependence of the excess Gibbs energy also suggests that the excess enthalpy (heat of mixing) must be equal to or slightly less than the excess Gibbs energy.

INTRODUCTION

The development and evaluation of liquid mixture (solution) theory depends heavily on the availability of precise data for mixtures of simple molecules. The most useful data are for binary mixtures at closely spaced temperatures over as wide a temperature range as possible, both above and below the critical temperature of the most volatile component. The nitrogen-methane mixture, which is technologically important as one of the more important binary mixtures in liquefied natural gas, is an excellent compromise between theoretical and practical considerations.

Key Words: Binary mixture, excess Gibbs energy, experimental phase equilibria data, heat of mixing, liquid-vapor equilibria, nitrogen-methane system.

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The interest in the phase equilibria properties of this particular system is apparent by the large number of studies reported in the literature. A number of experimental investigations have been conducted to determine the liquid-vapor equilibria properties of nitrogen-methane mixtures [1-15]. In addition, several investigations have been conducted to determine the solid-liquid equilibria and the three phase (solid-liquid-vapor) locus [16-19]. In the liquid-vapor region the data of Bloomer and Parent [1] and of Cines et al. [3] cover most of the methane liquid range, and consequently, one or the other of these data sets frequently has been used in correlations and for testing computation methods for the nitrogen-methane system [20-23]. Since the data of Bloomer and Parent are isobaric and those of Cines et al. are isothermal, direct comparisons are not possible. However, from comparisons made by Bloomer and Parent of isothermal crossplots of their data and those of Cines et al., these data sets appear to be in fairly good agreement at the lower temperatures, but are in less satisfactory agreement at the higher temperatures.

Of the remainder of the data reported prior to 1972, most studies were too limited to add independently to the description of the liquid-vapor equilibria behavior of this system. In addition, the method of investigation, i.e. isobaric dew-point, bubble-point measurements versus isothermal vapor-recirculation measurements, and the method of reporting data, i.e. graphical versus tabular, further complicate evaluation and comparison of all of the data.

The recent investigations of Miller et al. [10] at 112.00 K and of Stryjek et al. [13] from 113.72 K up to the methane critical temperature add new isothermal data which readily can be compared with some of the previous data sets. In the mutual liquid range of the two components, with which we are concerned in the present study, these newer data tend to highlight the discordant aspects of some of the previous data more clearly.

In addition to phase equilibria data, density or more specifically excess molar volumes are vital to the development of liquid mixture theory. Liu and Miller [24] recently reported excess molar volumes for the nitrogen-methane system between 90 and 120 K. Subsequently, Massengill and Miller [25] provided an interesting theoretical discussion of the effects of adjustments to the combining rules and of predictions of excess molar volume and excess Gibbs energy as a function of temperature with a modified hard sphere equation of state. Because of the lack of consistency of phase equilibria data for the nitrogen-methane system in the same temperature region, it is difficult to draw definitive conclusions from their treatise. Thus, the need for a consistent set of phase equilibria data for the nitrogen-methane system between 90 and 120 K was clearly indicated.

The purpose of the present study was to obtain liquid-vapor equilibria data for the nitrogen-methane system at 5 K increments of temperature between the triple point of methane and the critical point of nitrogen, and from these data to obtain the magnitude and temperature dependence of the excess Gibbs energy. These values of excess Gibbs energy provide the basis of comparison with the corresponding values derived from other data and with the qualitative temperature dependence of the excess Gibbs energy predicted from the hard sphere model by Massengill and Miller [25].

EXPERIMENTAL

The liquid-vapor equilibria measurements were made in a closed-loop vapor-recirculating system described previously [26]. Thus, other than some minor differences, discussion of experimental details need not be included here.

The equilibrium pressures were measured with a standard laboratory, double-revolution, 0-20 bar Bourdon gage and a 0-100 psia spiral quartz Bourdon gage. The 20 bar gage has a claimed accuracy of ± 0.1% of full scale and was found to be consistently better than these limits when compared with the 100 psia gage. The latter instrument was calibrated against an air dead-weight gage in this laboratory giving a maximum uncertainty of less than ± 0.1 psia over the full range. The pressure tap was a small tube connected directly to the top of the equilibrium cell and was independent of the recirculation system.

Temperatures were controlled as described previously [26]. However, the reported temperatures are those determined by vapor pressure measurements of pure methane and pure nitrogen as compared with the new methane data of Prydz and Goodwin [27] and the nitrogen values from the equation of Strobridge [28]. For our purposes, nitrogen vapor pressure values from the equation of Strobridge are in excellent agreement with the newer data of Weber [29]. Within experimental uncertainties of the present study, the temperatures reported here are consistent with the IPTS-68 temperature scale.

Compositions were determined chromatographically with helium elution gas and thermal conductivity detector. Calibration gas mixtures were prepared on a pressure basis, corrected for nonideality, at 4.94, 9.90, and 49.89 mole % methane in nitrogen. These calibration mixtures and pure methane and pure nitrogen were analyzed at a number of different sample pressures to determine analyzer response as a function of component partial pressure. It was determined that a linear calibration based on the pure species at near atmospheric pressure (60 cm Hg) satisfactorily reproduced compositions over the entire composition range of interest, based on peak areas, within 0.5% of the actual composition of the minor component. Since this difference is approximately equivalent to the precision of analysis, the results reported here are based entirely on pure component calibrations. The experimental liquid and vapor compositions are thought to be accurate within ± 1% of the actual composition or within ± 0.1 mole %, whichever is greater.

Liquid samples were withdrawn directly from the bottom of the equilibrium cell through a stainless steel capillary tube, while the vapor samples were isolated in a room temperature sample loop which included the pump free volume. In all cases, compositions were determined by analysis of both components in the mixture. The total sample pressure was taken as the sum of the partial pressures determined in the analysis. Though total sample pressure was measured, the sum of the partial pressures was used to compensate for slight variations in analyzer sensitivity and for any lack of sample thermal equilibrium.

It is also worth noting that the apparatus and chromatograph used in this study were the same as those used in the study of Miller et al. [10]. However, there were significant differences. The more precise 100 psia quartz Bourdon gage was acquired for the present study to improve the measurement of the lower pressures. The standard mixtures, except the pure component species, were prepared separately for each study using different methods. The calibration mixtures used in the earlier study were only equimolar mixtures prepared by weight. However, it was determined in both studies that assuming linear response based on calibration of the chromatograph with the pure fluid species represented the compositions of the prepared standard mixtures within the precision of analysis. In addition, temperatures reported in the earlier study were taken from the platinum thermometer readings, while in the present study the control point and thus the experimental temperature were determined by the vapor pressures of the pure component species. Thus, the two investigations are significantly different to be considered as two independent investigations.

RESULTS AND DISCUSSION

Equilibrium liquid and vapor compositions were measured at 95.00, 100.00, 105.00, 110.00, 115.00, and 120.00 K. The results of these measurements, along with the vapor pressures of the pure components, are given in Table 1.

A negative departure from Raoult's law occurs on the nitrogen rich end at the higher temperatures, consistent with the data of Bloomer and Parent [1], Cines et al. [3], Stryjek et al. [13], and Miller et al. [10]. However, the isotherm of Chang and Lu [4] at 122.05 K does not show this negative departure. Extrapolation of the data of Chang and Lu to the pure nitrogen axis suggests a higher nitrogen vapor pressure than that for 122 K and thus a slightly higher temperature than that reported, which could easily account for the discrepancy.

In figure 1, the liquid and vapor phase compositions at 100.00 K from the present investigation are compared with the smoothed values of Cines, et al. [3] at 99.82 K. This is the only direct comparison that can be made with the experimental data of other investigators. The significant point worth noting is that, even though the data of Cines et al. are for a slightly lower temperature, their vapor phase compositions are lower in nitrogen content than the present data. From the temperature dependence of the vapor phase compositions of the present study, the nitrogen content should be higher at the lower temperature. This is significant since the activity coefficient of methane is strongly affected by this inconsistency.

A sensitive method for comparing close-boiling liquid-vapor equilibria data is through the derived excess Gibbs energy, G^E, as a function of temperature and composition. This topic was discussed in some detail in an earlier paper by Duncan and Hiza [30]. The composition dependence of G^E is obtained from

$$G^E = x_1 RT \ln\gamma_1 + x_2 RT \ln\gamma_2 \tag{1}$$

where x is the liquid phase mole fraction and γ is the activity coefficient. The equation selected here for calculating the activity coefficient for each component is the one given in reference 30 and will not be repeated here. This equation is based on the virial equation of state and includes third virial coefficient effects. The activity coefficients thus calculated are corrected to a reference pressure, which for our purposes has been taken as one bar.

Second virial coefficients for pure nitrogen and the interaction second virial coefficients for nitrogen-methane were calculated from the corresponding states equation of McGlashan and Potter [31]. The mixture characteristic temperature was calculated from

$$T_{c_{12}} = (1 - k_{12})\ (T_{c_1}\ T_{c_2})^{1/2} \tag{2}$$

in which the value of k_{12} of 0.03 was taken. The characteristic volume of the mixture was calculated from the arithmetic mean rule

$$V_{c_{12}} = 1/8\ (V_{c_1}^{1/3} + V_{c_2}^{1/3})^3 \tag{3}$$

For pure methane, second virial coefficients were taken from Goodwin [32]. Molar volumes for pure liquid methane and for pure liquid nitrogen were taken from Goodwin and Prydz [33] and from Strobridge [28], respectively. Isothermal compressibility for the pure liquids were taken from Rowlinson [34]. For purposes of the present calculations, it was assumed that the molar volume and compressibility of each component in the mixture are the same as those of the pure fluid.

Values of the equimolar G^E for much of the previous data on the nitrogen-methane system are shown in figure 2. The values given include those obtained using both experimental liquid and vapor phase data (filled symbols) and those obtained from the liquid phase data only by the method attributed to Barker [35]. In both methods, the derived values of G^E were fitted by the method of least squares to the following equation

$$G^E = x_1 x_2 RT\ [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \tag{4}$$

where 1 refers to nitrogen. The values shown in figure 2 were calculated from the fit of equation (4) obtained by each method. The two values shown for Fastovskii and Petrovskii [6], however, were calculated from the smoothed equimolar liquid and vapor compositions tabulated in their paper, interpolated from the original isobaric data.

The curve shown in figure 2 was calculated by Massengill [36] from the hard sphere model applied by Snider and Herrington [37]. This curve was adjusted by Massengill to fit approximately the equimolar G^E value of Miller et al. [10] at 112.00 K by including a k_{12} correction for the "a" parameter of 0.035, similar to the correction indicated in equation (2).

Though values of G^E obtained from the two methods are not expected to be exactly equal, the results from both methods should exhibit the same temperature dependence if the data were internally and mutually consistent. It is not possible to conclude from the data presented in figure 2 that the temperature dependence of the excess Gibbs energy predicted from the hard sphere model is either reasonable or incorrect.

The values of G^E calculated from the present liquid and vapor phase data are given in Table 1 also. The constants of equation (4) obtained from these values and from the Barker method are given in Table 2. The equimolar G^E values from both methods are compared in figure 3 with those from the previous data of Miller et al. [10] and the calculated curve taken from Massengill [36]. The values of the equimolar G^E from the present study are in excellent agreement with those from Miller et al. Furthermore, the results obtained from both methods give the same temperature dependence, though the absolute values differ by about 10%. It thus can be concluded that the calculated curve is a reasonable representation of the temperature dependence of G^E.

The fact that the heat of mixing, H^E, is related to the excess Gibbs energy and its temperature dependence by

$$H^E = G^E - T(\partial G^E/\partial T)_P \tag{5}$$

also allows a conclusion about the heat of mixing for this system. From approximately 90 to 110 K, the value of G^E remains essentially constant. Thus, the temperature dependence is zero and H^E and G^E are equal. Above 110 K the temperature dependence becomes slightly positive; thus, the value of H^E would become less than the value of G^E in this region. Unfortunately, there are no calorimetric heat of mixing data for this system to substantiate this deduction.

Additional comparisons are given in figures 4, 5, and 6 between the isothermal G^E values from the liquid and vapor phase data of the present study at 95.00, 115.00, and 120.00 K and the corresponding values from four other investigations at approximately the same temperatures. It is apparent that the G^E values from the present study are more symmetrical about the equimolar value than those from the other investigations. The values from Stryjek et al. and Cines et al. are in reasonably good agreement with the present results at these temperatures. Those from Sprow and Prausnitz, however, are significantly lower than the present results. With the exception of two points, the G^E values from the data of Chang and Lu are in reasonable agreement with values from the present study, which is surprising considering the qualitative difference apparent in their data in the nitrogen rich end.

SUMMARY

The results of this investigation provide a single set of closely spaced and consistent liquid-vapor equilibria data for the nitrogen-methane system between the triple point temperature of methane and the critical point of nitrogen. The derived excess Gibbs energy values substantiate the qualitative temperature dependence of the equimolar Gibbs energy predicted by the hard sphere model of Snider and Herrington as applied by Massengill. From the temperature dependence of the excess Gibbs energy, it can be concluded that the nitrogen-methane system closely approximates a regular solution over much of the temperature range examined, i.e. $H^E = G^E$ and $S^E = 0$. These conclusions strongly suggest the desireability of calorimetric heat of mixing measurements for the nitrogen-methane system, at least in the lower temperature region of this investigation.

ACKNOWLEDGEMENTS

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TABLE 1. Experimental nitrogen-methane liquid-vapor equilibria properties.

T, K	x_{N_2}	P, bars	y_{N_2}	γ_{N_2}	γ_{CH_4}	G^E, J/mol
95.00	0.0000	0.199	0.0000			
	0.2679	2.254	0.9216	1.5755	1.0950	148.67
	0.3562	2.737	0.9374	1.4433	1.1790	186.99
	0.4249	3.018	0.9460	1.3355	1.2384	194.24
	0.5271	3.431	0.9573	1.2238	1.3271	189.77
	0.5889	3.646	0.9618	1.1621	1.4361	187.42
	0.7495	4.247	0.9756	1.0600	1.7038	139.92
	0.8271	4.580	0.9823	1.0327	1.9007	108.73
	1.0000	5.400	1.0000			
100.00	0.0000	0.343	0.0000			
	0.1329	1.988	0.8336	1.8662	1.0275	88.48
	0.2397	2.960	0.8907	1.6059	1.0987	153.91
	0.3301	3.621	0.9168	1.4436	1.1286	168.15
	0.3831	3.989	0.9277	1.3734	1.1547	174.87
	0.4463	4.396	0.9372	1.2987	1.2099	184.71
	0.5069	4.706	0.9448	1.2241	1.2614	180.44
	0.5638	5.032	0.9508	1.1742	1.3398	181.37
	0.6671	5.598	0.9618	1.1002	1.4799	161.46
	0.8133	6.451	0.9764	1.0320	1.8111	113.52
	1.0000	7.778	1.0000			
105.00	0.0000	0.565	0.0000			
	0.2101	3.649	0.8533	1.6242	1.0605	129.47
	0.2869	4.512	0.8855	1.4960	1.0963	158.15
	0.4108	5.664	0.9149	1.3191	1.1835	186.00
	0.4836	6.298	0.9275	1.2444	1.2478	192.13
	0.6012	7.242	0.9440	1.1455	1.3831	184.21
	0.7548	8.417	0.9626	1.0511	1.6684	142.43
	0.8990	9.805	0.9829	1.0148	2.0457	74.64
	1.0000	10.835	1.0000			

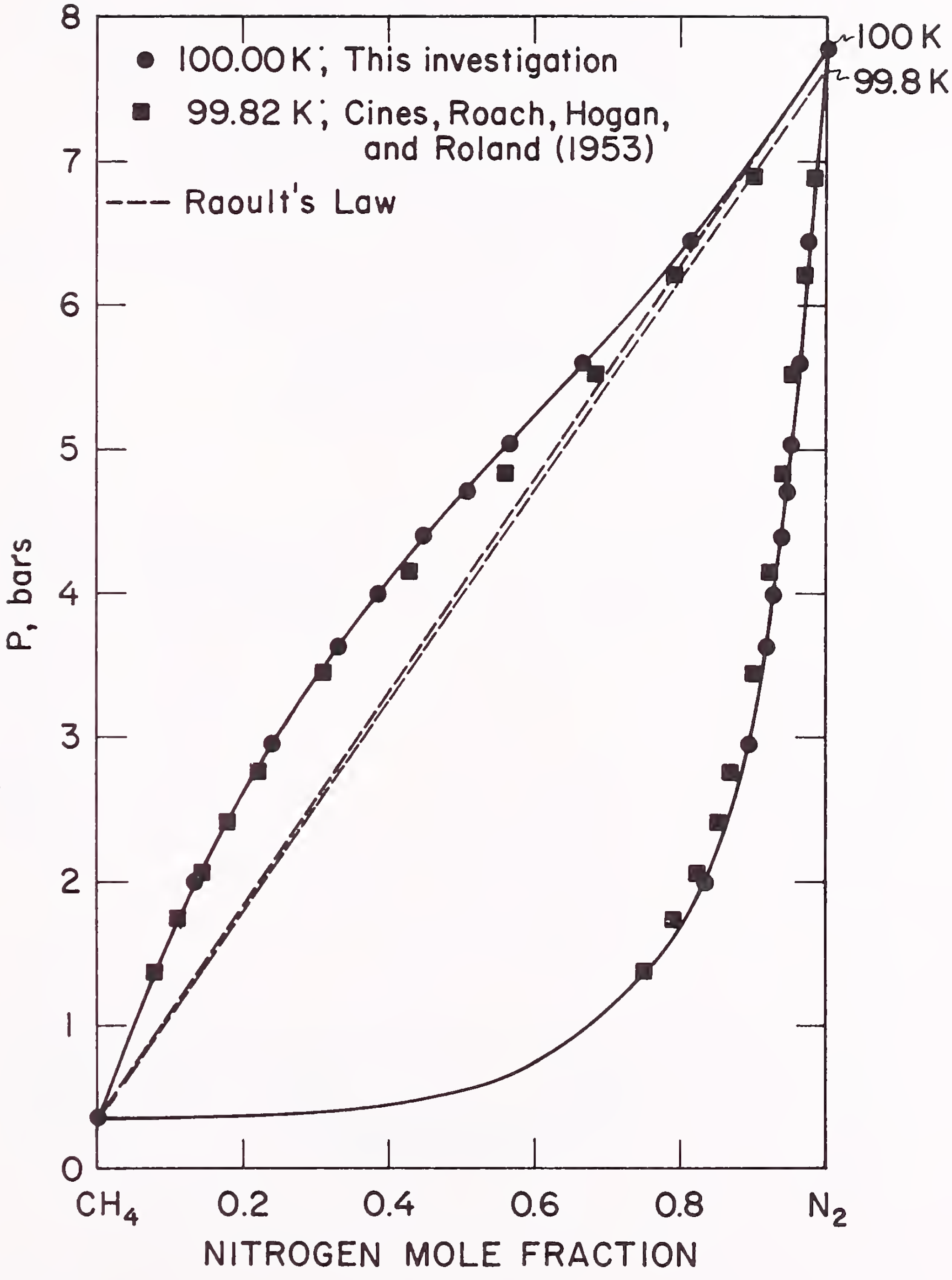
TABLE 1. (continued)

T, K	x_{N_2}	P, bars	y_{N_2}	γ_{N_2}	CH_4	G^E, J/mol
110.00	0.0000	0.844	0.0000			
	0.2093	4.810	0.8237	1.6008	1.0546	128.53
	0.2856	5.916	0.8615	1.4743	1.0850	154.66
	0.4061	7.450	0.8950	1.3129	1.1799	190.96
	0.4843	8.366	0.9113	1.2342	1.2477	197.60
	0.5008	8.479	0.9147	1.2112	1.2516	190.24
	0.6056	9.603	0.9319	1.1278	1.3765	181.88
	0.6948	10.580	0.9456	1.0756	1.5125	161.82
	0.7956	11.797	0.9612	1.0364	1.7208	127.47
	0.8978	13.179	0.9790	1.0131	1.9841	74.76
	1.0000	14.680	1.0000			
115.00	0.0000	1.327	0.0000			
	0.1891	5.882	0.7782	1.6384	1.0465	124.51
	0.2868	7.725	0.8363	1.4712	1.0873	162.93
	0.3989	9.580	0.8739	1.3218	1.1606	192.05
	0.5027	11.130	0.8983	1.2148	1.2501	199.65
	0.5789	12.218	0.9129	1.1515	1.3398	195.85
	0.7110	14.170	0.9377	1.0736	1.5208	164.16
	0.8043	15.650	0.9538	1.0344	1.7540	131.17
	0.9040	17.474	0.9750	1.0116	2.0407	75.40
	1.0000	19.389	1.0000			
120.00	0.0000	1.919	0.0000			
	0.0977	4.984	0.6122	1.8083	1.0174	73.31
	0.1938	7.549	0.7458	1.6058	1.0490	130.07
	0.2990	9.982	0.8125	1.4348	1.0956	171.53
	0.3978	12.100	0.8512	1.3177	1.1523	194.66
	0.4959	13.942	0.8773	1.2136	1.2381	203.17
	0.5938	15.919	0.9000	1.1444	1.3476	200.81
	0.7055	18.029	0.9225	1.0748	1.5323	176.16
	0.7877	19.880	0.9414	1.0459	1.6785	144.97
	1.0000	25.128	1.0000			

Table 2. Constants for equation (4) from the Barker method and from both liquid and vapor data.

T K	Data Used	A	Std Dev. A	B	Std Dev. B	C	Std Dev. C
95.00	x-P	0.856566	0.018181	0.048882	0.026564	-0.006273	0.030452
	x-y-P	0.989270	0.000249	-0.039063	0.001553	-0.060026	0.011018
100.00	x-P	0.834333	0.004510	0.012843	0.006889	0.019011	0.011753
	x-y-P	0.883896	0.0001627	-0.064193	0.001080	0.127218	0.005988
105.00	x-P	0.797382	0.011029	0.036777	0.018664	0.028248	0.026115
	x-y-P	0.877361	0.000017	0.001976	0.000084	0.058049	0.000487
110.00	x-P	0.769161	0.010578	0.024975	0.017310	0.017785	0.024585
	x-y-P	0.844515	0.000072	0.001095	0.000416	0.018386	0.002345
115.00	x-P	0.773121	0.006625	0.030019	0.011782	0.045115	0.016687
	x-y-P	0.832951	0.000019	0.014834	0.000086	0.066556	0.000489
120.00	x-P	0.753117	0.006021	0.048651	0.010289	0.058088	0.016019
	x-y-P	0.819650	0.000008	0.037988	0.000023	0.086550	0.000145

LIST OF FIGURES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■ 99.82 K; Cines, Roach, Hogan, and Roland (1953)
--- Raoult's Law
100 K
99.8 K
P, bars
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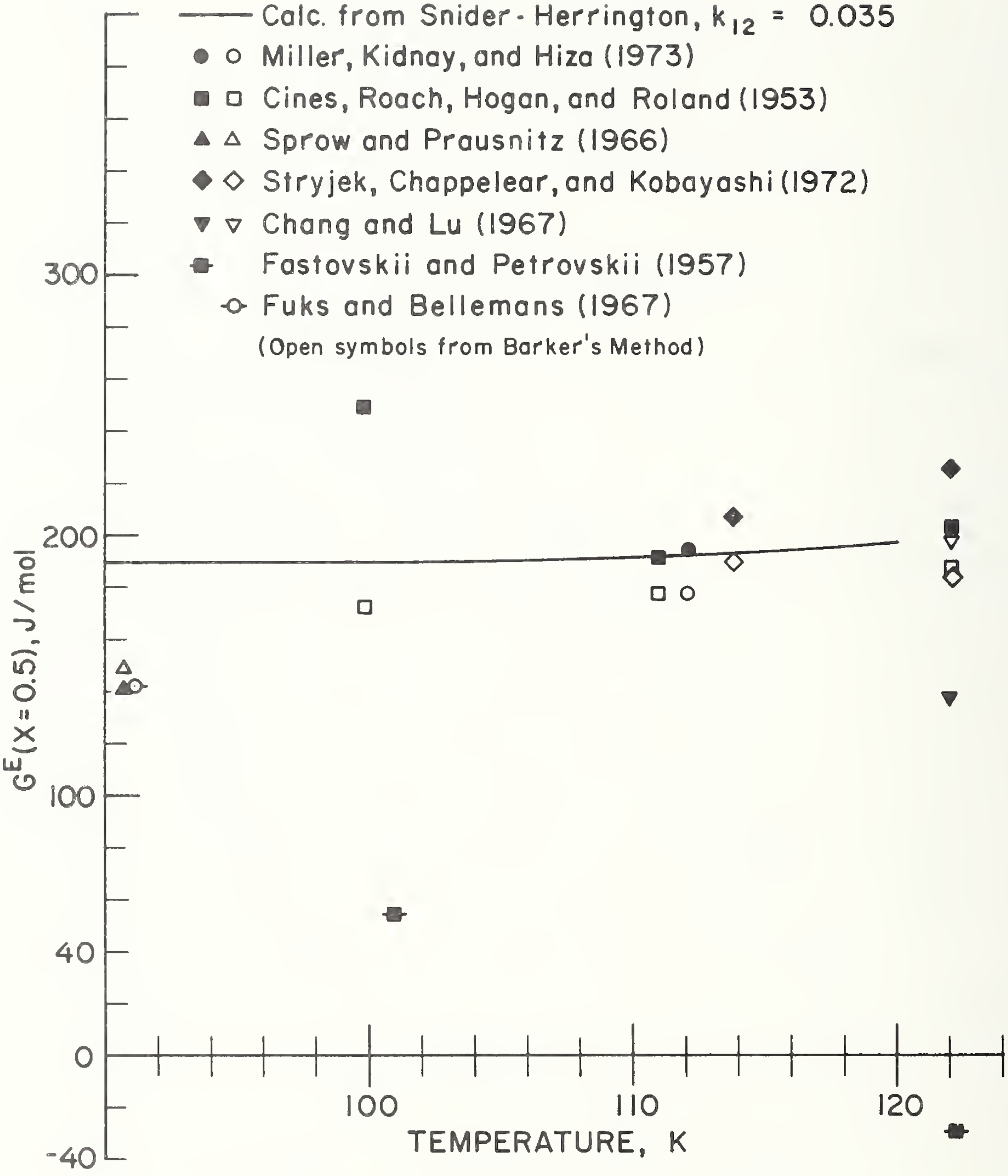
1
2
3
4
5
6
7
8
CH$_4$
0.2
0.4
0.6
0.8
N$_2$
NITROGEN MOLE FRACTION

Figure 1.


Calc. from Snider - Herrington, k_{12} = 0.035
Miller, Kidnay, and Hiza (1973)
Cines, Roach, Hogan, and Roland (1953)
Sprow and Prausnitz (1966)
Stryjek, Chappelear, and Kobayashi (1972)
Chang and Lu (1967)
Fastovskii and Petrovskii (1957)
Fuks and Bellemans (1967)
(Open symbols from Barker's Method)
$G^E(X=0.5)$, J/mol
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200
100
40
0
-40
100
110
120
TEMPERATURE, K

Figure 2.

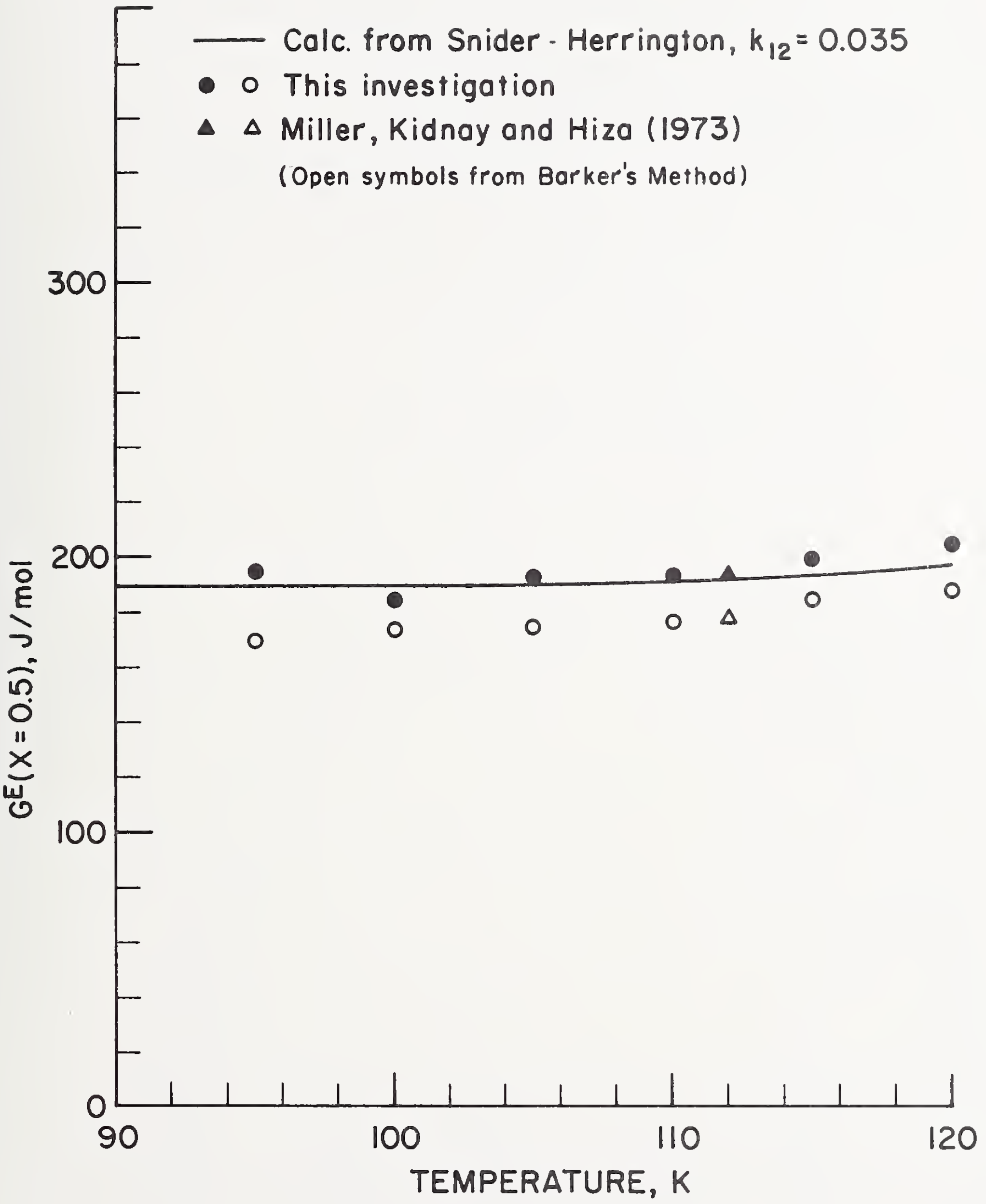
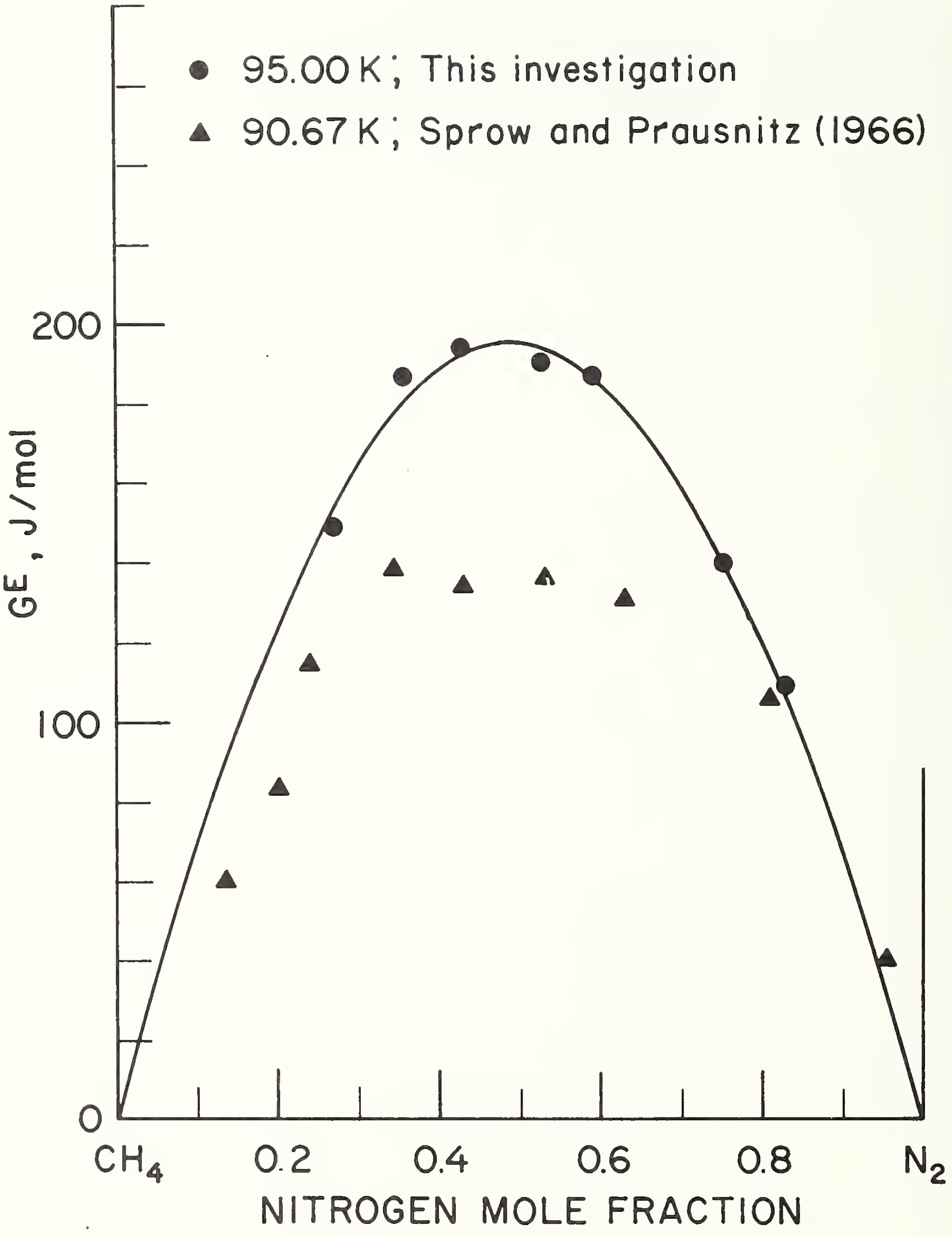

Calc. from Snider - Herrington, k_{12} = 0.035
● ○ This investigation
▲ △ Miller, Kidnay and Hiza (1973)
(Open symbols from Barker's Method)
G^E(X = 0.5), J/mol
300
200
100
0
90
100
110
120
TEMPERATURE, K

Figure 3.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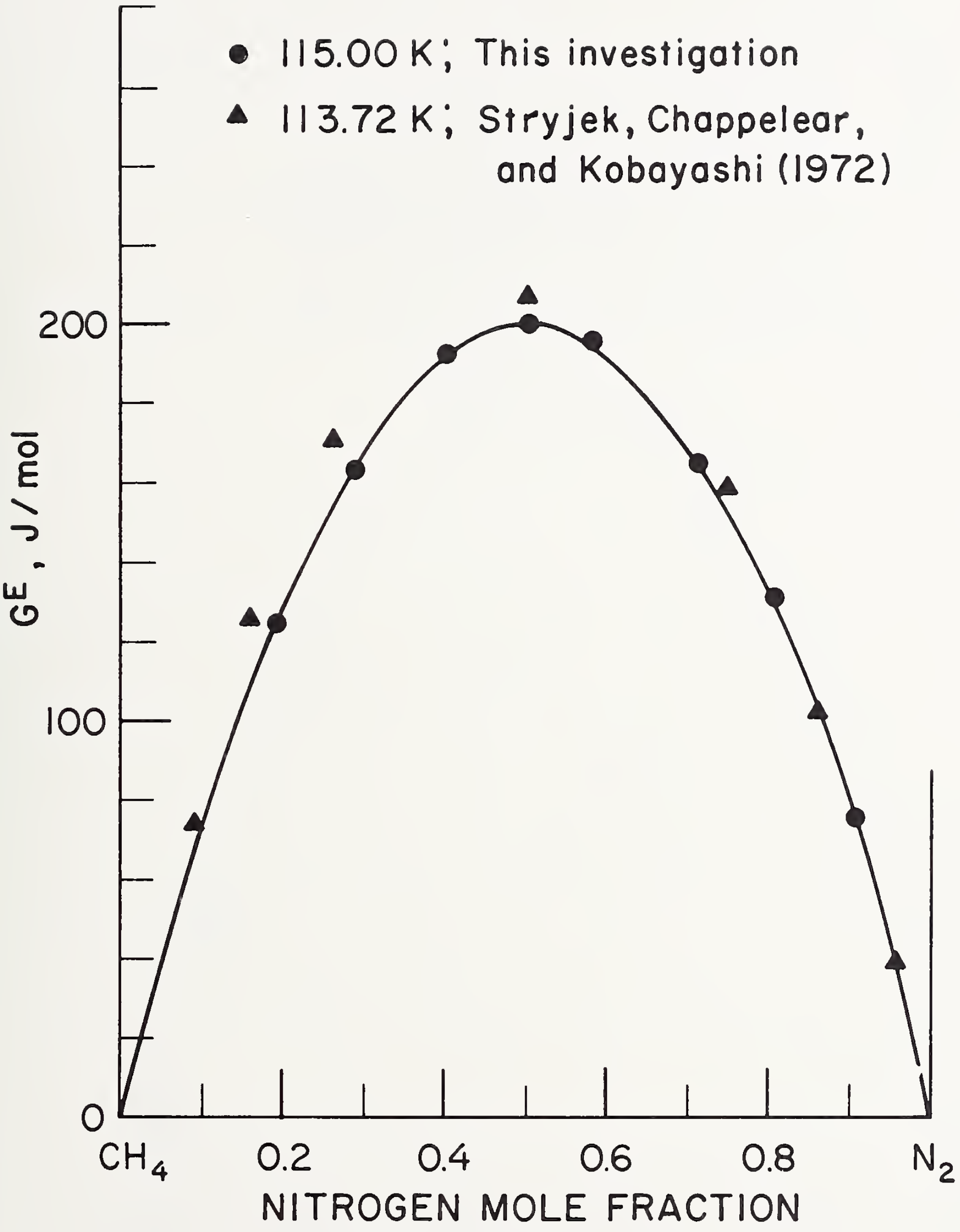
200
100
0
GE, J/mol
CH$_4$
0.2
0.4
0.6
0.8
N$_2$
NITROGEN MOLE FRACTION

Figure 4.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G^E, J/mol
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100
0
CH_4
0.2
0.4
0.6
0.8
N_2
NITROGEN MOLE FRACTION

Figure 5.

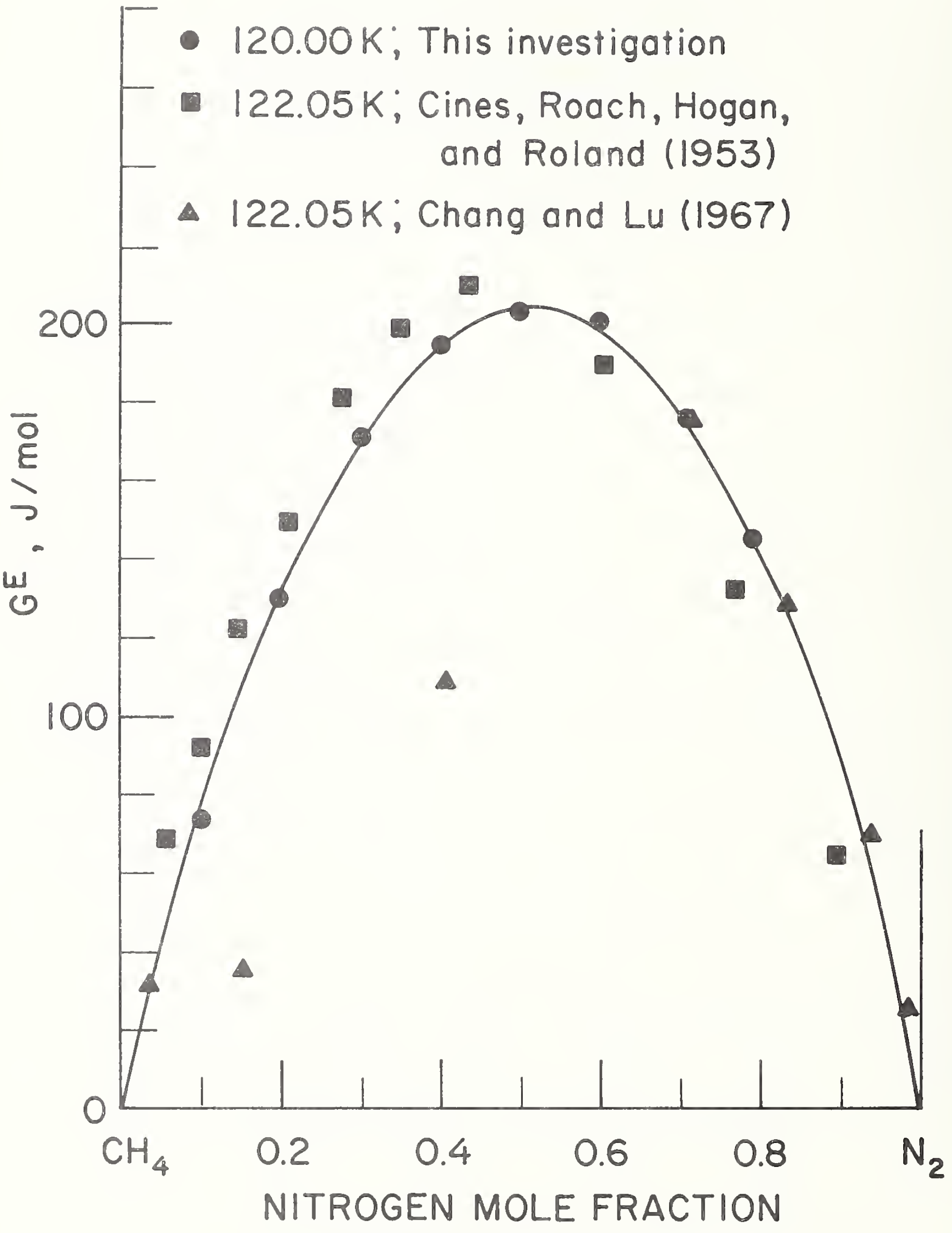
● 120.00 K; This investigation
■ 122.05 K; Cines, Roach, Hogan, and Roland (1953)
▲ 122.05 K; Chang and Lu (1967)
G^E, J/mol
200
100
0
CH_4
0.2
0.4
0.6
0.8
N_2
NITROGEN MOLE FRACTION

Figure 6.

APPENDIX J

Cryogenics Division – NBS Institute for Basic Standards LABORATORY NOTE	PROJECT NO. 2750364	FILE NO. 73-3	PAGE 1
SUBJECT The Vapor Pressures of Ethane	NAME R. D. Goodwin DATE July 9, 1973		

This is the first of several reports planned on the physical properties of ethane. Our ultimate purpose is to compute tables of thermodynamic functions over the entire range of fluid states. We first will discover regions where data are inadequate or lacking by attempting to compute provisional tables based on existing data.

Accurate vapor pressures, and a proper analytical representation of these data, are essential for computing heats of vaporization via the Clapeyron equation.

In this note we give a limited bibliography. Not all of these references were available at this writing. We compare several sets of data by use of our new, non-analytic vapor pressure equation. We make a choice of the best for least squares, and we give deviations from this selected equation.

At the triple point near 90 K the vapor pressure of ethane is about 0.00001 atm (10 μ-atm). Experimental methods therefore differ for the range below one atm (184.5K) and for the range of higher pressures to 48 atm at T_c = 305 K.

Data to about 1960 are reviewed by Tester [19], who selected the representation of Barkelew et al. [3] for the entire range from triple- to critical point.

Below one atm the data to 1964 are reviewed by Ziegler et al., who give their own, high quality set of data computed for thermodynamic consistency with all related or derived data, in a work for the National Standard Reference Data Program [23]. More recently we have the measurements of Carruth, obtained by the gas saturation flow technique, employing a flame ionization detector for analysis of the gas mixture [4]. See also J. J. Chen et al. (Rice University), paper G-1, 1972 Cryogenic Engineering Conference, on the same technique.

For high pressures the only new data of which we presently are aware are those of Pope (Table 25)[13], and those attributed to Dr. A. K. Pal by Pope [13] in Table 31. For these latter data there is no description of experimental method.

After this note was written we received the new precise measurements of Douslin and Harrison [24], and therefore have recomputed our results including these data. Douslin and Harrison note especially the new, precise measurements of Miniovich and Sorina [25], which were not available to us at this writing.

SUBJECT The Vapor Pressures of Ethane

NAME R. D. Goodwin
DATE July 9, 1973

Our vapor pressure equation [6] uses the reduced argument,

$$x(T) \equiv (1-T_t/T)/(1-T_t/T_c) ,$$

where subscripts t and c refer to triple- and critical points,

$$\ell n\,(P/P_t) = a\cdot x + b\cdot x^2 + c\cdot x^3 + d\cdot x^4 + e\cdot x\cdot(1-x)^{\epsilon} \qquad (1)$$

and the exponent is $\epsilon = 1.5$ for methane [15] and for oxygen [16]. Originally the term $d\cdot x^4$ was absent. It has been added here to improve representation of the ethane data.

The following discoveries are found with the original equation of four terms. Optimum exponents in the range $1.1 \leq \epsilon \leq 1.9$ are obtained merely by changing the sets of data used for least squares. Hence we must rely on the more precise methane and oxygen data to select $\epsilon = 1.5$. Varying the critical-point temperature within reasonable limits has no significant effect on the overall, rms relative pressure deviations.

By examining numerous results we have selected for least squares only the data of Ziegler at $P \leq 1$ atm [23], and the data of Pope, Pal [13] and Douslin [24] at $P > 1.9$ atm. Whereas the temperature scale of Ziegler may be thermodynamic (the report is not clear), we nevertheless find that deviations (rms in relative P) are minimized by converting both sets of data to T-1968 as if they had been on T-1948 [1]. All T used in the following are T-68.

The triple-point temperature was reviewed by Ziegler et al. Their selection of 89.89 K becomes 89.899 on the 1968 scale. The critical-point temperature 305.42 K of Pope has been changed to 305.33 K for consistency with the data of Douslin [24]. A value $T_c = 305.33 \pm 0.005$ K is given by P. Sliwinski, Zeit. Phys. Chem. 68, 91 (1969) based on analysis of dielectric constants. This was kindly pointed out by D. E. Diller. We obtain pressures at these end points from the vapor pressure equation:

	T, K (1968)	P, atm
Triple point	89.899	$9.616.10^{-6}$
Critical point	305.33	48.07695

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SUBJECT: The Vapor Pressures of Ethane

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The constants for eq (1) were obtained via the data of Ziegler, Pope, Pal and Douslin. They include $\epsilon = 1.6$ as shown at the head of table 1.

$a = 8.4549\,8734$
$b = 12.4880\,3978$
$c = -4.1042\,8155$
$d = -1.4138\,6053$
$e = 8.5265\,2253$

In the following tables we give the author's ID, his temperature and as converted to T-68, and the published and calculated pressures. Next is the deviation of his temperature from our calculated value,

$$DT \equiv T_{xpt} - T_{calc} = -(P_{xpt} - P_{calc})/(dP/dT),$$

and finally his relative pressure deviation,

$$P, PCT \equiv 100 \cdot (P_{xpt} - P_{calc})/P_{calc}.$$

At the bottom of each table we give the number of datum pairs, NP, and the rms of relative pressure deviations in percent.

The source of data in each table is identified by the numerical code, ID, in the first column--

Table No.	I.D.	Authors	Reference
1	4	A. K. Pal	[13]
	7	Ziegler et al.	[23]
	9	G. A. Pope	[13]
	10	Douslin, Harrison	[24]
2	1	Tickner, Lossing	[20]
	2	API Proj. 44	[2]
	3	Carruth	[4]
3	5	Loomis, Walters	[11]
4	6	F. Porter	[14]
	8	Barkelew et al	[3]
5	Calculated vapor pressures (this report)		
6	Reduced v.p. functions (this report)		

As additional data may be found, we reserve comment on the deviations of individual authors, and omit the labor of preparing deviation plots.

Calculated pressures, slopes and curvatures are given at uniform temperatures by Table 5.

For comparison with functions in our original vapor pressure publication [6], we give these functions in Table 6, as computed via eq (1) namely

$$x(T) \equiv (T - T_t/T)/(1 - T_t/T_c),$$

$$Y(P) \equiv \ln(P/P_t)/\ln(P_c/P_t). \tag{2}$$

These variables range from zero to unity. The equation

$$Y = x \tag{3}$$

represents the basic vapor pressure equation

$$\ln(P) = a - b/T \tag{4}$$

when this is constrained to the end-points (triple and critical). Hence (Y-x) is the deviation of data from (4).

Finally, we give the computer programs used in this work as a means to check for errors, and to facilitate resumption of this research.

Addendum. Following work shows that the second virial coefficient used by Ziegler et al. to obtain vapor pressures is not consistent with our selection. At 200°K his B(T) = - 455 cc/mol, whereas our B(T) = - 417.5. We therefore have recomputed our vapor pressure constants using Ziegler's vapor pressure data from his Table IX for "Curve B" of his Figure 1, for which B(T) = - 410 cc/mol at 200 K. The difference in his vapor pressures at 90 K is (7.80-7.33)/7.33 = 6.4 percent, the new values being the greater. Our new results for eq (1) are given in Table 7, (pages 20, 21) and tables 8, 9 on pages 22, 23 of this report. We prefer these constants for future use.

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SUBJECT The Vapor Pressures of Ethane
Table 1. Data of Pal (4), Ziegler (7), Pope (9), and Douslin (10).

NAME R. D. Goodwin
DATE July 9, 1973

```
ETHANE VAPOR PRESSURES, E = 1.60
TTRP = 89.899, TCRT = 305.330
PTRP,MUATM = 9.61600, PCRT,ATM = 48.07695
  8.454987344      12.488039775      -4.104281551
 -1.413860533       8.526522526       0.000000000

ID    T,XPTL      T-68        P,ATM        CALCD      DEL T      P,PCT
 7     94.000     94.013   0.0000274   0.0000274   -0.001       0.02
 7     98.000     98.012   0.0000693   0.0000694    0.002      -0.05
 7    102.000    102.008   0.0001618   0.0001619    0.002      -0.05
 7    106.000    106.002   0.0003526   0.0003522   -0.006       0.11
 7    110.000    109.998   0.0007207   0.0007205   -0.002       0.03
 7    114.000    113.995   0.0013947   0.0013947   -0.000       0.00
 7    118.000    117.991   0.0025697   0.0025698    0.000      -0.00
 7    122.000    121.988   0.0045303   0.0045293   -0.002       0.02
 7    126.000    125.987   0.0076737   0.0076734   -0.000       0.00
 7    130.000    129.987    0.012538    0.012540    0.001      -0.01
 7    134.000    133.988    0.019830    0.019834    0.002      -0.02
 7    138.000    137.990    0.030447    0.030460    0.004      -0.04
 7    142.000    141.993    0.045504    0.045527    0.005      -0.05
 7    146.000    145.996    0.066355    0.066389    0.006      -0.05
 7    150.000    150.000    0.094608    0.094657    0.006      -0.05
 7    154.000    154.004     0.13213     0.13220    0.007      -0.05
 7    158.000    158.008     0.18109     0.18117    0.005      -0.04
 7    162.000    162.012     0.24392     0.24397    0.003      -0.02
 7    166.000    166.015     0.32333     0.32330   -0.001       0.01
 7    170.000    170.019     0.42230     0.42214   -0.006       0.04
 7    174.000    174.023     0.54409     0.54371   -0.011       0.07
 7    178.000    178.026     0.69224     0.69145   -0.020       0.11
 7    182.000    182.028     0.87047     0.86905   -0.029       0.16
 7    184.520    184.550     1.00000     0.99803   -0.036       0.20
 9    198.181    198.216      1.9737      1.9758    0.023      -0.11
 4    214.302    214.334      3.9209      3.9176   -0.021       0.08
 4    224.102    224.130      5.6367      5.6429    0.031      -0.11
 4    229.756    229.782      6.8569      6.8629    0.026      -0.09
 4    234.556    234.581      8.0335      8.0423    0.034      -0.11
 9    234.692    234.715      8.0741      8.0772    0.012      -0.04
10    238.150    238.150      9.0097      9.0108    0.004      -0.01
 9    238.771    238.792      9.1843      9.1935    0.032      -0.10
 4    239.844    239.864      9.4959      9.5049    0.030      -0.09
 4    240.514    240.534      9.6960      9.7032    0.024      -0.07
10    243.150    243.150     10.5063     10.5071    0.003      -0.01
 4    243.359    243.377     10.5760     10.5790    0.009      -0.03
 4    246.814    246.830     11.7137     11.7183    0.014      -0.04
 4    247.816    247.831     12.0502     12.0648    0.042      -0.12
10    248.150    248.150     12.1756     12.1766    0.003      -0.01
 4    249.741    249.755     12.7620     12.7512   -0.030       0.08
 4    250.146    250.160     12.8985     12.8991    0.002      -0.01
 4    251.587    251.600     13.4425     13.4356   -0.018       0.05
 4    252.544    252.556     13.8065     13.8008   -0.015       0.04
10    253.150    253.150     14.0310     14.0310   -0.000       0.00
 4    254.290    254.301     14.4898     14.4854   -0.011       0.03
 4    257.543    257.552     15.8252     15.8264    0.003      -0.01
10    258.150    258.150     16.0835     16.0823   -0.003       0.01
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Table 1--continued.

ID	T,XPTL	T-68	P,ATM	CALCD	DEL T	P,PCT
10	263.150	263.150	18.3464	18.3433	-0.007	0.02
4	263.380	263.386	18.4543	18.4553	0.002	-0.01
4	267.536	267.539	20.5197	20.5113	-0.016	0.04
10	268.150	268.150	20.8318	20.8274	-0.009	0.02
4	271.749	271.750	22.7661	22.7618	-0.008	0.02
9	272.949	272.949	23.4515	23.4347	-0.030	0.07
10	273.150	273.150	23.5549	23.5488	-0.011	0.03
4	275.922	275.921	25.1584	25.1648	0.011	-0.03
4	276.363	276.362	25.4558	25.4293	-0.044	0.10
4	276.385	276.384	25.4491	25.4425	-0.011	0.03
4	276.514	276.513	25.5472	25.5203	-0.044	0.11
4	277.813	277.811	26.3185	26.3133	-0.008	0.02
10	278.150	278.150	26.5309	26.5233	-0.012	0.03
4	280.041	280.038	27.7039	27.7158	0.019	-0.04
4	282.247	282.243	29.1537	29.1588	0.008	-0.02
10	283.150	283.150	29.7763	29.7681	-0.012	0.03
4	284.635	284.630	30.7664	30.7836	0.025	-0.06
9	284.845	284.840	30.9555	30.9296	-0.037	0.08
4	287.653	287.648	32.9289	32.9340	0.007	-0.02
10	288.150	288.150	33.3110	33.3030	-0.011	0.02
4	288.263	288.257	33.3899	33.3822	-0.010	0.02
4	290.040	290.034	34.6873	34.7148	0.036	-0.08
9	290.214	290.208	34.8748	34.8474	-0.036	0.08
4	292.236	292.229	36.4440	36.4182	-0.033	0.07
4	293.098	293.091	37.0816	37.1044	0.028	-0.06
10	293.150	293.150	37.1583	37.1518	-0.008	0.02
9	293.266	293.259	37.2672	37.2394	-0.035	0.07
4	296.347	296.339	39.7598	39.7842	0.029	-0.06
10	298.150	298.150	41.3494	41.3450	-0.005	0.01
4	299.665	299.657	42.6543	42.6822	0.031	-0.07
9	299.863	299.855	42.8863	42.8606	-0.028	0.06
4	300.205	300.196	43.1650	43.1703	0.006	-0.01
4	301.251	301.242	44.1085	44.1297	0.023	-0.05
10	302.150	302.150	44.9809	44.9778	-0.003	0.01
10	303.150	303.150	45.9327	45.9295	-0.003	0.01
4	303.471	303.462	46.2032	46.2300	0.028	-0.06
4	303.477	303.468	46.2798	46.2358	-0.046	0.10
9	304.012	304.002	46.7736	46.7558	-0.018	0.04
4	304.049	304.039	46.7698	46.7920	0.023	-0.05
10	304.150	304.150	46.9040	46.9010	-0.003	0.01
4	304.360	304.350	47.0931	47.0974	0.004	-0.01
4	304.446	304.435	47.2198	47.1822	-0.038	0.08
4	304.519	304.508	47.2025	47.2544	0.052	-0.11
4	304.734	304.723	47.4310	47.4677	0.037	-0.08
4	304.796	304.785	47.5185	47.5294	0.011	-0.02
4	304.924	304.913	47.6846	47.6572	-0.027	0.06
4	304.980	304.969	47.7131	47.7132	0.000	-0.00
4	305.121	305.110	47.8496	47.8547	0.005	-0.01
4	305.135	305.124	47.8251	47.8688	0.043	-0.09
10	305.150	305.150	47.8992	47.8950	-0.004	0.01
4	305.153	305.142	47.8807	47.8869	0.006	-0.01
10	305.250	305.250	47.9994	47.9959	-0.003	0.01

NP = 99, RMSPCT = 0.061

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Table 2. Data of Tickner (1), API (2), and Carruth (3).

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```
 ID     T,XPTL       T-68         P,ATM          CALCD       DEL T      P,PCT
  1     91.350      91.361     0.0000132     0.0000141      0.265      -6.86
  1     94.450      94.463     0.0000263     0.0000306      0.582     -13.98
  1     98.550      98.562     0.0000658     0.0000783      0.730     -15.98
  1    101.850     101.858     0.0001316     0.0001571      0.797     -16.23
  1    105.350     105.353     0.0002632     0.0003118      0.825     -15.60
  1    110.550     110.548     0.0006579     0.0007914      0.992     -16.87
  1    114.650     114.644     0.0013158     0.0015453      0.947     -14.85
  1    119.050     119.040     0.0026316     0.0029942      0.839     -12.11
  1    125.550     125.537     0.0065789     0.0072450      0.717      -9.19
  1    130.650     130.637      0.013158      0.013539      0.240      -2.81

 NP =   10, RMSPCT = 13.226
 ID     T,XPTL       T-68         P,ATM          CALCD       DEL T      P,PCT
  2    130.270     130.257      0.013158      0.012947     -0.138       1.63
  2    136.460     136.449      0.026316      0.025909     -0.148       1.57
  2    140.410     140.402      0.039474      0.038925     -0.141       1.41
  2    143.370     143.364      0.052632      0.051945     -0.139       1.32
  2    145.760     145.756      0.065789      0.064946     -0.142       1.30
  2    147.790     147.788      0.078947      0.078018     -0.134       1.19
  2    151.120     151.121       0.10526       0.10415     -0.127       1.07
  2    153.820     153.824       0.13158       0.13028     -0.122       0.99
  2    159.030     159.039       0.19737       0.19591     -0.099       0.74
  2    162.960     162.973       0.26316       0.26140     -0.094       0.67
  2    166.170     166.185       0.32895       0.32708     -0.084       0.57
  2    168.900     168.918       0.39474       0.39284     -0.074       0.48
  2    173.410     173.432       0.52632       0.52422     -0.064       0.40
  2    177.100     177.125       0.65789       0.65574     -0.056       0.33
  2    180.250     180.277       0.78947       0.78743     -0.046       0.26
  2    183.010     183.039       0.92105       0.91908     -0.039       0.21
  2    184.520     184.550       1.00000       0.99803     -0.036       0.20
  2    185.480     185.510        1.0526        1.0509     -0.031       0.16
  2    187.710     187.741        1.1842        1.1821     -0.034       0.18
  2    189.770     189.802        1.3158        1.3143     -0.023       0.11
  2    193.440     193.473        1.5789        1.5777     -0.017       0.08
  2    198.150     198.185        1.9737        1.9729     -0.008       0.04

 NP =   22, RMSPCT =   0.857
 ID     T,XPTL       T-68         P,ATM          CALCD       DEL T      P,PCT
  3     91.340      91.351     0.0000152     0.0000141     -0.315       8.14
  3     93.700      93.712     0.0000270     0.0000255     -0.237       5.80
  3     96.240      96.253     0.0000491     0.0000466     -0.235       5.42
  3    100.700     100.710     0.0001297     0.0001239     -0.222       4.64
  3    105.600     105.603     0.0003263     0.0003268      0.009      -0.16
  3    114.240     114.235     0.0014461     0.0014487      0.012      -0.19
  3    120.380     120.369     0.0036066     0.0036185      0.023      -0.33
  3    129.810     129.797      0.012312      0.012260     -0.036       0.42
  3    135.770     135.759      0.024197      0.024065     -0.051       0.55
  3    140.550     140.542      0.040211      0.039472     -0.188       1.87
  3    144.140     144.135      0.056289      0.055871     -0.080       0.75

 NP =   11, RMSPCT =   3.759
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Table 3. Data (5) of Loomis, Walters [11].

```
ID    T,XPTL      T-68       P,ATM        CALCD      DEL T       P,PCT
 5   135.736   135.725    0.024500     0.023977    -0.203        2.18
 5   143.267   143.261    0.052200     0.051437    -0.156        1.48
 5   147.324   147.321    0.075900     0.074840    -0.158        1.42
 5   154.546   154.550     0.14000      0.13816    -0.166        1.33
 5   158.385   158.393     0.18860      0.18657    -0.143        1.09
 5   162.629   162.641     0.25730      0.25528    -0.110        0.79
 5   165.529   165.544     0.31600      0.31300    -0.139        0.96
 5   167.836   167.853     0.36930      0.36606    -0.133        0.89
 5   169.175   169.193     0.40330      0.40000    -0.126        0.82
 5   171.700   171.721     0.47430      0.47084    -0.116        0.74
 5   170.602   170.622     0.44300      0.43890    -0.145        0.93
 5   174.062   174.085     0.54980      0.54579    -0.119        0.73
 5   175.708   175.732     0.60730      0.60338    -0.108        0.65
 5   177.623   177.649     0.68040      0.67631    -0.103        0.61
 5   178.621   178.647     0.72100      0.71696    -0.097        0.56
 5   179.750   179.777     0.76960      0.76525    -0.099        0.57
 5   181.506   181.534     0.84990      0.84537    -0.096        0.54
 5   182.463   182.492     0.89630      0.89172    -0.093        0.51
 5   183.776   183.807     0.96340      0.95860    -0.092        0.50
 5   184.539   184.569     1.00400      0.99906    -0.091        0.49
 5   185.137   185.167      1.0366       1.0318    -0.087        0.47
 5   185.914   185.944      1.0800       1.0755    -0.078        0.42
 5   186.609   186.640      1.1208       1.1158    -0.084        0.44
 5   187.302   187.333      1.1619       1.1572    -0.077        0.40
 5   187.726   187.757      1.1881       1.1831    -0.081        0.42
 5   188.379   188.410      1.2289       1.2239    -0.080        0.41
 5   189.114   189.146      1.2757       1.2710    -0.072        0.37
 5   189.656   189.690      1.3248       1.3202    -0.069        0.35
 5   190.791   190.823      1.3885       1.3839    -0.057        0.33
 5   191.430   191.463      1.4334       1.4288    -0.064        0.32
 5   192.286   192.319      1.4953       1.4908    -0.061        0.30
 5   192.777   192.810      1.5318       1.5273    -0.060        0.29
 5   196.244   196.278      1.8088       1.8049    -0.046        0.22
 5   199.909   199.944      2.1417       2.1384    -0.034        0.15

NP =  34, RMSPCT =  0.789
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SUBJECT The Vapor Pressures of Ethane Table 4. Data of Porter (6), and Barkelew (8).	NAME R. D. Goodwin DATE July 9, 1973		

ID	T,XPTL	T-68	P,ATM	CALCD	DEL T	P,PCT
6	184.470	184.500	0.99940	0.99534	-0.075	0.41
6	203.490	203.524	2.4960	2.5076	0.106	-0.46
6	205.620	205.653	2.7330	2.7489	0.135	-0.58
6	210.960	210.992	3.4140	3.4308	0.121	-0.49
6	216.310	216.341	4.2250	4.2338	0.054	-0.21
6	221.880	221.910	5.2070	5.2104	0.018	-0.06
6	225.100	225.128	5.8380	5.8456	0.037	-0.13
6	226.180	226.207	6.0730	6.0709	-0.010	0.03
6	234.580	234.603	8.0440	8.0481	0.016	-0.05
6	238.900	238.921	9.2290	9.2305	0.005	-0.02
6	243.220	243.238	10.5360	10.5350	-0.003	0.01
6	248.650	248.665	12.3540	12.3588	0.013	-0.04
6	253.030	253.042	14.0430	13.9889	-0.139	0.39
6	258.800	258.809	16.4210	16.3679	-0.122	0.32
6	263.280	263.286	18.4480	18.4078	-0.085	0.22
6	268.730	268.732	21.1850	21.1317	-0.101	0.25
6	273.090	273.090	23.5440	23.5147	-0.051	0.12
6	278.640	278.638	26.8370	26.8276	-0.015	0.04
6	283.580	283.576	30.1060	30.0575	-0.071	0.16
6	288.260	288.254	33.4680	33.3800	-0.119	0.26

NP = 20, RMSPCT = 0.274

ID	T,XPTL	T-68	P,ATM	CALCD	DEL T	P,PCT
8	110.000	109.998	0.00076000	0.0007205	-0.319	5.49
8	120.000	119.989	0.00346000	0.0034295	-0.063	0.89
8	130.000	129.987	0.012720	0.012540	-0.121	1.44
8	140.000	139.992	0.037850	0.037359	-0.131	1.31
8	150.000	150.000	0.095600	0.094657	-0.116	1.00
8	160.000	160.010	0.21200	0.21068	-0.084	0.63
8	170.000	170.019	0.42360	0.42214	-0.053	0.35
8	180.000	180.027	0.77780	0.77628	-0.034	0.20
8	190.000	190.032	1.3300	1.3297	-0.004	0.02
8	200.000	200.035	2.1462	2.1472	0.011	-0.05
8	210.000	210.033	3.2970	3.2998	0.020	-0.08
8	220.000	220.030	4.8580	4.8639	0.033	-0.12
8	230.000	230.025	6.9120	6.9196	0.032	-0.11
8	240.000	240.020	9.5510	9.5508	-0.001	0.00
8	250.000	250.014	12.8500	12.8456	-0.012	0.03
8	260.000	260.008	16.9100	16.8973	-0.028	0.08
8	270.000	270.001	21.8000	21.8065	0.012	-0.03
8	280.000	279.997	27.6500	27.6895	0.062	-0.14
8	290.000	289.994	34.6500	34.6843	0.045	-0.10

NP = 19, RMSPCT = 1.383

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SUBJECT The Vapor Pressures of Ethane Table 5. Calculated Ethane Vapor Pressures.	NAME R. D. Goodwin DATE July 9, 1973		

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ETHANE VAPOR PRESSURES

      T,K       P,ATM       DP/DT       D2P/DT2
   89.899   0.0000096   0.0000026   0.00000063
   90.000   0.0000099   0.0000026   0.00000064
   95.000   0.0000348   0.0000083   0.00000177
  100.000   0.0001067   0.0000226   0.00000430
  105.000   0.0002916   0.0000555   0.00000942
  110.000   0.0007207   0.0001239   0.00001881
  115.000   0.0016337   0.0002545   0.00003475
  120.000   0.0034347   0.0004868   0.00005997
  125.000   0.0067606   0.0008749   0.00009759
  130.000    0.012559    0.001489    0.0001508
  135.000    0.022167    0.002414    0.0002228
  140.000    0.037390    0.003753    0.0003164
  145.000    0.060574    0.005618    0.0004339
  150.000    0.094659    0.008135    0.0005771
  155.000     0.14323     0.01143     0.000747
  160.000     0.21052     0.01565     0.000944
  165.000     0.30146     0.02091     0.001167
  170.000     0.42162     0.02736     0.001415
  175.000     0.57722     0.03511     0.001688
  180.000     0.77507     0.04428     0.001984
  185.000      1.0226      0.0550      0.00230
  190.000      1.3276      0.0673      0.00263
  195.000      1.6984      0.0813      0.00298
  200.000      2.1439      0.0972      0.00335
  205.000      2.6731      0.1148      0.00372
  210.000      3.2954      0.1344      0.00411
  215.000      4.0205      0.1560      0.00451
  220.000      4.8585      0.1795      0.00492
  225.000      5.8194      0.2052      0.00533
  230.000      6.9136      0.2329      0.00576
  235.000      8.1519      0.2628      0.00619
  240.000      9.5450      0.2948      0.00664
  245.000     11.1040      0.3292      0.00710
  250.000     12.8406      0.3658      0.00757
  255.000     14.7664      0.4049      0.00806
  260.000     16.8936      0.4465      0.00858
  265.000     19.2357      0.4907      0.00913
  270.000     21.8056      0.5378      0.00972
  275.000     24.6190      0.5880      0.01036
  280.000     27.6914      0.6416      0.01108
  285.000     31.0410      0.6990      0.01192
  290.000     34.6895      0.7610      0.01294
  295.000     38.6612      0.8289      0.01429
  300.000     42.9922      0.9053      0.01649
  305.000     47.7442      1.0029      0.02894
  305.330     48.0770      1.0160      0.00000
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SUBJECT The Vapor Pressures of Ethane Table 6. Reduced Vapor Pressure Functions.	NAME R. D. Goodwin DATE July 9, 1973		

ETHANE REDUCED VAPOR PRESSURE FUNCTIONS

T,K	X	Y	(Y-X)
89.899	0.00	0.00000	0.00000
91.186	0.02	0.02199	0.00199
92.510	0.04	0.04392	0.00392
93.873	0.06	0.06578	0.00578
95.277	0.08	0.08759	0.00759
96.723	0.10	0.10934	0.00934
98.215	0.12	0.13102	0.01102
99.753	0.14	0.15264	0.01264
101.339	0.16	0.17419	0.01419
102.977	0.18	0.19568	0.01568
104.569	0.20	0.21710	0.01710
106.418	0.22	0.23845	0.01845
108.226	0.24	0.25972	0.01972
110.096	0.26	0.28093	0.02093
112.032	0.28	0.30205	0.02205
114.037	0.30	0.32310	0.02310
116.116	0.32	0.34406	0.02406
118.272	0.34	0.36495	0.02495
120.509	0.36	0.38574	0.02574
122.832	0.38	0.40645	0.02645
125.247	0.40	0.42706	0.02706
127.759	0.42	0.44758	0.02758
130.373	0.44	0.46800	0.02800
133.097	0.46	0.48832	0.02832
135.937	0.48	0.50854	0.02854
138.901	0.50	0.52866	0.02866
141.997	0.52	0.54866	0.02856
145.234	0.54	0.56855	0.02855
148.622	0.56	0.58833	0.02833
152.172	0.58	0.60800	0.02800
155.896	0.60	0.62755	0.02755
159.807	0.62	0.64698	0.02698
163.919	0.64	0.66629	0.02629
168.248	0.66	0.68548	0.02548
172.812	0.68	0.70455	0.02455
177.630	0.70	0.72350	0.02350
182.725	0.72	0.74233	0.02233
188.121	0.74	0.76105	0.02105
193.845	0.76	0.77965	0.01965
199.928	0.78	0.79815	0.01815
206.405	0.80	0.81655	0.01655
213.317	0.82	0.83486	0.01486
220.707	0.84	0.85309	0.01309
228.527	0.86	0.87126	0.01126
237.138	0.88	0.88938	0.00938
246.306	0.90	0.90749	0.00749
256.212	0.92	0.92562	0.00562
266.948	0.94	0.94381	0.00381
278.623	0.96	0.96216	0.00216
291.366	0.98	0.98078	0.00078
305.330	1.00	1.00000	0.00000

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      PROGRAM PSATFIT
C    ETHANE VAPOR PRESSURES,     X = (1-TT/T)/(1-TT/TC),
C    LN(P/PTRP) = A1*X + A2*X2 + A3*X3 + A4*X4 + A5*X*(1-X)**E.
C    AUTHORS ID = (1)TICKNER, (2)ROSSINI, (3)CARRUTH, (4)PAL/POPE,
C    (5)LOOMIS, (6)PORTER, (7)ZIEGLER, (8)BARKELEW/TESTER
C    (9)POPE, (10)DOUSLIN,PREPRINT(1973).
C
      COMMON TTRP,TCRT,PTRP, E,A(9), FZ,F1,F2, DLPDT,D2LPDT2
      COMMON/999/NFUN,Y,F(30)
      DIMENSION TEMP(130),DELT(130)
      DIMENSION ID(999),T(999),TX(999),P(999)
      DIMENSION G(30)
    1 FORMAT(I5, 2F10.0)
    2 FORMAT(1H1 17X *ETHANE VAPOR PRESSURES, E =* F5.2//
     1 18X 6HTTRP =F7.3, 8H, TCRT =F8.3//
     2 18X 12HPTRP,MUATM =F9.5, 12H, PCRT,ATM =F9.5// 2(15X 3F16.9/) )
    3 FORMAT(     18X 2HID 4X6HT,XPTL 6X4HT-68 7X5HP,ATM 7X5HCALCD
     1 5X5HDEL T  5X5HP,PCT)
    4 FORMAT(1H1 17X 2HID 4X6HT,XPTL 6X4HT-68 7X5HP,ATM 7X5HCALCD
     1 5X5HDEL T  5X5HP,PCT)
    5 FORMAT(15X I5, 2F10.3, 2F12.7, F10.3, F10.2)
    6 FORMAT(15X I5, 2F10.3, 2F12.6, F10.3, F10.2)
    7 FORMAT(15X I5, 2F10.3, 2F12.5, F10.3, F10.2)
    8 FORMAT(15X I5, 2F10.3, 2F12.4, F10.3, F10.2)
    9 FORMAT(1H0 17X 4HNP =I4, 10H, RMSPCT =F7.3)
   10 FORMAT(F8.3, F9.5, 63X)
   11 FORMAT(1H1 16X *ETHANE VAPOR PRESSURES* // 17X3HT,K 6X5HP,ATM
     1 6X5HDP/DT 5X7HD2P/DT2 )
   12 FORMAT(10X F10.3, 2F11.7, F12.8)
   13 FORMAT(10X F10.3, 2F11.6, F12.7)
   14 FORMAT(10X F10.3, 2F11.5, F12.6)
   15 FORMAT(10X F10.3, 2F11.4, F12.5)
   16 FORMAT(1H1 15X *ETHANE REDUCED VAPOR PRESSURE FUNCTIONS* //
     1 17X 3HT,K 7X1HX 9X1HY 5X5H(Y-X) )
   17 FORMAT(10X F10.3, F8.2, 2F10.5)
   18 FORMAT(18X 2HEP 6X2HSS)
   19 FORMAT(10X 2F10.4)
C    READ-IN THE T48 - T68 TEMP. CONVERSION TABLE.
   20 READ 10, ((TEMP(J),DELT(J)),J=1,130)
   21 TTRP=89.899 $ TCRT=305.33 $ PTRP=9.638E-6   $  E=1.5   $  N=0
C
C    READ (7)ZIEGLER, KELVIN, MM HG.
   22 DO 24 J=1,99   $  READ 1, IDD,TT,PP   $  IF(IDD) 23,25
   23 N = N+1   $  ID(N)=IDD   $  P(N)=PP/760   $  TX(N)=TT
   24 T(N) = T68(TT,DELT,TEMP)
   25 NF1 = N
C    READ MIXED (4)PAL, (9)POPE, (10)DOUSLIN DATA.
C    (4)KELVIN,PSIA,  (9)KELVIN,ATMOS,   (10)CENTIG.,ATMOS.
   26 DO 35 J=1,200   $  READ 1, IDD,TT,PP   $  IF(IDD) 27,36
   27 N = N+1   $  ID(N) = IDD   $  IF(IDD-4) 28,30
   28 IF(IDD-9) 34,32
   30 P(N) = PP/14.69595   $  T(N) = T68(TT,DELT,TEMP)
   31 TX(N) = TT   $  GO TO 35
   32 P(N) = PP   $  T(N) = T68(TT,DELT,TEMP)
   33 TX(N) = TT   $  GO TO 35
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        PSATFIT                                                 07/23/73

   34 P(N) = PP  $  T(N) = TX(N) = TT + 273.15
   35 CONTINUE
   36 NP = N   $   NF = 5
C    READ (1) DATA, CENTIGRADE, MM HG.
   38 DO 40 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 39,41
   39 N = N+1  $  ID(N) = IDD  $  P(N) = PP/760  $  TX(N) = 273.15 + TT
   40 T(N) = T68(TX(N),DELT,TEMP)
   41 NP2 = N
C    READ (2) DATA, CENTIGRADE, MM HG.
   42 DO 44 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 43,45
   43 N = N+1  $  ID(N) = IDD  $  P(N) = PP/760  $  TX(N) = 273.15 + TT
   44 T(N) = T68(TX(N),DELT,TEMP)
   45 NP3 = N
C    READ (3) DATA, KELVIN, MM HG.
   46 DO 48 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 47,49
   47 N = N+1  $  ID(N) = IDD  $  P(N) = PP/760  $  TX(N) = TT
   48 T(N) = T68(TT,DELT,TEMP)
   49 NP4 = N
C    READ (5) DATA, KELVIN, ATMOS.
   50 DO 52 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 51,53
   51 N = N+1  $  ID(N) = IDD  $  P(N) = PP  $  TX(N) = TT
   52 T(N) = T68(TT,DELT,TEMP)
   53 NP5 = N
C    READ (6) DATA, KELVIN, ATMOS.
   54 DO 56 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 55,57
   55 N = N+1  $  ID(N) = IDD  $  P(N) = PP  $  TX(N) = TT
   56 T(N) = T68(TT,DELT,TEMP)
   57 NP6 = N
C    READ (8)DATA, KELVIN, ATMOS.
   60 DO 62 J=1,99  $  READ 1, IDD,TT,PP  $  IF(IDD) 61,63
   61 N = N+1  $  ID(N)=IDD $ P(N)=PP $ TX(N)=TT
   62 T(N) = T68(TT,DELT,TEMP)
   63 NPP = NP7 = N
C
C    EXPLORE VALUES FOR PTPP.
   79 E = 1.6  $  PRINT 18  $  SSK = 1.0E+010
   80 XK = 1 - TTRP/TCRT
   81 DO 92 IP=1,25  $  PTR  = 9.600 + 0.001*IP  $  PTRP = PTR*1.0E-6
   82 NFUN = NF  $  DO 85 J=1,NP  $  X = (1-TTRP/T(J))/XK
   83 F(1)=X $ F(2)=X**2 $ F(3)=X**3 $ F(4)=X**4 $ F(5)=X*(1-X)**E
   84 Y = LOGF(P(J)/PTPP)
   85 CALL FIT  $  CALL COEFF  $  SS = 0  $  DO 86 K=1,9
   86 A(K) = F(K)
   87 DO 88 J=1,NP  $  PC=PSATF(T(J))  $  SS = SS+(P(J)/PC-1)**2
   88 CONTINUE  $  SS=100*SQRTF(SS/NP)  $  IF(SS.LT.SSK) 89,92
   89 SSK=SS $ EK=E $ TCK=TCRT $ TTK=TTRP $ PTK=PTRP
   90 DO 91 K=1,9
   91 G(K) = F(K)
   92 PRINT 19, PTR, SS
   93 E=EK $ TCRT=TCK $ TTRP=TTK $ PTRP=PTK  $  DO 94 K=1,9
   94 A(K) = G(K)  $  PCRT = PTRP*EXPF(A(1)+A(2)+A(3)+A(4))
   95 PTR = 1.0E6*PTRP
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C     PRINT DEVIATIONS, INCLUDING DT = -DP/(DP/DT).
  105 L = 9  $  SS = 0
  106 PRINT 2, E,TTRP,TCRT,PTR,PCRT, (A(K),K=1,6)  $  PRINT 3
  107 DO 125 J=1,NP  $  L = L+1  $  IF(L-57) 112,108
  108 L = 0  $  PRINT 4
  112 PC = PSATF(T(J))  $  DPDT = PC*DLPDT
  113 DP = P(J)-PC  $  DT = -DP/DPDT
  114 PCT = 100*DP/PC  $  SS = SS + PCT**2
  117 IF(PC-0.01) 120,118,118
  118 IF(PC-0.1) 121,119,119
  119 IF(PC-1.0) 122,123,123
  120 PRINT 5, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GOTO 125
  121 PRINT 6, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GOTO 125
  122 PRINT 7, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GOTO 125
  123 PRINT 8, ID(J),TX(J),T(J),P(J),PC,DT,PCT
  125 CONTINUE
  126 SS = SQRTF(SS/NP)  $  PRINT 9, NP,SS
C
C     PRINT OTHER DATA DEVIATIONS.
  140 K = NP+1  $  SS = N = 0  $  PRINT 4
  141 DO 157 J=K,NPP  $  IF(J-NPP) 143,142
  142 SS = SQRTF(SS/N)  $  PRINT 9, N,SS  $  GO TO 158
  143 N = N+1  $  PC=PSATF(T(J))  $  DPDT = PC*DLPDT
  144 DP = P(J)-PC  $  DT = -DP/DPDT
  145 PCT = 100*DP/PC  $  SS = SS + PCT**2
  146 IF(PC-0.01) 150,147,147
  147 IF(PC-0.1) 151,148,148
  148 IF(PC-1.0) 152,153,153
  150 PRINT 5, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GO TO 155
  151 PRINT 6, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GO TO 155
  152 PRINT 7, ID(J),TX(J),T(J),P(J),PC,DT,PCT  $  GO TO 155
  153 PRINT 8, ID(J),TX(J),T(J),P(J),PC,DT,PCT
  155 IF(ID(J+1)-ID(J)) 156,157
  156 SS = SQRTF(SS/N)  $  PRINT 9, N,SS  $  SS=N=0  $  PRINT 4
  157 CONTINUE
  158 CONTINUE
C
C     PRINTOUT UNIFORM TABLE FOR PUBLICATION.
  200 PRINT 11  $  DO 220 J=1,46  $  IF(J-1) 202,201
  201 TT = TTRP  $  GO TO 205
  202 IF(J-46) 204,203
  203 TT = TCRT  $  GO TO 205
  204 TT = 80 + 5*J
  205 PS=PSATF(TT) $ DPDT=PS*DLPDT $ D2PDT2=PS*(DLPDT**2 + D2LPDT2)
  207 IF(PS-0.01) 210,208,208
  208 IF(PS-0.1) 211,209,209
  209 IF(PS-1.0) 212,213,213
  210 PRINT 12, TT,PS,DPDT,D2PDT2  $  GOTO 220
  211 PRINT 13, TT,PS,DPDT,D2PDT2  $  GOTO 220
  212 PRINT 14, TT,PS,DPDT,D2PDT2  $  GOTO 220
  213 IF(J-46) 215,214
  214 D2PDT2 = 0
  215 PRINT 15, TT,PS,DPDT,D2PDT2
  220 CONTINUE
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       PSATFIT                                                      07/23/73

C    PRINT UNIFORM REDUCED TABLE.
C    Y = LN(P/PTRP)/YN.    YN = LN(PCRT/PTRP).
C    YC = (A(1)*X + . . . + A(5)*X*(1-X)**E)/YN.
  250 XN = 1-TTRP/TCRT  $  YN = A(1) + A(2) + A(3) + A(4)
  251 PRINT 16  $  DO 270 J=1,51  $  X = 0.02*(J-1)
  252 IF(J-1) 254,253
  253 TT = TTRP  $  GOTO 257
  254 IF(J-51) 256,255
  255 TT = TCRT  $  GOTO 257
  256 TT = TTRP/(1-X*XN)
  257 IF(J-51) 259,258
  258 Z = 0  $  GO TO 260
  259 Z = X*(1-X)**E
  260 YC = A(5)*Z  $  DO 261 K=1,4
  261 YC = YC + A(K)*X**K
  262 YC = YC/YN  $  YX = YC - X
  270 PRINT 17, TT, X, YC, YX
  999 CONTINUE   $   STOP   $   END

SINGLE-BANK COMPILATION.
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```
       FUNCTION PSATF(T)
C    LN(P/PTRP) = A1*X + A2*X2 + A3*X3 + A4*X4 + A5*X*(1-X)**E.
C    ARGUMENT,  X = (1-TT/T)/(1-TT/TC).
C    YIELDS ALSO DLPDT = (DP/DT)/P,  AND D2LPT = (D2P/DT2)/P.
       COMMON TTRP,TCRT,PTRP, E,A(9), FZ,F1,F2, DLPDT,D2LPDT2
     1 FORMAT(1H0 9X *PSATF = 0, T EXCEEDS TCRT. * / )
     2 XN=1-TTRP/TCRT $ X=(1-TTRP/T)/XN $ X2=X**2 $ X3=X**3 $ X4=X**4
     3 DXDT = TTRP/XN/T**2  $  D2XDT2 = -2*DXDT/T
     4 Q = 1-X   $   IF(Q) 5,6,7
     5 PSATF = DLPDT = D2LPDT2 = 0  $  PRINT 1  $  RETURN
     6 Z = Z1 = Z2 = 0  $  GOTO 9
     7 W = Q**E  $  W1 = -E*W/Q  $  W2 = (1-E)*W1/Q
     8 Z = X*W  $  Z1 = X*W1 + W  $  Z2 = X*W2 + 2*W1
     9 FZ = A(1)*X + A(2)*X2 + A(3)*X3 + A(4)*X4 + A(5)*Z
    10 PSATF = PTRP*EXPF(FZ)
    11 F1 = A(1) + 2*A(2)*X + 3*A(3)*X2 + 4*A(4)*X3 + A(5)*Z1
    12 DLPDT = F1*DXDT
    13 F2 = 2*A(2) + 6*A(3)*X + 12*A(4)*X2 + A(5)*Z2
    15 D2LPDT2 = F1*D2XDT2 + F2*DXDT**2   $   RETURN  $  END
```

SUBJECT The Vapor Pressures of Ethane

NAME R. D. Goodwin

DATE July 9, 1973

```
      FUNCTION T68(X,YMAT,XMAT)
      THIS PROGRAM HAS BEEN CHANGED SO THAT THE OSCILLATING NATURE OF
      THE MATRIX TO BE INTERPOLATED EXISTS ONLY AT THE UPPER END OF THE
      TABLE
      THIS ROUTINE WILL TAKE INPUT MATRICES OF UP TO 999 ELEMENTS EACH,
      ARRANGED SO THAT THE X MATRIX(XMAT) IS IN EITHER ASCENDING OR
      DESCENDING ORDER,SELECT NMAX OF THESE POINTS,CHOSEN SO THAT
      SUCESSIVE X VALUES OSCILATE ABOUT THE VALUE OF THE ARGUMENT X
      UNLESS THE ENDS OF THE XMATRIX INTERFERE (IN THIS CASE THE
      OSCILATORY NATURE IS LOST BUT THE PROGRAM WILL STILL PERFORM AN
      INTERPOLATION), INTERPOLATE ON THESE NMAX PAIRS OF DATA BY
      AN OSCILATING VARIABLE POINT AITKEN INTERPOLATION ALGORITHM
      EITHER UNTIL THE PERCENTAGE CHANGE IN THE INTERPOLANT IS LESS
      THAN THE ACRCY ARGUMENT(THE ARGUMENT NESSY INDICATES THE
      NUMBER OF THE POINT JUST BEFORE THE LAST ONE CHECKED) OR UNTIL
      THE NMAX POINTS ARE ALL USED.  IT IS SUGGESTED THAT NMAX
      BE LESS THAN 10, AND OF COURSE LESS THAN NELMTS.  NELMTS
      INDICATES THE NUMBER OF ELEMENTS IN XMAT OR YMAT.
      IF NESSY IS ZERO IT INDICATES THAT THE INTERPOLATION REQUIREMENT
      HAS NOT BEEN SATISFIED.  IF NESSY IS 1 IT MEANS THAT THE VALUE OF
      X LIES OUT SIDE THE RANGE OF XMAT.
      DIMENSION YMAT(999), XMAT(999),A(21,20)
  100 FORMAT(42HINTERPOLATION REQUIREMENT NOT SATISFIED(X=,E16.8,1H)/33H
     1LAST 2 APPROXIMATIONS OF Y ARE(Y=,E16.8,1H,,E16.8,1H))
  200 FORMAT(55HTHIS REPRESENTS AN EXTRAPOLATION OF THE  XMAT MATRIX(X=,
     1E16.8,1H)/33HNO CALCULATION HAS BEEN PERFORMED)
  300 FORMAT(24HNELMTS IS LESS THAN NMAX)
  400 FORMAT(22HNMAX IS LARGER THAN 20)
      NELMTS=130 $ NMAX=9 $ ACRCY=0.01
      IF(NMAX-20)71,71,69
   69 WRITE OUTPUT TAPE 6,400
      T68 = X   $  RETURN
   71 IF(NMAX-NELMTS)75,75,73
   73 WRITE OUTPUT TAPE 6,300
      T68 = X   $  RETURN
   75 CONTINUE
      FIRST TWO SUCCESSIVE VALUES OF THE XMATRIX THAT STRADDLE THE
      VALUE X WILL BE SOUGHT
      JJ1=NELMTS-1
      DO 20 I=1,JJ1
      DIF1=X-XMAT(I)
      DIF2=XMAT(I+1)-X
      IF(DIF1)16,15,16
   15 T68 = X  + YMAT(I)
      NESSY =NMAX
      RETURN
   16 IF(DIF2)18,17,18
   17 T68 = X  + YMAT(I+1)
      NESSY =NMAX
      RETURN
   18 RATIO=DIF1/ DIF2
      IF(RATIO)20,20,19
   19 IMID=I
      GO TO 32
   20 CONTINUE
```

```
     AT THIS POINT ONE COULD PRINT THE FOLLOWING STATEMENT
     WRITE OUTPUT TAPE 6,200,X
     NESSY=1
     T68 = X   $  RETURN
  32 CONTINUE
     NOTE THAT RATIO IS POSITIVE IF THE TWO POINTS STRADDLE X
     REGARDLESS WHICH IS LARGER
     JJJ=IMID
     JUP=IMID
     JDN=IMID
     IF(JJJ+NMAX-NELMTS+1)98,98,102
  98 DO 201 J=1,NMAX
     JJJ=IMID+J-1
     A(1,J)=XMAT(JJJ)
 201 A(2,J)=YMAT(JJJ)
     GO TO 203
 102 DO 41 J=1,NMAX
     JJ=J/2
     JOE=J-2*JJ
     JOE IS 0 IF J IS EVEN AND 1 IF J IS ODD
     IF(J-1)33,40,33
  33 IF(JDN-1)34,36,34
  34 IF(JUP-NELMTS)35,37,35
  35 IF(JOE)37,36,37
  36 JUP=JUP+1
     JJJ=JUP
     GO TO 40
  37 JDN=JDN-1
     JJJ=JDN
     GO TO 40
  40 A(1,J)=XMAT(JJJ)
     A(2,J)=YMAT(JJJ)
  41 CONTINUE
 203 NNN=NMAX+1
     DO 6 J=3,NNN
     L=J-1
     DO 5 K=L,NMAX
     J IS THE COLUMN NUMBER
     K IS THE ROW NUMBER
    0A(J,K)=(A(J-1,K)-A(J-1,J-2))*(X-A(1,J-2))/(A(1,K)-A(1,J-2))
    1     +A(J-1,J-2)
     IF(K-L)3,2,3
   2 IF(ABSF((A(J,L)-A(J-1,L-1))/A(J,L))-ACRCY/100.0)7,7,3
   3 CONTINUE
   5 CONTINUE
   6 CONTINUE
     NESSY=0
     AT THIS POINT ONE COULD PRINT OUT THE FOLLOWING STATEMENT.
     WRITE OUTPUT TAPE 6,100,X,A(NNN,NMAX),A(NNN-1,NMAX-1)
     T68 = X + A(NNN,NMAX)
     RETURN
   7 NESSY=J-1
     T68 = X + A(J,L)    $   RETURN   $  END
```

This program by
Rolf Prydz.

Cryogenics Division – NBS Institute for Basic Standards
LABORATORY NOTE

PROJECT NO. 2750364
FILE NO. 73-3
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SUBJECT The Vapor Pressures of Ethane

NAME R. D. Goodwin

DATE July 9, 1973

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ETHANE VAPOR PRESSURES, E = 1.50
TTRP = 89.899,   TCRT = 305.330

PTRP,MUATM = 9.96700, PCRT, ATM = 48.07723

  10.806922651        8.344715938       -3.119603823
  -0.642995191        6.059966098        0.000000000

  ID     T,XPTL      T-68        P,ATM        CALCD       DEL T       P,PCT
   7     90.000     90.010    0.0000103    0.0000103     0.000       -0.01
   7    100.000    100.010    0.0001098    0.0001098    -0.001        0.01
   7    110.000    109.998    0.0007364    0.0007363    -0.001        0.02
   7    120.000    119.989    0.0034934    0.0034939     0.001       -0.01
   7    130.000    129.987     0.012728     0.012732     0.003       -0.04
   7    140.000    139.992     0.037792     0.037803     0.003       -0.03
   7    150.000    150.000     0.095474     0.095476     0.000       -0.00
   7    160.000    160.010      0.21196      0.21192    -0.003        0.02
   7    170.000    170.019      0.42387      0.42369    -0.007        0.04
   7    180.000    180.027      0.77824      0.77783    -0.009        0.05
   7    184.520    184.550      1.00000      0.99944    -0.010        0.06
   9    198.181    198.216       1.9737       1.9761     0.027       -0.12
   4    214.302    214.334       3.9209       3.9159    -0.032        0.13
   4    224.102    224.130       5.6367       5.6402     0.017       -0.06
   4    229.756    229.782       6.8569       6.8598     0.012       -0.04
   4    234.558    234.581       8.0335       8.0392     0.022       -0.07
   9    234.692    234.715       8.0741       8.0741    -0.000        0.00
  10    238.150    238.150       9.0097       9.0077    -0.007        0.02
   9    238.771    238.792       9.1843       9.1905     0.021       -0.07
   4    239.844    239.864       9.4959       9.5019     0.020       -0.06
   4    240.514    240.534       9.6960       9.7003     0.014       -0.04
  10    243.150    243.150      10.5063      10.5045    -0.006        0.02
   4    243.359    243.377      10.5760      10.5764     0.001       -0.00
   4    246.814    246.830      11.7137      11.7162     0.007       -0.02
   4    247.816    247.831      12.0502      12.0628     0.036       -0.10
  10    248.150    248.150      12.1756      12.1747    -0.003        0.01
   4    249.741    249.755      12.7620      12.7496    -0.034        0.10
   4    250.146    250.160      12.8985      12.8976    -0.002        0.01
   4    251.587    251.600      13.4425      13.4344    -0.022        0.06
   4    252.544    252.556      13.8065      13.7997    -0.018        0.05
  10    253.150    253.150      14.0310      14.0301    -0.002        0.01
   4    254.290    254.301      14.4898      14.4848    -0.012        0.03
   4    257.543    257.552      15.8252      15.8266     0.003       -0.01
  10    258.150    258.150      16.0835      16.0827    -0.002        0.00
  10    263.150    263.150      18.3464      18.3452    -0.003        0.01
   4    263.380    263.386      18.4543      18.4573     0.006       -0.02
   4    267.536    267.539      20.5197      20.5145    -0.010        0.03
  10    268.150    268.150      20.8318      20.8308    -0.002        0.00
   4    271.749    271.750      22.7661      22.7662     0.000       -0.00
   9    272.949    272.949      23.4515      23.4394    -0.021        0.05
  10    273.150    273.150      23.5549      23.5536    -0.002        0.01
   4    275.922    275.921      25.1584      25.1702     0.020       -0.05
   4    276.363    276.362      25.4558      25.4347    -0.035        0.08
   4    276.385    276.384      25.4491      25.4479    -0.002        0.00
   4    276.514    276.513      25.5472      25.5257    -0.036        0.08
   4    277.813    277.811      26.3185      26.3189     0.001       -0.00
  10    278.150    278.150      26.5309      26.5290    -0.003        0.01
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SUBJECT The Vapor Pressure of Ethane

NAME R. D. Goodwin

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```
 IO    T,XPTL      T-68        P,ATM        CALCD       DEL T      P,PCT
  4   280.041    280.038     27.7039      27.7217      0.028      -0.06
  4   282.247    282.243     29.1537      29.1647      0.016      -0.04
 10   283.150    283.150     29.7763      29.7739     -0.003       0.01
  4   284.635    284.630     30.7664      30.7893      0.033      -0.07
  9   284.845    284.840     30.9555      30.9353     -0.029       0.07
  4   287.653    287.648     32.9289      32.9392      0.014      -0.03
 10   288.150    288.150     33.3110      33.3080     -0.004       0.01
  4   288.263    288.257     33.3899      33.3872     -0.004       0.01
  4   290.040    290.034     34.6873      34.7192      0.042      -0.09
  9   290.214    290.208     34.8748      34.8518     -0.030       0.07
  4   292.236    292.229     36.4440      36.4216     -0.028       0.06
  4   293.098    293.091     37.0816      37.1074      0.032      -0.07
 10   293.150    293.150     37.1583      37.1547     -0.005       0.01
  9   293.266    293.259     37.2672      37.2422     -0.031       0.07
  4   296.347    296.339     39.7598      39.7852      0.030      -0.06
 10   298.150    298.150     41.3494      41.3446     -0.005       0.01
  4   299.665    299.657     42.6543      42.6808      0.030      -0.06
  9   299.863    299.855     42.8863      42.8591     -0.030       0.06
  4   300.205    300.196     43.1650      43.1686      0.004      -0.01
  4   301.251    301.242     44.1085      44.1274      0.020      -0.04
 10   302.150    302.150     44.9809      44.9751     -0.006       0.01
 10   303.150    303.150     45.9327      45.9268     -0.006       0.01
  4   303.471    303.462     46.2032      46.2273      0.025      -0.05
  4   303.477    303.468     46.2798      46.2331     -0.048       0.10
  9   304.012    304.002     46.7736      46.7533     -0.021       0.04
  4   304.049    304.039     46.7698      46.7896      0.020      -0.04
 10   304.150    304.150     46.9040      46.8987     -0.005       0.01
  4   304.360    304.350     47.0931      47.0953      0.002      -0.00
  4   304.446    304.435     47.2198      47.1802     -0.040       0.08
  4   304.519    304.508     47.2025      47.2525      0.050      -0.11
  4   304.734    304.723     47.4310      47.4661      0.035      -0.07
  4   304.796    304.785     47.5185      47.5280      0.009      -0.02
  4   304.924    304.913     47.6846      47.6560     -0.028       0.06
  4   304.980    304.969     47.7131      47.7122     -0.001       0.00
  4   305.121    305.110     47.8496      47.8541      0.004      -0.01
 10   305.150    305.150     47.8992      47.8945     -0.005       0.01
  4   305.153    305.142     47.8807      47.8864      0.006      -0.01
 10   305.250    305.250     47.9994      47.9958     -0.004       0.01

 NP =   85, RMSPCT =   0.050
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LABORATORY NOTE

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SUBJECT: The Vapor Pressures of Ethane

NAME: R. D. Goodwin

DATE: July 9, 1973

ETHANE VAPOR PRESSURES

T,K	P,ATM	DP/DT	D2P/DT2
89.899	0.0000100	0.0000027	0.00000064
90.000	0.0000102	0.0000027	0.00000066
95.000	0.0000358	0.0000085	0.00000181
100.000	0.0001095	0.0000232	0.00000439
105.000	0.0002985	0.0000567	0.00000960
110.000	0.0007365	0.0001264	0.00001915
115.000	0.0016670	0.0002592	0.00003529
120.000	0.0034991	0.0004948	0.00006077
125.000	0.0068762	0.0008875	0.00009864
130.000	0.012752	0.001507	0.0001521
135.000	0.022468	0.002439	0.0002242
140.000	0.037834	0.003785	0.0003177
145.000	0.061192	0.005656	0.0004350
150.000	0.095478	0.008177	0.0005776
155.000	0.14426	0.01148	0.000747
160.000	0.21176	0.01569	0.000942
165.000	0.30288	0.02095	0.001165
170.000	0.42317	0.02738	0.001412
175.000	0.57882	0.03511	0.001684
180.000	0.77662	0.04426	0.001979
185.000	1.0239	0.0549	0.00229
190.000	1.3287	0.0672	0.00263
195.000	1.6991	0.0812	0.00298
200.000	2.1440	0.0970	0.00334
205.000	2.6726	0.1147	0.00372
210.000	3.2943	0.1343	0.00411
215.000	4.0188	0.1558	0.00451
220.000	4.8561	0.1794	0.00492
225.000	5.8165	0.2051	0.00534
230.000	6.9105	0.2329	0.00577
235.000	8.1487	0.2628	0.00620
240.000	9.5420	0.2949	0.00665
245.000	11.1016	0.3293	0.00711
250.000	12.8390	0.3660	0.00758
255.000	14.7659	0.4052	0.00807
260.000	16.8947	0.4468	0.00858
265.000	19.2381	0.4910	0.00913
270.000	21.8098	0.5381	0.00971
275.000	24.6242	0.5882	0.01034
280.000	27.6972	0.6416	0.01105
285.000	31.0467	0.6989	0.01187
290.000	34.6934	0.7607	0.01288
295.000	38.6630	0.8283	0.01425
300.000	42.9905	0.9046	0.01657
305.000	47.7433	1.0055	0.03283
305.330	48.0772	1.0228	0.00000

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SUBJECT The Vapor Pressures of Ethane

NAME R. D. Goodwin
DATE July 9, 1973

ETHANE REDUCED VAPOR PRESSURE FUNCTIONS

T,K	X	Y	(Y-X)
89.899	0.00	0.00000	0.00000
91.186	0.02	0.02190	0.00190
92.510	0.04	0.04376	0.00376
93.873	0.06	0.06558	0.00558
95.277	0.08	0.08734	0.00734
96.723	0.10	0.10906	0.00906
98.215	0.12	0.13073	0.01073
99.753	0.14	0.15234	0.01234
101.339	0.16	0.17389	0.01389
102.977	0.18	0.19538	0.01538
104.669	0.20	0.21680	0.01680
106.418	0.22	0.23816	0.01816
108.226	0.24	0.25945	0.01945
110.096	0.26	0.28066	0.02066
112.032	0.28	0.30180	0.02180
114.037	0.30	0.32285	0.02285
116.116	0.32	0.34382	0.02382
118.272	0.34	0.36471	0.02471
120.509	0.36	0.38551	0.02551
122.832	0.38	0.40621	0.02621
125.247	0.40	0.42682	0.02682
127.759	0.42	0.44733	0.02733
130.373	0.44	0.46774	0.02774
133.097	0.46	0.48805	0.02805
135.937	0.48	0.50825	0.02825
138.901	0.50	0.52835	0.02835
141.997	0.52	0.54833	0.02833
145.234	0.54	0.56820	0.02820
148.622	0.56	0.58796	0.02796
152.172	0.58	0.60760	0.02760
155.896	0.60	0.62713	0.02713
159.807	0.62	0.64654	0.02654
163.919	0.64	0.66583	0.02583
168.248	0.66	0.68501	0.02501
172.812	0.68	0.70406	0.02406
177.630	0.70	0.72301	0.02301
182.725	0.72	0.74184	0.02184
188.121	0.74	0.76056	0.02056
193.845	0.76	0.77917	0.01917
199.928	0.78	0.79769	0.01769
206.405	0.80	0.81611	0.01611
213.317	0.82	0.83445	0.01445
220.707	0.84	0.85272	0.01272
228.627	0.86	0.87093	0.01093
237.138	0.88	0.88910	0.00910
246.306	0.90	0.90726	0.00726
256.212	0.92	0.92544	0.00544
266.948	0.94	0.94369	0.00369
278.623	0.96	0.96208	0.00208
291.366	0.98	0.98074	0.00074
305.330	1.00	1.00000	0.00000

APPENDIX K

Cryogenics Division – NBS Institute for Basic Standards
LABORATORY NOTE

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SUBJECT
Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin

DATE August 14, 1973

1. Introduction

The virial equation of state for low densities is needed for thermal computations to generate P-ρ-T data, and to obtain saturated vapor densities via the vapor pressure equation.

In this report we develop analytical representations for the virial coefficients of ethane and obtain the corresponding saturated vapor densities.

In the truncated virial equation,

$$Z(T,d) \equiv P/(R\cdot T\cdot d) = 1 + B(x)\cdot\sigma + C(x)\cdot\sigma^2 + D(x)\cdot\sigma^3, \qquad (1)$$

P is pressure, R the gas constant, T the absolute temperature, d the density, and $\sigma \equiv d/d_c$ is reduced density. The second, third, and fourth coefficients B(x), C(x), D(x) are dimensionless functions of reduced temperature $x \equiv T/T_c$. We use $T_c \equiv 305.33$ K, and $V_c \equiv 1/d_c = 145.56$ cc/mol from Douslin [2]. In the tables we use symbols B^*, C^* and D^* for the coefficients of (1).

2. The Second Virial Coefficient

Data for B(x) through about 1960 are reviewed by Tester [16]. Since then we have data from Gunn [8], Hoover [9], Pope [15], McGlashan [12], and Douslin [2]. Data of Gunn and of Douslin extend from 273 K upwards to 623 K. McGlashan gives outstanding experimental work on the hydrocarbon series (but not on ethane) down to $T/T_c = 0.5$. From his formulations he concludes that the low-temperature data of Eucken and Parts [4] are wrong. This suspicion also was expressed by Ziegler et al. [17].

For least squares we have selected for low temperatures only the data from McGlashan's formula because all other data diverge widely therefrom (Table 2). For high temperatures we have selected Douslin's recent data because the experimental work [2] was executed with great care. Table 2 shows that Michels (1D=3) and Gunn (1D=8) are in substantial agreement with Douslin. For consistency with Douslin, we have increased the absolute values of McGlashan's data by one percent, well within the uncertainty of his $V_c = 148$ cc/mol.

Our formula for B(x), selected from many variations, finally is similar to that developed for methane [6],

$$B(x) = \left[B_1 + B_2/x^{1/4} + B_3/x + B_4/x^2 + B_5/x^3\right] \cdot \left[1-(T_o/T)^{1/4}\right], \qquad (2)$$

T_o = 740.0 K,
B_1 = 7.99 3156,
B_2 = -10.67 2497,
B_3 = 9.21 7322,
B_4 = -2.48 1668,
B_5 = 0.84 2328.

Table 1 gives results for (2) with the data used for least squares: (6) McGlashan; (10) Douslin. Data not used for ℓ.s. are compared with (2) in Table 2: (1) Eucken; (2) Lambert; (3) Michels: (4) Hoover; (5) Pope; (8) Gunn.

3. The Third Virial Coefficient

For C(x) relatively few data are known to us. The data of Michels [13] and Hoover [9] were generalized in 1967 by Chueh [1], using a formula similar to that developed by Goodwin [5]. In 1971 Pope [15] gave five low-temperature values from 210 to 306 K. For temperatures above 273 K we are fortunate to have the recent, carefully-derived data of Douslin [2].

A comparison of Chueh's generalized function with Douslin's data at $T/T_c = 2$ shows $C^* = 0.20$ (Chueh), and $C^* = 0.15$ (Douslin). Whereas the Chueh formula gives nearly constant values at high temperatures, the Douslin data are trending asymptotically toward zero.

For least squares we have selected the data of Douslin at high temperatures, and data generated by Chueh's formula at low temperatures. For consistency we have diminished these latter values by two percent. (Chueh fails to give his critical densities.) At low temperatures the third virial coefficient is not important in the computation of eq (1) because the maximum possible density (saturated vapor) is diminishing exponentially with temperature, $e^{-\alpha/T}$, (see Table 4).

Our formula for C(x) is much simpler than that of Chueh, and is similar to that developed for methane [6],

$$C(x) = \left[C_1/x + C_2/x^3 + C_3/x^5\right]\cdot\left(1-T_o/T\right), \tag{3}$$

T_o = 217.80 K, C_2 = 0.865 299,

C_1 = 0.253 773, C_3 = 0.556 075.

Least squares results are in the upper part of Table 3: (7) Chueh; (10) Douslin. Other data in the lower part are: (4) Hoover; (5) Pope.

4. The Fourth Virial Coefficient

Recent data of Douslin [2] are plotted in Figure 1. The general behavior expected for D^* is shown in the book by Mason and Spurling [11]. As present data exist only at $T > T_c$, we use the simple formula,

$$100\cdot D^* = x^{-1/4}\cdot\exp\left[a-b/(x-1)\right], \tag{4}$$

where $x \equiv T/T_c$, and a = 4.00, b = 1.84 from Figure 1.

5. Examination of the Virial Equation

It is valuable to know the relative importance of the terms of eq (1). In Table 4 we compute these for the saturated vapor, using densities from the formula of Plank and Kambeitz quoted by Tester [16]. We have increased the P.K. densities by 0.088% to agree with the virial equation at 90 K. Pressures are from our vapor pressure equation [7].

In the fourth column of Table 4 we give the ratio DI/DN of ideal gas density to the P.K calculated densities. Fifth and sixth columns give $B(x)\cdot\sigma$ and $C(x)\cdot\sigma^2$. If all data were accurate, we should expect Z(T, d) in the last column to be the same as DI/DN.

The vapor pressures of Ziegler [17] were based on second virial coefficients of Eucken and Parts [4], the accuracy of which Ziegler questioned. Our selection for B^* also disagrees with Eucken and Parts. We therefore have recomputed our vapor

SUBJECT Ethane Virial Coefficients and Saturated Vapor Densities

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pressure constants using alternate vapor pressure data of Ziegler, as shown in the addendum to our Laboratory Note [7]. This revised vapor pressure equation is used in the following to obtain the densities of saturated vapor.

6. Derivation of the Saturated Vapor Densities

For a given temperature we iterate density in the virial equation to obtain a pressure therefrom which is the same as the vapor pressure. Results are in Table 5. In previous work we have found that this method gives acceptable results at densities up to about $\rho_c/3$, which for ethane occurs near T = 286 K. We see that data from the Plank-Kambeitz formula diverge increasingly from our results on approach to T_c. The highest temperature at which our results are accurate remains to be seen by comparison with data from other sources. Figure 2 shows,however, that in the region of overlap with Douslin's vapor densities [2], our results (the filled circles) appear reasonable.

Figure 3 shows the results at lower temperatures. We see that powers of (1/T) greater than the first will be needed to describe these data.

7. Discussion of Uncertainties

Experimental uncertainties for virial coefficients vary inversely as the significance of these coefficients in giving departure from ideal gas behavior, see Table 4. For the second coefficient only, for example,

$$\delta B/B = \frac{\delta Z}{Z} \cdot \frac{Z}{Z-1} ,$$

where δB and δZ are small variations in B and Z. Assume a tolerable error of 0.01 percent in Z. From Table 4 we compute the approximate tolerable uncertainty in B, neglecting the effect of C(T),

T, K	mol/ℓ	δB/B, %
100	0.000013	357.0
120	0.000349	21.6
140	0.00327	3.37
160	0.01626	0.915
180	0.05434	0.352
200	0.1401	0.170
220	0.3035	0.096
240	0.5864	0.060
260	1.057	0.040

Not all authors give estimates of uncertainty for experimental virial coefficients. Hoover et al, however, give these estimates for ethane,

T, K	δB/B, %	δC/C, %
215	1.0	10.0
240	0.4	4.0
273	0.1	1.0

and we believe these to be reasonable estimates for very careful work. In Table 2, however, we see that Hoover's data, ID=4, differ from our selection by up to five percent at low temperatures (215 and 240 K).

Our derived densities depend on the vapor pressure equation. This we estimate to be uncertain by several percent at the lowest temperatures approaching the triple point. The virial equation, on the other hand, approaches ideal gas behavior at these low temperatures. At the higher temperatures above 270 K, we believe the virial coefficients and vapor pressures of Douslin to be accurate as can be derived from the best of PVT measurements.

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Table Captions

Table 1. Second virial data of (6) McGlashan, (10) Douslin.

Table 2. Second virial, (1) Eucken, (2) Lambert, (3) Michels, (4) Hoover, (5) Pope, (8) Gunn.

Table 3. Third virial, (7) Chueh, (10) Douslin, (4) Hoover, (5) Pope.

Table 4. Terms of the virial equation for saturated vapor.

Table 5. Saturated vapor densities derived via V.P. and virial equations.

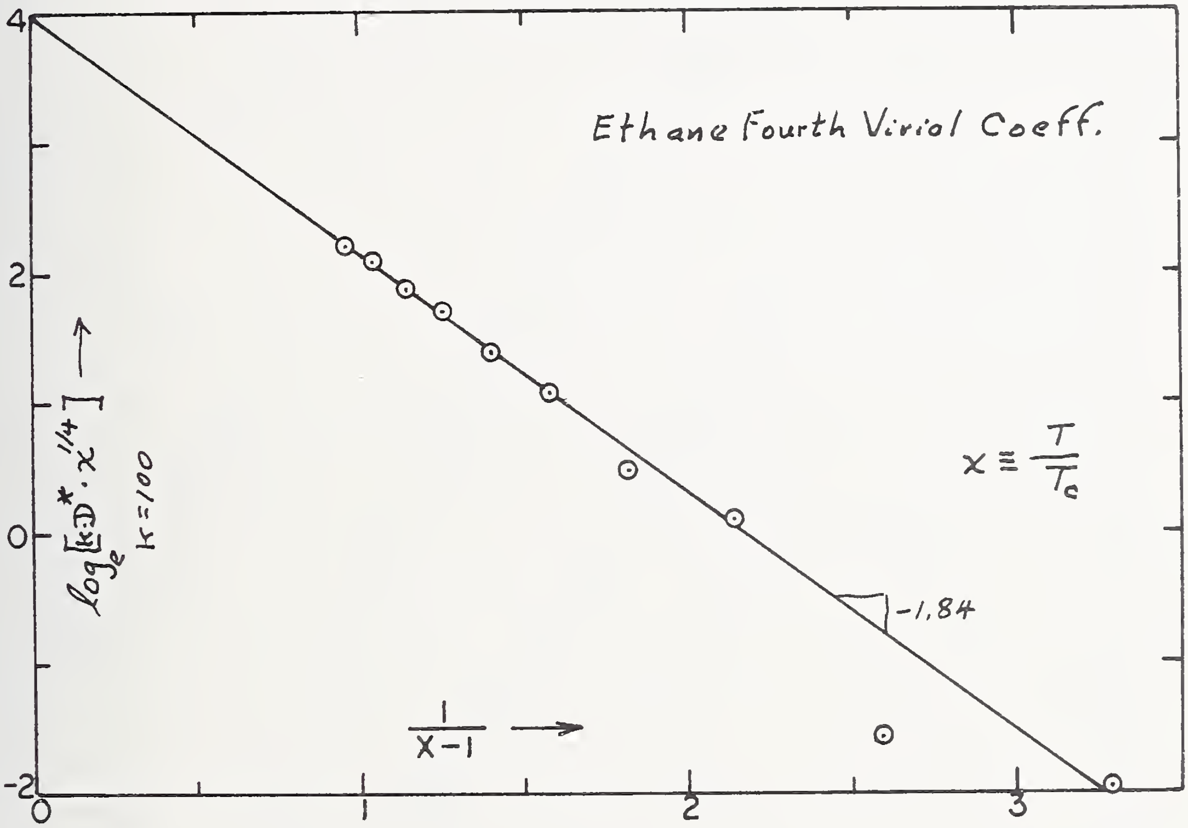

Figure 1. Ethane fourth virial coefficients of Douslin [2],

$$100\cdot D^* = x^{-1/4}\cdot\exp[4.0 - 1.84/(x-1)].$$

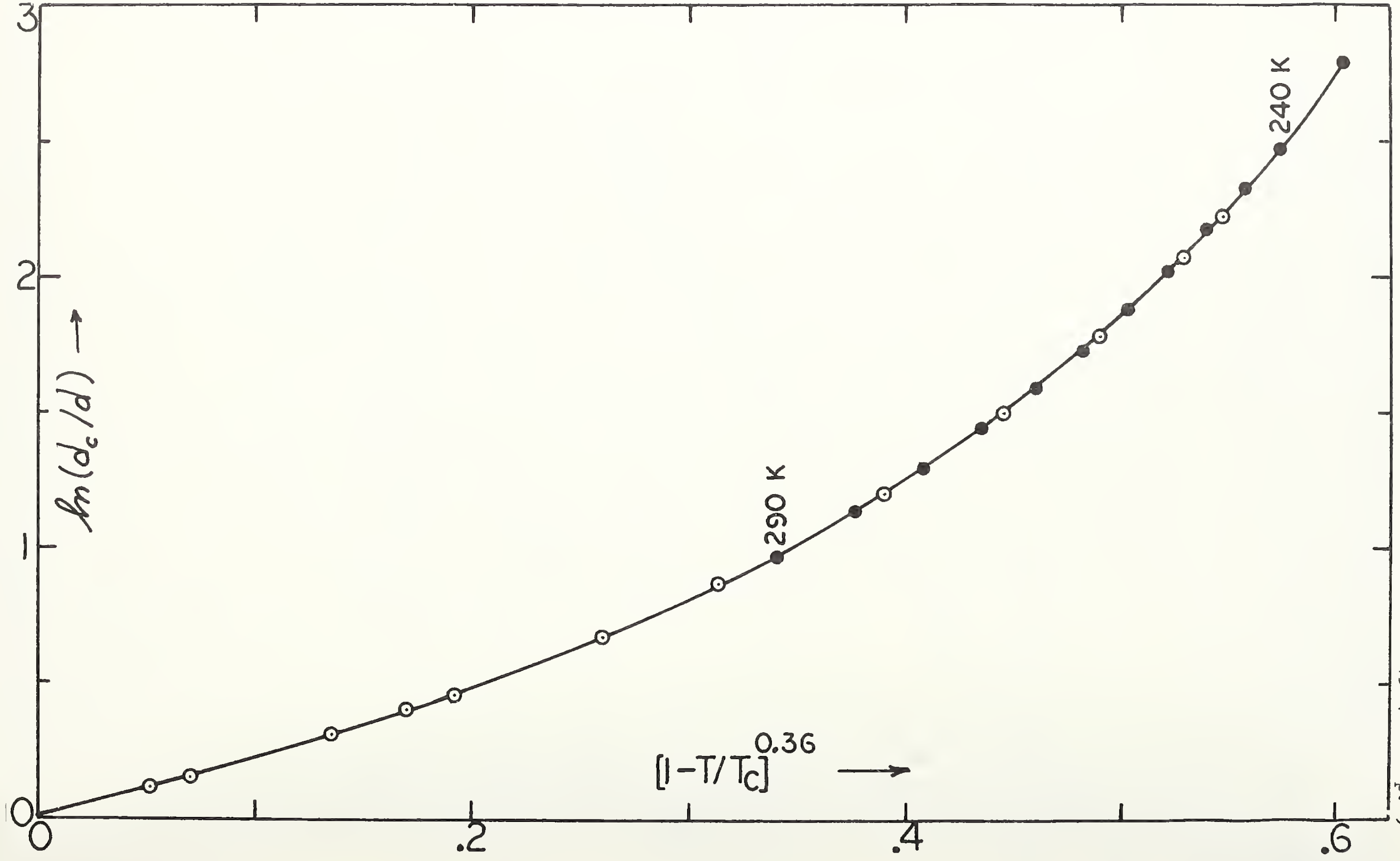

Figure 2. Ethane saturated vapor densities. Open circles from Douslin [2]; filled circles from Table 5, this report.

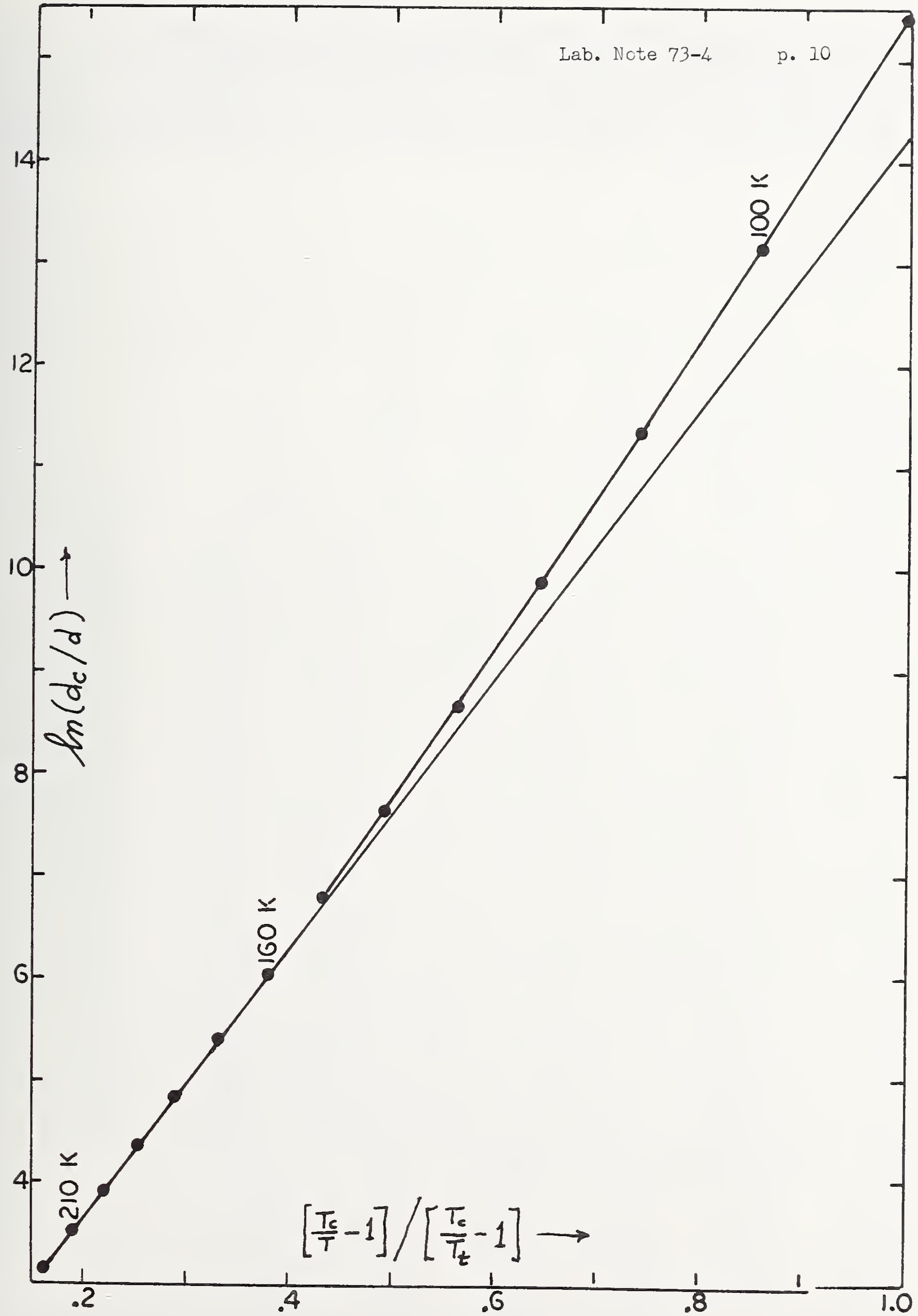

Figure 3. Ethane saturated vapor densities from Table 5, this report.

SUBJECT Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin

DATE August 14, 1973

Table 1. Second virial data of (6) McGlashan, (10) Douslin.

```
ETHANE SECOND VIRIAL COEFFICIENT

EB = 0.250, TZ = 740.0

 7.993156  -10.672497    9.217322   -2.481668     0.842328

ID        T,K       T/TC        B*       CALC       DIFF       PCNT
 6    150.000     0.4913    -5.309    -5.310      0.001       0.01
 6    160.000     0.5240    -4.598    -4.597     -0.001      -0.01
 6    170.000     0.5568    -4.031    -4.030     -0.001      -0.02
 6    180.000     0.5895    -3.569    -3.569     -0.000      -0.01
 6    190.000     0.6223    -3.188    -3.188      0.000       0.01
 6    200.000     0.6550    -2.868    -2.869      0.001       0.02
 6    210.000     0.6878    -2.597    -2.597      0.001       0.03
 6    220.000     0.7205    -2.353    -2.364      0.001       0.03
 6    230.000     0.7533    -2.161    -2.162      0.000       0.02
 6    240.000     0.7860    -1.984    -1.984     -0.000      -0.00
 6    250.000     0.8188    -1.828    -1.828     -0.001      -0.04
 6    260.000     0.8515    -1.690    -1.688     -0.002      -0.09
10    273.150     0.8946    -1.527    -1.527      0.001       0.06
10    298.150     0.9765    -1.276    -1.275     -0.001      -0.08
10    303.150     0.9929    -1.232    -1.232     -0.001      -0.05
10    323.150     1.0584    -1.077    -1.076     -0.001      -0.06
10    348.150     1.1402    -0.914    -0.914      0.001       0.08
10    373.150     1.2221    -0.780    -0.781      0.001       0.10
10    398.150     1.3040    -0.668    -0.670      0.001       0.16
10    423.150     1.3859    -0.574    -0.575      0.000       0.06
10    448.150     1.4678    -0.493    -0.493      0.000       0.10
10    473.150     1.5496    -0.423    -0.422     -0.000      -0.08
10    498.150     1.6315    -0.360    -0.360     -0.000      -0.01
10    523.150     1.7134    -0.306    -0.305     -0.001      -0.27
10    548.150     1.7953    -0.256    -0.256     -0.000      -0.19
10    573.150     1.8771    -0.212    -0.212     -0.001      -0.30
10    598.150     1.9590    -0.172    -0.172     -0.000      -0.02
10    623.150     2.0409    -0.135    -0.135      0.001       0.53
NP = 28, MEANPCT = 0.088
```

Table 2. Second Virial, (1) Eucken, (2) Lambert, (3) Michels, (4) Hoover (5) Pope, (8) Gunn.

ID	T,K	T/TC	B*	CALC	DIFF	PCNT
1	200.000	0.6550	-3.112	-2.869	-0.243	-8.48
2	200.000	0.6550	-3.119	-2.869	-0.250	-8.72
5	209.534	0.6863	-2.533	-2.609	0.076	2.93
1	210.000	0.6878	-2.817	-2.597	-0.219	-8.44
2	210.000	0.6878	-2.817	-2.597	-0.219	-8.44
4	215.000	0.7042	-2.340	-2.477	0.137	5.52
1	220.000	0.7205	-2.542	-2.364	-0.178	-7.52
2	220.000	0.7205	-2.576	-2.364	-0.212	-8.97
1	230.000	0.7533	-2.288	-2.162	-0.126	-5.84
2	230.000	0.7533	-2.343	-2.162	-0.181	-8.38
5	238.769	0.7820	-1.972	-2.005	0.033	1.63
1	240.000	0.7860	-2.095	-1.984	-0.111	-5.61
2	240.000	0.7860	-2.116	-1.984	-0.132	-6.65
4	240.000	0.7860	-1.900	-1.984	0.085	4.26
1	250.000	0.8188	-1.924	-1.828	-0.096	-5.26
2	250.000	0.8188	-1.944	-1.828	-0.117	-6.39
5	254.807	0.8345	-1.733	-1.759	0.026	1.45
1	260.000	0.8515	-1.759	-1.688	-0.070	-4.17
2	260.000	0.8515	-1.786	-1.688	-0.098	-5.80
1	270.000	0.8843	-1.614	-1.564	-0.051	-3.23
2	270.000	0.8843	-1.649	-1.564	-0.085	-5.43
3	273.150	0.8946	-1.521	-1.527	0.006	0.39
4	273.150	0.8946	-1.535	-1.527	-0.007	-0.48
5	273.150	0.8946	-1.507	-1.527	0.020	1.33
8	273.200	0.8948	-1.527	-1.527	0.000	0.02
1	280.000	0.9170	-1.470	-1.452	-0.018	-1.25
2	280.000	0.9170	-1.511	-1.452	-0.059	-4.09
2	290.000	0.9498	-1.408	-1.351	-0.058	-4.26
3	298.138	0.9764	-1.275	-1.275	0.000	0.03
8	298.200	0.9766	-1.284	-1.275	-0.009	-0.71
2	300.000	0.9825	-1.305	-1.259	-0.046	-3.68
5	306.062	1.0024	-1.204	-1.207	0.003	0.27
3	322.748	1.0570	-1.078	-1.079	0.001	0.07
8	323.200	1.0585	-1.032	-1.076	-0.006	-0.60
3	347.652	1.1386	-0.916	-0.917	0.002	0.19
3	372.522	1.2201	-0.784	-0.784	0.001	0.09
8	377.600	1.2367	-0.752	-0.760	0.008	1.10
3	397.844	1.3030	-0.671	-0.671	-0.001	-0.08
8	410.900	1.3458	-0.616	-0.619	0.004	0.61
3	422.700	1.3844	-0.576	-0.576	-0.000	-0.04
8	444.300	1.4551	-0.508	-0.505	-0.003	-0.69
8	477.600	1.5642	-0.423	-0.411	-0.013	-3.09
8	510.900	1.6733	-0.350	-0.331	-0.019	-5.83

Table 1. Second virial data of (6) McGlashan, (10) Douslin.

```
ETHANE SECOND VIRIAL COEFFICIENT

EB = 0.250, TZ = 740.0

 7.993156  -10.672497    9.217322   -2.481668     0.842328

ID        T,K      T/TC        B*      CALC       DIFF      PCNT
 6    150.000    0.4913    -5.309    -5.310      0.001      0.01
 6    160.000    0.5240    -4.598    -4.597     -0.001     -0.01
 6    170.000    0.5568    -4.031    -4.030     -0.001     -0.02
 6    180.000    0.5895    -3.569    -3.569     -0.000     -0.01
 6    190.000    0.6223    -3.188    -3.188      0.000      0.01
 6    200.000    0.6550    -2.868    -2.869      0.001      0.02
 6    210.000    0.6878    -2.597    -2.597      0.001      0.03
 6    220.000    0.7205    -2.353    -2.364      0.001      0.03
 6    230.000    0.7533    -2.161    -2.162      0.000      0.02
 6    240.000    0.7860    -1.984    -1.984     -0.000     -0.00
 6    250.000    0.8188    -1.828    -1.828     -0.001     -0.04
 6    260.000    0.8515    -1.690    -1.688     -0.002     -0.09
10    273.150    0.8946    -1.527    -1.527      0.001      0.06
10    298.150    0.9765    -1.276    -1.275     -0.001     -0.08
10    303.150    0.9929    -1.232    -1.232     -0.001     -0.05
10    323.150    1.0584    -1.077    -1.076     -0.001     -0.06
10    348.150    1.1402    -0.914    -0.914      0.001      0.08
10    373.150    1.2221    -0.780    -0.781      0.001      0.10
10    398.150    1.3040    -0.668    -0.670      0.001      0.16
10    423.150    1.3859    -0.574    -0.575      0.000      0.06
10    448.150    1.4678    -0.493    -0.493      0.000      0.10
10    473.150    1.5496    -0.423    -0.422     -0.000     -0.08
10    498.150    1.6315    -0.360    -0.360     -0.000     -0.01
10    523.150    1.7134    -0.306    -0.305     -0.001     -0.27
10    548.150    1.7953    -0.256    -0.256     -0.000     -0.19
10    573.150    1.8771    -0.212    -0.212     -0.001     -0.30
10    598.150    1.9590    -0.172    -0.172     -0.000     -0.02
10    623.150    2.0409    -0.135    -0.135      0.001      0.53
NP = 28, MEANPCT = 0.088
```

SUBJECT
Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin
DATE August 14, 1973

Table 2. Second Virial, (1) Eucken, (2) Lambert, (3) Michels, (4) Hoover (5) Pope, (8) Gunn.

ID	T,K	T/TC	B*	CALC	DIFF	PCNT
1	200.000	0.6550	-3.112	-2.869	-0.243	-8.48
2	200.000	0.6550	-3.119	-2.869	-0.250	-8.72
5	209.534	0.6863	-2.533	-2.609	0.076	2.93
1	210.000	0.6878	-2.817	-2.597	-0.219	-8.44
2	210.000	0.6878	-2.817	-2.597	-0.219	-8.44
4	215.000	0.7042	-2.340	-2.477	0.137	5.52
1	220.000	0.7205	-2.542	-2.364	-0.178	-7.52
2	220.000	0.7205	-2.576	-2.364	-0.212	-8.97
1	230.000	0.7533	-2.288	-2.162	-0.126	-5.84
2	230.000	0.7533	-2.343	-2.162	-0.181	-8.38
5	238.769	0.7820	-1.972	-2.005	0.033	1.63
1	240.000	0.7860	-2.095	-1.984	-0.111	-5.61
2	240.000	0.7860	-2.116	-1.984	-0.132	-6.65
4	240.000	0.7860	-1.900	-1.984	0.085	4.26
1	250.000	0.8188	-1.924	-1.828	-0.096	-5.26
2	250.000	0.8188	-1.944	-1.828	-0.117	-6.39
5	254.807	0.8345	-1.733	-1.759	0.026	1.45
1	260.000	0.8515	-1.759	-1.688	-0.070	-4.17
2	260.000	0.8515	-1.786	-1.688	-0.098	-5.80
1	270.000	0.8843	-1.614	-1.564	-0.051	-3.23
2	270.000	0.8843	-1.649	-1.564	-0.085	-5.43
3	273.150	0.8946	-1.521	-1.527	0.006	0.39
4	273.150	0.8946	-1.535	-1.527	-0.007	-0.48
5	273.150	0.8946	-1.507	-1.527	0.020	1.33
8	273.200	0.8948	-1.527	-1.527	0.000	0.02
1	280.000	0.9170	-1.470	-1.452	-0.018	-1.25
2	280.000	0.9170	-1.511	-1.452	-0.059	-4.09
2	290.000	0.9498	-1.408	-1.351	-0.058	-4.26
3	298.138	0.9764	-1.275	-1.275	0.000	0.03
8	298.200	0.9766	-1.284	-1.275	-0.009	-0.71
2	300.000	0.9825	-1.305	-1.259	-0.046	-3.68
5	306.062	1.0024	-1.204	-1.207	0.003	0.27
3	322.748	1.0570	-1.078	-1.079	0.001	0.07
8	323.200	1.0585	-1.082	-1.076	-0.006	-0.60
3	347.652	1.1386	-0.916	-0.917	0.002	0.19
3	372.522	1.2201	-0.784	-0.784	0.001	0.09
8	377.600	1.2367	-0.752	-0.760	0.008	1.10
3	397.844	1.3030	-0.671	-0.671	-0.001	-0.08
8	410.900	1.3458	-0.616	-0.619	0.004	0.61
3	422.700	1.3844	-0.576	-0.576	-0.000	-0.04
8	444.300	1.4551	-0.508	-0.505	-0.003	-0.69
8	477.600	1.5642	-0.423	-0.411	-0.013	-3.09
8	510.900	1.6733	-0.350	-0.331	-0.019	-5.83

SUBJECT
Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin
DATE August 14, 1973

Table 3. Third virial, (7) Chueh, (10) Douslin, (4) Hoover, (5) Pope.

```
THIRD VIRIAL,

 217.800   0.253773   0.865299   0.556075   0.000000

ID        T,K      T/TCRT         C*      CALCD        DIFF
 7    210.000      0.6878     -0.251     -0.247      -0.004
 7    220.000      0.7205      0.055      0.055       0.000
 7    230.000      0.7533      0.249      0.247       0.002
 7    240.000      0.7860      0.367      0.366       0.001
 7    250.000      0.8188      0.436      0.438      -0.002
 7    260.000      0.8515      0.472      0.477      -0.006
10    273.150      0.8946      0.489      0.499      -0.010
10    298.150      0.9765      0.500      0.489       0.011
10    303.150      0.9929      0.491      0.483       0.008
10    323.150      1.0584      0.455      0.453       0.003
10    348.150      1.1402      0.409      0.410      -0.001
10    373.150      1.2221      0.364      0.369      -0.004
10    398.150      1.3040      0.328      0.332      -0.003
10    423.150      1.3859      0.295      0.299      -0.004
10    448.150      1.4678      0.268      0.271      -0.003
10    473.150      1.5496      0.250      0.247       0.002
10    498.150      1.6315      0.228      0.227       0.002
10    523.150      1.7134      0.212      0.209       0.004
10    548.150      1.7953      0.195      0.193       0.002
10    573.150      1.8771      0.182      0.180       0.002
10    598.150      1.9590      0.167      0.168      -0.001
10    623.150      2.0409      0.154      0.157      -0.003
NP = 22, MEANDIFF =    0.004



ID        T,K      T/TCRT         C*      CALCD        DIFF
 5    209.534      0.6863     -2.770     -0.264      -2.506
 4    215.000      0.7042     -3.356     -0.079      -3.277
 5    238.769      0.7820      0.175      0.354      -0.180
 4    240.000      0.7860     -0.121      0.366      -0.487
 5    254.807      0.8345      0.401      0.460      -0.059
 5    273.150      0.8946      0.489      0.499      -0.010
 4    273.150      0.8946      0.501      0.499       0.002
 4    273.150      0.8946      0.537      0.499       0.038
 4    298.138      0.9764      0.507      0.489       0.017
 5    306.062      1.0024      0.473      0.479      -0.006
 4    322.748      1.0570      0.456      0.453       0.003
 4    347.652      1.1386      0.405      0.411      -0.006
 4    372.522      1.2201      0.364      0.370      -0.006
 4    397.844      1.3030      0.330      0.332      -0.002
 4    422.700      1.3844      0.301      0.300       0.001
```

SUBJECT
Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin
DATE August 14, 1973

Table 4. Terms of the virial equation for saturated vapor.

TERMS OF THE VIRIAL EQUATION FOR SATURATED VAPOR

T,K	P,ATM	MOL/L	DI/DN	B*S	C*S2	Z(T,D)
90	0.0000099	0.0000013	0.999996	-0.000004	-0.000000	0.999996
95	0.0000348	0.0000045	0.999987	-0.000011	-0.000000	0.999989
100	0.0001057	0.0000130	0.999966	-0.000028	-0.000000	0.999972
105	0.0002916	0.0000338	0.999920	-0.000064	-0.000000	0.999936
110	0.0007207	0.0000799	0.999831	-0.000133	-0.000000	0.999867
115	0.0016337	0.0001732	0.999670	-0.000256	-0.000000	0.999744
120	0.0034347	0.0003490	0.999398	-0.000462	-0.000000	0.999538
125	0.0067608	0.0006598	0.998969	-0.000787	-0.000000	0.999213
130	0.0125592	0.0011793	0.998323	-0.001276	-0.000001	0.998723
135	0.0221670	0.0020063	0.997397	-0.001982	-0.000002	0.998016
140	0.0373903	0.0032674	0.996119	-0.002961	-0.000005	0.997034
145	0.0605738	0.0051196	0.994420	-0.004276	-0.000009	0.995715
150	0.0946592	0.0077508	0.992228	-0.005991	-0.000016	0.993994
155	0.1432275	0.0113809	0.989479	-0.008171	-0.000026	0.991803
160	0.2105236	0.0162608	0.986113	-0.010882	-0.000042	0.989077
165	0.3014633	0.0226721	0.982082	-0.014185	-0.000063	0.985752
170	0.4216243	0.0309256	0.977343	-0.018141	-0.000090	0.981769
175	0.5772221	0.0413607	0.971866	-0.022806	-0.000124	0.977070
180	0.7750743	0.0543439	0.965625	-0.028233	-0.000164	0.971603
185	1.0225573	0.0702692	0.958606	-0.034470	-0.000206	0.965324
190	1.3275563	0.0895573	0.950796	-0.041563	-0.000248	0.958189
195	1.6984137	0.1126577	0.942186	-0.049554	-0.000281	0.950164
200	2.1438785	0.1400503	0.932771	-0.058485	-0.000299	0.941217
205	2.6730575	0.1722494	0.922541	-0.068395	-0.000287	0.931318
210	3.2953721	0.2098093	0.911484	-0.079325	-0.000230	0.920445
215	4.0205218	0.2533319	0.899587	-0.091321	-0.000107	0.908571
220	4.8584553	0.3034770	0.886826	-0.104432	0.000108	0.895676
225	5.8193516	0.3609763	0.873177	-0.118715	0.000448	0.881732
230	6.9136108	0.4266509	0.858605	-0.134238	0.000952	0.866714
235	8.1518573	0.5014347	0.843069	-0.151085	0.001671	0.850586
240	9.5449551	0.5864036	0.826523	-0.169358	0.002667	0.833309
245	11.1040386	0.6828144	0.808912	-0.189185	0.004017	0.814832
250	12.8405603	0.7921552	0.790174	-0.210725	0.005818	0.795093
255	14.7663588	0.9162120	0.770240	-0.234180	0.008194	0.774014
260	16.8937542	1.0571595	0.749033	-0.259804	0.011305	0.751500
265	19.2356771	1.2176851	0.726466	-0.287925	0.015361	0.727436
270	21.8058475	1.4011641	0.702440	-0.318963	0.020642	0.701679
275	24.6190249	1.6119133	0.676839	-0.353469	0.027531	0.674063
280	27.6913739	1.8555713	0.649528	-0.392177	0.036563	0.644386
285	31.0410283	2.1396901	0.620339	-0.436086	0.048505	0.612418
290	34.6890345	2.4747097	0.589059	-0.486600	0.064498	0.577898
295	38.6611522	2.8756823	0.555393	-0.545771	0.086320	0.540549
300	42.9921502	3.3657409	0.518891	-0.616818	0.115916	0.500098
305	47.7441963	3.9859334	0.478608	-0.705645	0.161805	0.456160

Table 5. Saturated vapor densities derived via V.P. and virial equations.

```
ETHANE SATD. VAPOR DENSITIES VIA V.P. AND VIRIAL EQNS.

ID       T,K       P,ATM    PLANK/KAMB        MOL/L         PCT
 1    89.899  9.9670-006   1.3511-006   1.3511-006        0.00
 1    90.000  1.0238-005   1.3863-006   1.3863-006        0.00
 1    95.000  3.5808-005   4.5936-006   4.5936-006        0.00
 1   100.000  1.0952-004   1.3347-005   1.3347-005        0.00
 1   105.000  2.9851-004   3.4649-005   3.4648-005        0.00
 1   110.000  7.3654-004   8.1615-005   8.1612-005        0.00
 1   115.000  1.6670-003   1.7671-004   1.7670-004        0.01
 1   120.000  3.4991-003   3.5558-004   3.5552-004        0.01
 1   125.000  6.8762-003   6.7110-004   6.7093-004        0.02
 1   130.000  1.2752-002   1.1974-003   1.1970-003        0.04
 1   135.000  2.2468-002   2.0336-003   2.0323-003        0.06
 1   140.000  3.7834-002   3.3064-003   3.3033-003        0.09
 1   145.000  6.1192-002   5.1721-003   5.1653-003        0.13
 1   150.000  9.5478-002   7.8184-003   7.8043-003        0.18
 1   155.000  1.4426-001   1.1464-002   1.1436-002        0.24
 1   160.000  2.1176-001   1.6358-002   1.6308-002        0.31
 1   165.000  3.0288-001   2.2781-002   2.2694-002        0.38
 1   170.000  4.2317-001   3.1042-002   3.0899-002        0.46
 1   175.000  5.7882-001   4.1479-002   4.1252-002        0.55
 1   180.000  7.7662-001   5.4457-002   5.4111-002        0.64
 1   185.000  1.0239+000   7.0369-002   6.9860-002        0.73
 1   190.000  1.3287+000   8.9635-002   8.8911-002        0.81
 1   195.000  1.6991+000   1.1271-001   1.1171-001        0.89
 1   200.000  2.1440+000   1.4006-001   1.3872-001        0.97
 1   205.000  2.6726+000   1.7222-001   1.7047-001        1.03
 1   210.000  3.2943+000   2.0973-001   2.0750-001        1.08
 1   215.000  4.0186+000   2.5321-001   2.5043-001        1.11
 1   220.000  4.8561+000   3.0331-001   2.9993-001        1.13
 1   225.000  5.8165+000   3.6077-001   3.5674-001        1.13
 1   230.000  6.9105+000   4.2642-001   4.2173-001        1.11
 1   235.000  8.1487+000   5.0120-001   4.9585-001        1.08
 1   240.000  9.5420+000   5.8618-001   5.8025-001        1.02
 1   245.000  1.1102+001   6.8262-001   6.7626-001        0.94
 1   250.000  1.2839+001   7.9203-001   7.8551-001        0.83
 1   255.000  1.4766+001   9.1618-001   9.0997-001        0.68
 1   260.000  1.6895+001   1.0572+000   1.0522+000        0.48
 1   265.000  1.9238+001   1.2179+000   1.2154+000        0.21
 1   270.000  2.1810+001   1.4016+000   1.4041+000       -0.18
 1   275.000  2.4624+001   1.6125+000   1.6245+000       -0.74
 1   280.000  2.7697+001   1.8563+000   1.8861+000       -1.58
 1   285.000  3.1047+001   2.1404+000   2.2047+000       -2.91
 1   290.000  3.4693+001   2.4754+000   2.6108+000       -5.19
```

Cryogenics Division – NBS Institute for Basic Standards
LABORATORY NOTE

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SUBJECT
Ethane Virial Coefficients and Saturated Vapor Densities

NAME R. D. Goodwin
DATE August 14, 1973

```
      PROGRAM VIRUS
C     ETHANE VIRIAL COEFFICIENTS,     X = T/TCRT,   Q = X**1/2,
C     BV = (B1 + B2/X**EB + B3/X + B4/X2 + B5/X3)*(1-(TZ/T)**1/4).
C     CV = (C1/X**EC + C2/X3 + C3/X5)*(1-TZ/T).
C    ID, (1)EUCKEN, (2)LAMBERT, (3)MICHELS, (4)HOOVER, (5)POPE,
C     (6)MCGLASHAN, (7)CHUEH, (8)GUNN, (10)DOUSLIN,PREPRINT.
C     VCRT,CC/MOL, ROSSINI(1953)/MCGLASHAM=148, EUBANK/POPE=146.2,
C                   TESTER(1961)=141.7, DOUSLIN(1973)=145.56.
      COMMON/1/M,EB,EC,TZB,TZC, BVS,CVS, B(5),C(4)
      COMMON/3/ DPSDT
      COMMON/999/NP,NF,H(15),Y(200),G(200,15)
      DIMENSION ID(200),T(200),BV(200),CV(200),X(200),XQ(200)
    1 FORMAT(I5, 2F10.0)
    2 FORMAT(1H1 13X 1HM 5X5HE(BC) 8X2HTZ 8X2HSS)
    3 FORMAT(10X I5, 2F10.3, F10.4)
    4 FORMAT(1H1 17X *ETHANE SECOND VIRIAL COEFFICIENT*//
     1 18X4HEB =F6.3, 5H, TZ =F6.1// 15X 5F12.6//
     2 18X2HID 7X3HT,K 5X4HT/TC 7X2HB* 5X4HCALC 5X4HDIFF 5X4HPCNT)
    5 FORMAT(15X I5, F10.3, F9.4, 3F9.3, F9.2)
    6 FORMAT(1H117X*THIRD VIRIAL, M =*I2, 6H, EC =F6.3// 16X F10.3,
     1 4F11.6// 18X2HID 7X3HT,K 4X6HT/TCRT 8X2HC* 5X5HCALCD 6X4HDIFF )
    7 FORMAT(15X I5, F10.3, F10.4, 3F10.3)
    8 FORMAT(18X 4HNP =I3, 12H, MEANDIFF = F7.3)
    9 FORMAT(18X 4HNP =I3, 11H, MEANPCT =F6.3)
   10 FORMAT(1H1 15X*TERMS OF THE VIRIAL EQUATION FOR SATURATED VAPOR*//
     1 17X3HT,K 7X5HP,ATM 7X5HMOL/L 5X5HDI/DN
     2 7X3HB*S 6X4HC*S2 4X6HZ(T,D)    )
   11 FORMAT(10X F10.0, 2F12.7, 4F10.6)
   12 FORMAT(1H1 17X 2HID 7X3HT,K 5X4HT/TC 7X2HB* 5X4HCALC
     1 5X4HDIFF 5X4HPCNT)
   13 FORMAT(1H117X2HID 7X3HT,K 4X6HT/TCRT 8X2HC* 5X5HCALCD 6X4HDIFF)
   15 TTRP=89.899 $ TCRT=305.33 $ DCRT=1.0/145.56
C     GENERATE MCGLASHAM DATA FOR BV(T), CC/MOL.
C     INCREASE ABS(MCGLASHAM) BY ONE PERCENT (148/145.56 = 1.017).
   16 N=0  $  DO 19 J=1,12  $  N = N+1  $  TT = T(N) = 140 + 10*J
   17 X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N))  $  ID(N) = 6
   18 BV(N) = 1.01*GLABF(TT)  $  Y(N) = BV(N)*DCRT
   19 CONTINUE
C     READ DOUSLIN(1973) DATA, CC/MOL.
   20 DO 23 J=1,99  $  READ 1, IDD,TT,BB  $  IF(IDD) 21,24
   21 N = N+1  $  ID(N)=IDD  $  T(N)=TT  $  BV(N)=BB
   22 X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ Y(N)=BB*DCRT
   23 CONTINUE
   24 NP = N  $  NF = 5  $  SSK = 1.0E+010
C     READ SECOND VIRIAL DATA.
   25 DO 28 J=1,99  $  READ 1, IDD,TT,BB  $  IF(IDD) 26,29
   26 N = N+1  $  ID(N)=IDD $ T(N)=TT $ BV(N)=BB
   27 X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N)) $ Y(N)=BB*DCRT
   28 CONTINUE
   29 NPP = N   $   M = 0
C     EXPLORE VALUES FOR EB AND FOR TZB.
C     MCGLASHAM TZB NEAR 2.7*TCRT = 824 K.
   30 EB = 0.25  $  TZ = TZB = 740  $  PRINT 2
C  31 DO 44 IE=1,3  $  EB = 0.25*IE
C  32 DO 44 IT=1,17  $  TZ = 640 + 10*IT
```

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```
   33 DO 36 J=1,NP  $  U=X(J)  $  Q=XQ(J)  $  W = 1-(TZ/T(J))**0.25
   34 G(J,1)=W $ G(J,2)=W/U**EB $ G(J,3)=W/U $ G(J,4)=W/U**2
   35 G(J,5)=W/U**3
   36 CONTINUE  $  CALL EGENFT  $  SS = 0
   37 DO 39 J=1,NP  $  YC = 0  $  DO 38 K=1,NF
   38 YC = YC + H(K)*G(J,K)
   39 SS = SS + ABSF(Y(J)/YC-1)  $  SS = 100*SS/NP
   40 IF(SS.LT.SSK) 41,44
   41 SSK=SS $ EK=EB $ TK=TZ  $  DO 42 K=1,5
   42 B(K) = H(K)
   44 PRINT 3, M,EB,TZ,SS  $  EB=EK $ TZ=TZB=TK  $  SS = 0
C     USE SAVED CONSTANTS FOR DEVIATIONS.
   45 PRINT 4, EB, TZ, (B(K),K=1,5)
   46 DO 51 J=1,NPP $  U=X(J)  $  Q=XQ(J)  $  W = 1-(TZ/T(J))**0.25
   47 YC = W*(B(1) + B(2)/U**EB + B(3)/U + B(4)/U**2 + B(5)/U**3)
   48 DIF=Y(J)-YC $ PCT=-100*DIF/YC $ SS=SS+ABSF(PCT)
   49 PRINT 5, ID(J),T(J),X(J),Y(J),YC,DIF,PCT  $  IF(J-NP) 51,50
   50 SS = SS/NP  $  PRINT 9, NP,SS  $  PRINT 12
   51 CONTINUE  $  N = 0
C     GENERATE THIRD VIRIAL DATA VIA CHUEH(1967), ID = 7.
C     DIMINISH CHUEH DATA BY 2 PERCENT.
   52 DO 55 J=1,6  $  N = N+1  $  TT = T(N) = 200 + 10*J
   53 X(N)=TT/TCRT $ XQ(N)=SQRTF(X(N))  $  ID(N) = 7
   54 CV(N) = 0.98*CHUCF(TT)  $  Y(N) = CV(N)*DCRT**2
   55 CONTINUE  $  K = N + 1
C     READ DOUSLIN(1973) DATA, (CC/MOL)**2.
   56 DO 58 J=K,99  $  READ 1, ID(J),T(J),CV(J)  $  IF(ID(J)) 57,59
   57 X(J)=T(J)/TCRT $ XQ(J)=SQRTF(X(J)) $ Y(J)=CV(J)*DCRT**2
   58 CONTINUE
   59 NP = J-1  $  NF = 3  $  SSK = 1.0E+010
C     READ THIRD VIRIAL DATA.   TZC NEAR 220 K.
   60 K = NP+1  $  DO 63 J=K,99
   61 READ 1, ID(J),T(J),CV(J)  $  IF(ID(J)) 62,64
   62 X(J) = T(J)/TCRT  $  XQ(J)=SQRTF(X(J))  $  Y(J)=CV(J)*DCRT**2
   63 CONTINUE
   64 NPP = J-1  $  EC = 1.0  $  PRINT 2
C     EXPLORE VALUES FOR EC AND FOR TZ.
C  65 DO 76 IE=1,4  $  EC = 0.5*IE
   66 DO 76 IT=1,11  $  TZ = 217.60 + 0.05*IT
   67 DO 69 J=1,NP  $  U = X(J)  $  W = 1-TZ/T(J)
   68 G(J,1)=W/U**EC  $  G(J,2)=W/U**3  $  G(J,3)=W/U**5
   69 CONTINUE  $  CALL EGENFT  $  SS = 0
   70 DO 72 J=1,NP  $  YC = 0  $  DO 71 K=1,NF
   71 YC = YC + H(K)*G(J,K)
   72 SS = SS + ABSF(Y(J)-YC)  $  SS = SS/NP
   73 IF(SS.LT.SSK) 74,76
   74 SSK=SS $ TK=TZ $ EK=EC $ MK=M  $  DO 75 K=1,4
   75 C(K) = H(K)
   76 PRINT 3, M,EC,TZ,SS  $  M = MK
   77 TZC = TZ = TK  $  EC = EK  $  SS = 0
C     USE SAVED CONSTANTS FOR DEVIATIONS.
   79 PRINT 6, M,EC,TZ, (C(K),K=1,4)
   80 DO 85 J=1,NPP $  U = X(J)  $  W = 1-TZ/T(J)
   81 YC = W*(C(1)/U**EC + C(2)/U**3 + C(3)/U**5)
   82 PCT = Y(J)-YC  $  SS = SS + ABSF(PCT)
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      VIRUS                                                      07/26/73

   83 PRINT 7, ID(J),T(J),X(J),Y(J),YC,PCT  $  IF(J-NP) 85,84
   84 SS = SS/NP  $  PRINT 8, NP,SS  $  PRINT 13
   85 CONTINUE
C     NOW EXAMINE TERMS OF THE VIRIAL EQUATION AT SATURATION.
C     THE IDEAL GAS DENSITY IS DI = P/(R*T),
   90 PRINT 10  $  DO 95 J=1,44  $  TT = 85 + 5*J
   91 PS=PSATF(TT)  $  DN=DNGSF(TT)  $  Z = ZIPF(TT,DN)
   92 DI = PS/TT/0.082056156  $  DR = DI/DN
   95 PRINT 11, TT,PS,DN, DR, BVS,CVS, Z
   99 STOP   $   END

SINGLE-BANK COMPILATION.




      FUNCTION CHUCF(T)
C     ETHANE THIRD VIRIAL VIA CHUEH FORMULA(1967), (CC/MOL)**2.
C     CV(T)/VCRT**2 = FA*FB + FC,  FA = A/Q + B/X5,
C     FB = 1 - EXP(1-AL*X2),  FC = EXP(-C + D*X - E*X2),  X = T/TCRT.
      DATA (TCRT=305.33),(VCRT=145.56),(AL=1.89)
      DATA (A=0.232),(B=0.468),(C=2.49),(D=2.30),(E=2.70)
    1 X=T/TCRT $ Q=SQRTF(SQRTF(X)) $ X2=X**2 $ X5=X**5
    2 FA = A/Q + B/X5  $  FB = 1 - EXPF(1-AL*X2)
    3 FC = EXPF(-C + D*X - E*X2)
    4 CHUCF = (FA*FB+FC)*VCRT**2    $    RETURN  $  END




      FUNCTION DNGSF(T)
C     PLANCK/KAMBEITZ VIA TESTER (P.171)/DIN.  VALID 170 TO 305 K.
C     V = R*T/P - C1/K**A - C2*P**2/X**B,   X = T/100,
C     V IN CC/GRAM,  T IN KELVINS,  P IN KG/CM**2,
C     1 ATM = 1.03323 KG/CM**2, R=2.822, C1=89.0, C2=27.9, A=2.4, B=9.0
      DATA (R=2.822),(C1=89.0),(C2=27.9),(A=2.4),(B=9.0),(WM=30.07)
    1 P = PSATF(T)  $  P = 1.03323*P  $  P2 = P**2
    2 X = T/100  $  XA = X**A  $  XB = X**B
    3 V = R*T/P - C1/XA - C2*P2/XB
    4 DNGSF = 1000.88/V/WM   $   RETURN  $  END
```

```
      FUNCTION GLABF(T)
C     ETHANE SECOND VIRIAL COEFF. VIA MC GLASHAM FORMULA (1962).
C     MC G. BELIEVES EUCKEN/PARTS ARE WRONG.
C     BV(T)/VCRT = B1 - B2/X - B3/X2 - B4/X**4.5,    X = T/TCRT.
      DATA (TCRT=305.4),(VCRT=148.0)
      DATA (B1=0.430),(B2=0.886),(B3=0.694),(B4=0.0375)
    1 X=T/TCRT $ X2=X**2 $ XN = X**4.5
    2 F = B1 - B2/X - B3/X2 - B4/XN
    9 GLABF = VCRT*F    $    RETURN  $  END
```

```
                                                              07/26/73

      FUNCTION PSATF(T)
C     LN(P/PTRP) = A*X + B*X2 + C*X3 + D*X4  + E*X*(1-X)**EP.
      COMMON/3/ DPSDT
      DATA (TTRP=89.899),(TCRT=305.33),(PTRP=9.616E-6),(EP=1.6)
      DATA (A=8.454987344),(B=12.48039775),(C=-4.104281551),
     1 (D=-1.413860533),(E=8.526522526)
    1 FORMAT(1H0 9X *PSATF = 0, T EXCEEDS TCRT. * / )
    2 XN=1-TTRP/TCRT $ X=(1-TTRP/T)/XN $ X2=X**2 $ X3=X**3 $ X4=X**4
    3 DXDT = TTRP/XN/T**2  $  Q = 1-X  $  IF(Q) 4,5,6
    4 PSATF = DPSDT = 0  $  PRINT 1  $  RETURN
    5 Z = Z1 = 0  $  GO TO 7
    6 W = Q**EP  $  W1 = -EP*W/Q  $  Z = X*W  $  Z1 = W + X*W1
    7 F = A*X + B*X2 + C*X3 + D*X4 + E*Z
    8 F1 = A + 2*B*X + 3*C*X2 + 4*D*X3 + E*Z1
    9 PSATF=PTRP*EXPF(F) $ DPSDT=F1*PSATF*DXDT  $  RETURN  $  END
```

```
                                                              07/26/73

      FUNCTION ZIPF(T,D)
C     Z(T,D) = 1 + BV(T)*S + CV(T)*S**2,    S = D/DCRT,   X = T/TCRT.
C     BV = (B1 + B2/X**EB + B3/X + B4/X2 + B5/X3)*(1-(TZ/T)**1/4).
C     CV = (C1/X**EC + C2/X3 + C3/X5)*(1-TZ/T).
      COMMON/1/M,EB,EC,TZB,TZC, BVS,CVS, B(5),C(4)
      DATA (TCRT=305.33),(VCRT=0.14556)
    1 S=D*VCRT $ X=T/TCRT $ Q=SQRTF(X) $ R=X**EC
    2 X2=X**2 $ X3=X**3 $ X4=X**4 $ X5=X**5
    3 ZB = 1 - (TZB/T)**0.25  $  ZC = 1 - TZC/T
    4 BV = ZB*(B(1) + B(2)/X**EB + B(3)/X + B(4)/X2 + B(5)/X3)
    5 CV = ZC*(C(1)/R + C(2)/X3 + C(3)/X5)
    6 BVS = BV*S  $  CVS = CV*S**2
    7 ZIPF = 1 + BVS + CVS    $    RETURN  $  END
```

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                                                                07/26/73

      PROGRAM VAPORDEN
C     ETHANE SATVAPORDEN VIA V.P. AND VIRIAL EQNS.
C     ON ISOTHERMS, ITERATE DEN IN VIRIAL EQN. TO MINIMIZE (P-PSAT).
      COMMON/3/ DPSDT
    1 FORMAT(18X *ETHANE SATD. VAPOR DENSITIES VIA V.P. AND VIRIAL EQNS.
     1 *//18X2HID 7X3HT,K 7X5HP,ATM 2X10HPLANK/KAMB 7X5HMOL/L 7X3HPCT)
    2 FORMAT(15X I5, F10.3, 3E12.4, F10.2)
    3 FORMAT(I5, F10.3, 2E15.5)
   19 ID = 1  $  TTRP = 89.899  $  PRINT 1
   20 DO 30 J=1,42  $  IF(J-1) 23,22
   22 T = TTRP  $  GO TO 24
   23 T = 80 + 5*J
   24 DI = DNGSF(T)  $  P = PSATF(T)  $  DEN = FINDF(T,P,DI)
   25 PUNCH 3, ID,T,DEN,P
   27 DIF = DI-DEN  $  PCT = 100*DIF/DEN
   28 PRINT 2, ID, T,P, DI,DEN, PCT
   30 CONTINUE  $  STOP  $  END

SINGLE-BANK COMPILATION.
```

```
      FUNCTION FINDF(T,P,DI)
C     ON ISOTHERM T, ITERATE DEN TO MINIMIZE (P-PCALC).
      COMMON DZDS
      DATA (GK=0.082056156),(VCRT=0.14556)
    1 FORMAT(1H0 9X *FINDF = 0, FAILS TO CONVERGE.* / )
    2 D = DI  $  GT = GK*T  $  DO 9 J=1,50
    3 Z = ZIPF(T,D)  $  PC = D*GT*Z  $  DP = P-PC  $  AP = ABSF(DP)
    4 Q = AP/P-1.0E-6  $  IF(Q) 10,10,5
    5 DPDD = GT*(Z + D*DZDS*VCRT)  $  ADP = ABSF(DPDD)
    6 Q = AP/ADP/D-1.0E-6  $  IF(Q) 10,10,7
    7 D = D + DP/DPDD  $  IF(D) 8,8,9
    8 D = P/T/GK
    9 CONTINUE  $  FINDF = 0  $  PRINT 1  $  RETURN
   10 FINDF = D    $    RETURN   $   END
```

```
      FUNCTION DNGSF(T)
C    PLANK/KAMBEITZ VIA TESTER.
      DATA (R=2.522),(C1=39.0),(C2=27.9),(A=2.4),(IB=9),(WM=30.07)
    1 P = 1.03323*PSATF(T)   $  P2 = P**2
    2 X = T/100   $  XA = X**A   $  XB = X**IB
    3 V = R*T/P - C1/XA - C2*P2/XB
    4 DNGSF = 1000.88/V/WM    $   RETURN  $  FND
```

08/01/73

```
      FUNCTION PSATF(T)
C    LN(P/PTRP) = A*X + B*X2 + C*X3 + D*X4 + E*X*(1-X)**EP.
      COMMON/3/ DPSDT
C    CONSTANTS VIA ZIEGLER TYPE B V.P. DATA.
      DATA (TTRP=89.899),(TCRT=305.33),(PTRP=9.967E-6),(EP=1.5)
      DATA (A=10.806922651),(B=8.344715938),(C=-3.119603823)
      DATA (D=-0.642995191),(E=6.059966098)
    1 FORMAT(1H0 9X *PSATF = 0, T EXCEEDS TCRT. * / )                4
    2 XN=1-TTRP/TCRT $ X=(1-TTRP/T)/XN $ X2=X**2 $ X3=X**3 $ X4=X**4
    3 DXDT = TTRP/XN/T**2   $  Q = 1-X   $  IF(Q) 4,5,6
    4 PSATF = DPSDT = 0   $  PRINT 1   $  RETURN
    5 Z = Z1 = 0   $   GO TO 7
    6 W = Q**EP   $  W1 = -EP*W/Q   $  Z = X*W   $  Z1 = W + X*W1
    7 F = A*X + B*X2 + C*X3 + D*X4 + E*Z
    8 F1 = A + 2*B*X + 3*C*X2 + 4*D*X3 + E*Z1
    9 PSATF=PTRP*EXPF(F) $ DPSDT=F1*PSATF*DXDT  $  RETURN  $  END
```

```
      FUNCTION ZIPF(T,D)
C    Z(T,D) = 1 + BV(X)*S + CV(X)*S**2.
C    BV = (B1 + B2/Q + B3/X + B4/X2 + B5/X3)*(1-(TZB/T)**1/4).
C    CV = (C1/X + C2/X3 + C3/X5)*(1-TZC/T).
      COMMON DZDS
      DATA (TCRT=305.33),(VCRT=0.14556),(TZB=740.0),(TZC=217.8),
     1 (B1=7.993156),(B2=-10.672497),(B3=9.217322),(B4=-2.481668),
     2 (B5=0.842328),(C1=0.253773),(C2=0.865299),(C3=0.556075)
    1 S=D*VCRT $ X=1/TCRT $ Q=X**0.25 $ X2=X**2 $ X3=X**3 $ X5=X**5
    2 ZB = 1 - (TZB/T)**0.25   $  ZC = 1 - TZC/T
    3 BV = ZB*(B1 + B2/Q + B3/X + B4/X2 + B5/X3)
    4 CV = ZC*(C1/X + C2/X3 + C3/X5)
    6 ZIPF = 1 + BV*S + CV*S**2   $  DZDS = BV + 2*CV*S
    9 RETURN   $   END
```

APPENDIX L

Cryogenics Division – NBS Institute for Basic Standards
LABORATORY NOTE

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SUBJECT
The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R. D. Goodwin

DATE Sept. 18, 1973

1. Introduction.

These densities, and accurate analytical descriptions thereof, are essential for the computation of thermodynamic functions, in particular to obtain heats of vaporization via the Clapeyron equation, and to formulate the equation of state which originates on this locus [4].

We have had difficulties in representing the available ethane data, and therefore have returned to fundamentals. For comparison we shall include oxygen [18], fluorine [13], and methane [4]. Previous formulations occur in [4, 7]. We start with the saturated liquid densities because their representation is much simpler than that of the saturated vapor densities.

2. The Saturated Liquids.

It is well known that these densities are described near the critical point by the form

$$\rho = \rho_c + a \cdot (T_c - T) + b \cdot (T_c - T)^{\epsilon} \tag{1}$$

wherein the first two terms are the rectilinear diameter, and the exponent is near $\epsilon = 0.35$.

Let us constrain (1) at the boundaries by use of the variables,

$$x(T) \equiv (T_c - T)/(T_c - T_t), \tag{2}$$

$$W(\rho) \equiv (\rho - \rho_c)/(\rho_t - \rho_c), \tag{3}$$

where subscripts c and t refer to critical and triple points. Equation (1) now becomes,

$$W(\rho) = a \cdot x + b \cdot x^{\epsilon}, \tag{4}$$

and the constraint requires that $a + b = 1$. If we solve this for the constant b, we may expect to obtain a function $Y(\rho, x)$ which is nearly constant over the entire range $0 \le x \le 1$,

$$Y(\rho, x) \equiv [W(\rho) - x]/(x^{\epsilon} - x). \tag{5}$$

This sensitive function is useful for examining data.

In past work we found that three arbitrary coefficients are required to describe saturated liquid densities. We now find the following results via many exploratory computations. For the smoothed data used here for oxygen and fluorine, the use of five arbitrary coefficients gives an improvement in the "fit". For the rough experimental data used here for methane and ethane, the use of five arbitrary coefficients gives virtually no improvement in the "fit" as compared with only three coefficients. With only three, the first equation used was,

$$Y(\rho, x) = A_1 + A_2 \cdot x + A_3 \cdot x^{\alpha}, \qquad (6)$$

and we found exponent $\alpha = 4/3$ for oxygen, fluorine and methane, but $\alpha = 8/3$ for ethane. After much exploration we have selected the following representation,

$$Y(\rho, x) = A_1 + A_2 \cdot x^{2/3} + A_3 \cdot x \qquad (7)$$

Table 1 gives the fixed-point constants. Table 2A gives the exponent ϵ found by trial, the least-squares coefficients, the rms of relative density deviations in percent, and the number of datum pairs, NP.

Tables 3, 4, 5, 6 compare calculated with experimental densities. No temperature-scale adjustments have been made in present work. Column YX gives the experimental value of $Y(\rho, x)$ via (5), whereas column YC gives the value calculated by the right side of (7). Table 7 compares ethane data not used for least squares.

Tables 8, 9, 10, 11 give saturated liquid densities computed by (7) at uniform temperatures, and also their slopes and curvatures.

The small deviations for oxygen and fluorine necessarily are systematic because the data were smoothed by the authors. The overall methane deviation is large because experimental data from various sources are included in the critical region.

The low-temperature ethane data of Miller were used to estimate the triple-point liquid density. Other data are from Canfield et al., and from Klosek/McKinley. The high-temperature "data" of Eubank are a correlation of available experimental data down to the boiling point 184.5 K, $(x = 0.561)$. We estimate uncertainty in our calculation of these densities to be about 0.1 percent over the entire range.

Concerning assignment of critical densities, we at first found both ρ_c and exponent ϵ simultaneously by trial to minimize the overall deviation. The results are rough because these two parameters are mutually compensating for data in the critical region. Hence we have adjusted ρ_c one step at a time for both saturated liquid and saturated vapor, examining the values of ϵ found by trial. We select that value of ρ_c which yields reasonable exponents ϵ for both liquid and vapor. For methane it thus is necessary to select $\rho_c = 10.2$ mol/ℓ, at the upper limit of uncertainty in the experimental values [4].

3. The Saturated Vapors

Densities of the ethane vapors range thru a factor of about 10^6. We have given reasons for using the logarithm of vapor densities, with arguments in powers of $(1/T)$, [7]. Define the normalized variables

$$z(T) \equiv (T_c/T - 1)/(T_c/T_t - 1), \qquad (8)$$

$$W(\rho) \equiv \ln(\rho_c/\rho)/\ln(\rho_c/\rho_t). \qquad (9)$$

We write the vapor densities equation for the critical region as follows,

$$-W(\rho) = (b-1) \cdot z - b \cdot z^{\epsilon} \qquad (10)$$

wherein the minus sign on the left arises merely from our definition of W(ρ). Solving (10) for b yields the dependent variable,

$$Y(\rho, z) \equiv [W(\rho) - z]/(z^{\epsilon} - z) \; . \qquad (11)$$

For the present work we have explored all kinds of representations, finally selecting the expression,

$$Y(\rho, z) = A_1 + \sum_{i=2}^{5} A_i \cdot z^{i/3} . \qquad (12)$$

Table 2B gives results for (12), analagous to table 2A for the liquid. Tables 12, 13, 14, 15 compare calculated with experimental vapor densities. Column YX is the experimental value of Y(ρ, z) via (11), whereas YC is calculated by the right side of (12). Table 16 compares ethane data not used for least squares. Tables 17, 18, 19, 20 give uniformly computed densities and derivatives via (12).

Computer programs used in this work are attached as an appendix.

4. Bibliography

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List of Tables

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SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R. D. Goodwin

DATE Sept. 18, 1973

List of Authors for Computer Tables

ID*	Author(s)	Reference
1	Goodwin (Virial + V.P.)	[6]
6	Porter	[12]
9	Tester	[16]
10	Douslin	[2]
11	Sliwinski	[15]
12	Canfield et al.	[1, 14]
13	Klosek	[9]
14	Miller	[11]
15	Eubank	[3]
16	Tomlinson	[17]
98	Prydz	[13]
99	Weber	[18]

* For METHANE, see references in [4].

Table 1. The fixed-point constants.

	Oxygen	Fluorine	Methane	Ethane
T_t, K	54.3507	53.4811	90.680	89.899
T_c, K	154.576	144.310	190.555	305.330
ρ_c, mol/ℓ	13.63	15.15	10.20	6.87
ρ_t, liquid	40.830	44.8623	28.147	21.680
ρ_t, vapor	$3.36122 \cdot 10^{-4}$	$5.670 \cdot 10^{-4}$	$1.567865 \cdot 10^{-2}$	$1.35114 \cdot 10^{-6}$

Table 2A. Constants for liquid equation (7)

	Oxygen	Fluorine	Methane	Ethane
ε	0.349	0.354	0.361	0.350
A_1	0.758 8805	0.791 3438	0.837 0910	0.761 7350
A_2	0.228 3200	0.112 9132	0.084 1613	0.298 6535
A_3	-0.230 4342	-0.100 6980	-0.074 7858	-0.327 6239
rms, %	0.014	0.010	0.084	0.142
NP	50	46	49	29

Table 2B. Constants for vapor equation (12)

	Oxygen	Fluorine	Methane	Ethane
ε	0.382	0.362	0.382	0.362
A_1	0.277 3707	0.257 1572	0.374 1014	0.192 7743
A_2	-0.338 6621	-0.227 0644	-0.261 5731	0.041 5501
A_3	0.769 0708	0.605 3864	0.675 3322	-0.789 2263
A_4	-1.576 1185	-1.391 6332	-1.012 2063	0.357 6675
A_5	0.939 8713	0.792 5719	0.439 8834	0.124 5438
rms, %	0.052	0.134	0.148	0.104
NP	50	46	96	29

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

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Table 3. Comparison of oxygen liquid densities.

ε = 0.349

```
          TCRT =  154.576,  TTRP =  54.3507

          DCRT =   13.630,  DTRP =  40.8300

       7.5888052-001  2.2832003-001 -2.3043415-001
       0.0000000+000  0.0000000+000  0.0000000+000

ID        T,K       MOL/L      CALC      PCNT            X        YX        YC       YDIF
99     56.000      40.601    40.603     -0.00      0.98354   0.75202   0.75805   -0.00603
99     58.000      40.323    40.326     -0.01      0.96359   0.75397   0.75958   -0.00561
99     60.000      40.048    40.049     -0.00      0.94363   0.76038   0.76109   -0.00072
99     62.000      39.777    39.770      0.02      0.92368   0.76779   0.76258    0.00520
99     64.000      39.494    39.491      0.01      0.90372   0.76630   0.76405    0.00225
99     66.000      39.216    39.210      0.01      0.88377   0.76840   0.76550    0.00291
99     68.000      38.926    38.928     -0.00      0.86381   0.76610   0.76692   -0.00081
99     70.000      38.655    38.644      0.03      0.84386   0.77243   0.76831    0.00411
99     72.000      38.358    38.358     -0.00      0.82390   0.76966   0.76969   -0.00002
99     74.000      38.081    38.071      0.03      0.80395   0.77392   0.77103    0.00289
99     76.000      37.779    37.782     -0.01      0.78399   0.77145   0.77235   -0.00090
99     78.000      37.495    37.491      0.01      0.76404   0.77482   0.77364    0.00118
99     80.000      37.202    37.197      0.01      0.74408   0.77614   0.77490    0.00124
99     82.000      36.900    36.901     -0.00      0.72413   0.77599   0.77613   -0.00014
99     84.000      36.603    36.602      0.00      0.70417   0.77750   0.77733    0.00017
99     86.000      36.298    36.301     -0.01      0.68422   0.77788   0.77850   -0.00061
99     88.000      35.997    35.996      0.00      0.66426   0.77979   0.77963    0.00016
99     90.000      35.689    35.688      0.00      0.64431   0.78081   0.78073    0.00007
99     92.000      35.373    35.377     -0.01      0.62435   0.78118   0.78180   -0.00061
99     94.000      35.063    35.062      0.00      0.60440   0.78305   0.78282    0.00023
99     96.000      34.734    34.742     -0.02      0.58444   0.78261   0.78381   -0.00120
99     98.000      34.412    34.418     -0.02      0.56449   0.78376   0.78475   -0.00099
99    100.000      34.083    34.090     -0.02      0.54453   0.78472   0.78565   -0.00093
99    102.000      33.750    33.756     -0.02      0.52458   0.78563   0.78651   -0.00088
99    104.000      33.411    33.417     -0.02      0.50462   0.78659   0.78732   -0.00072
99    106.000      33.069    33.072     -0.01      0.48467   0.78772   0.78807   -0.00035
99    108.000      32.712    32.720     -0.02      0.46471   0.78780   0.78878   -0.00098
99    110.000      32.362    32.361      0.00      0.44476   0.78960   0.78943    0.00017
99    112.000      31.990    31.995     -0.02      0.42480   0.78946   0.79001   -0.00056
99    114.000      31.616    31.620     -0.01      0.40485   0.79005   0.79054   -0.00049
99    116.000      31.230    31.236     -0.02      0.38489   0.79038   0.79100   -0.00062
99    118.000      30.845    30.842      0.01      0.36494   0.79169   0.79138    0.00031
99    120.000      30.441    30.438      0.01      0.34498   0.79208   0.79169    0.00039
99    122.000      30.021    30.021     -0.00      0.32503   0.79190   0.79192   -0.00001
99    124.000      29.595    29.591      0.01      0.30507   0.79239   0.79205    0.00034
99    126.000      29.146    29.147     -0.00      0.28512   0.79203   0.79209   -0.00006
99    128.000      28.686    28.685      0.00      0.26516   0.79210   0.79201    0.00008
99    130.000      28.209    28.205      0.01      0.24521   0.79216   0.79182    0.00033
99    132.000      27.709    27.704      0.02      0.22525   0.79192   0.79150    0.00042
99    134.000      27.181    27.179      0.01      0.20530   0.79129   0.79103    0.00026
99    136.000      26.631    26.625      0.02      0.18534   0.79103   0.79039    0.00063
99    138.000      26.042    26.037      0.02      0.16539   0.78999   0.78956    0.00043
99    140.000      25.413    25.410      0.01      0.14543   0.78883   0.78851    0.00032
99    142.000      24.734    24.733      0.01      0.12548   0.78733   0.78719    0.00014
99    144.000      23.992    23.993     -0.00      0.10552   0.78549   0.78555   -0.00006
99    146.000      23.164    23.170     -0.02      0.08557   0.78287   0.78350   -0.00063
99    148.000      22.227    22.230     -0.01      0.06561   0.78057   0.78090   -0.00033
99    150.000      21.106    21.108     -0.01      0.04566   0.77724   0.77753   -0.00029
99    152.000      19.646    19.647     -0.00      0.02570   0.77280   0.77284   -0.00004
99    154.000      17.106    17.104      0.01      0.00575   0.76528   0.76488    0.00040
                NP =  50,  RMSPCT =   0.014
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NATIONAL BUREAU OF STANDARDS, CRYOGENIC ENGINEERING LABORATORY

LABORATORY NOTE

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NAME R.D.Goodwin

DATE Sept. 18, 1973

Table 4. Comparison of fluorine liquid densities.

```
                                             E = 0.354

                 TCRT = 144.310, TTRP = 53.4811

                 DCRT =  15.150, DTRP = 44.8623

             7.9134383-001  1.1291315-001 -1.0069804-001
             0.0000000+000  0.0000000+000  0.0000000+000

ID        T,K      MOL/L      CALC     PCNT              X        YX        YC       YDIF
98     54.000     44.781    44.781     0.00        0.99429   0.80556   0.80370   0.00186
98     56.000     44.465    44.464     0.00        0.97227   0.80524   0.80425   0.00099
98     58.000     44.146    44.146     0.00        0.95025   0.80550   0.80479   0.00071
98     60.000     43.825    43.825     0.00        0.92823   0.80574   0.80532   0.00042
98     62.000     43.501    43.501     0.00        0.90621   0.80603   0.80583   0.00021
98     64.000     43.174    43.174    -0.00        0.88419   0.80632   0.80633  -0.00000
98     66.000     42.845    42.845    -0.00        0.86217   0.80662   0.80681  -0.00019
98     68.000     42.512    42.513    -0.00        0.84015   0.80693   0.80728  -0.00034
98     70.000     42.176    42.177    -0.00        0.81813   0.80728   0.80773  -0.00045
98     72.000     41.836    41.838    -0.01        0.79611   0.80760   0.80817  -0.00056
98     74.000     41.493    41.496    -0.01        0.77409   0.80796   0.80859  -0.00063
98     76.000     41.146    41.149    -0.01        0.75207   0.80831   0.80899  -0.00068
98     78.000     40.795    40.799    -0.01        0.73005   0.80868   0.80938  -0.00069
98     80.000     40.440    40.444    -0.01        0.70803   0.80903   0.80974  -0.00071
98     82.000     40.081    40.085    -0.01        0.68602   0.80941   0.81009  -0.00068
98     84.000     39.717    39.720    -0.01        0.66400   0.80977   0.81042  -0.00065
98     86.000     39.347    39.351    -0.01        0.64198   0.81011   0.81073  -0.00061
98     88.000     38.973    38.976    -0.01        0.61996   0.81047   0.81101  -0.00054
98     90.000     38.592    38.596    -0.01        0.59794   0.81080   0.81127  -0.00047
98     92.000     38.206    38.209    -0.01        0.57592   0.81112   0.81151  -0.00039
98     94.000     37.813    37.815    -0.01        0.55390   0.81143   0.81172  -0.00029
98     96.000     37.413    37.415    -0.00        0.53188   0.81171   0.81191  -0.00019
98     98.000     37.005    37.006    -0.00        0.50986   0.81197   0.81206  -0.00009
98    100.000     36.590    36.590     0.00        0.48784   0.81220   0.81219   0.00001
98    102.000     36.165    36.164     0.00        0.46582   0.81240   0.81229   0.00012
98    104.000     35.731    35.729     0.01        0.44380   0.81256   0.81235   0.00021
98    106.000     35.286    35.283     0.01        0.42178   0.81268   0.81238   0.00030
98    108.000     34.829    34.826     0.01        0.39976   0.81274   0.81236   0.00038
98    110.000     34.361    34.356     0.01        0.37774   0.81276   0.81231   0.00045
98    112.000     33.878    33.873     0.01        0.35572   0.81272   0.81221   0.00050
98    114.000     33.379    33.374     0.02        0.33370   0.81261   0.81206   0.00055
98    116.000     32.864    32.858     0.02        0.31168   0.81243   0.81186   0.00056
98    118.000     32.330    32.324     0.02        0.28967   0.81218   0.81161   0.00057
98    120.000     31.774    31.768     0.02        0.26765   0.81183   0.81129   0.00055
98    122.000     31.193    31.188     0.02        0.24563   0.81139   0.81090   0.00049
93    124.000     30.584    30.579     0.02        0.22361   0.81086   0.81042   0.00043
98    126.000     29.942    29.939     0.01        0.20159   0.81020   0.80986   0.00034
98    128.000     29.262    29.260     0.01        0.17957   0.80942   0.80920   0.00022
98    130.000     28.535    28.534     0.00        0.15755   0.80850   0.80842   0.00009
98    132.000     27.750    27.751    -0.00        0.13553   0.80742   0.80749  -0.00007
98    134.000     26.891    26.894    -0.01        0.11351   0.80617   0.80638  -0.00022
98    136.000     25.935    25.939    -0.01        0.09149   0.80470   0.80506  -0.00036
98    138.000     24.839    24.843    -0.02        0.06947   0.80300   0.80343  -0.00043
98    140.000     23.521    23.524    -0.01        0.04745   0.80096   0.80137  -0.00040
98    142.000     21.769    21.770    -0.00        0.02543   0.79843   0.79855  -0.00012
98    144.000     18.327    18.328    -0.00        0.00341   0.79340   0.79356  -0.00016
                  NP = 46, RMSPCT =   0.010
```

Table 5. Comparison of methane liquid densities.

```
                                         E = 0.361

          TCRT = 190.555, TTRP = 90.6800

          DCRT =  10.200, DTRP = 28.1470

      8.3709103-001  8.4161267-002 -7.4785753-002
      0.0000000+000  0.0000000+000  0.0000000+000

 ID      T,K       MOL/L      CALC     PCNT          X        YX        YC        YDIF
  1    93.512     27.910     27.912   -0.01      0.97164   0.84050   0.84699  -0.00649
  1    97.173     27.605     27.605    0.00      0.93499   0.84830   0.84764   0.00066
  1   101.434     27.243     27.240    0.01      0.89233   0.85043   0.84836   0.00207
  1   105.165     26.916     26.916    0.00      0.85497   0.84900   0.84896   0.00003
  1   109.611     26.527     26.521    0.02      0.81045   0.85231   0.84964   0.00267
  1   113.772     26.146     26.144    0.01      0.76879   0.85112   0.85023   0.00089
  1   117.746     25.782     25.775    0.03      0.72900   0.85327   0.85074   0.00252
  1   121.893     25.388     25.380    0.03      0.68748   0.85373   0.85123   0.00249
  1   125.825     24.999     24.995    0.02      0.64811   0.85272   0.85165   0.00107
  1   129.657     24.611     24.610    0.01      0.60974   0.85236   0.85201   0.00035
101   130.000     24.558     24.575   -0.07      0.60631   0.84803   0.85204  -0.00400
  1   133.773     24.186     24.182    0.01      0.56853   0.85313   0.85233   0.00080
  1   133.878     24.176     24.171    0.02      0.56748   0.85338   0.85234   0.00104
102   135.000     24.041     24.052   -0.05      0.55625   0.85002   0.85242  -0.00240
  1   139.352     23.578     23.579   -0.00      0.51267   0.85249   0.85266  -0.00017
103   140.000     23.500     23.507   -0.03      0.50618   0.85132   0.85269  -0.00137
104   145.000     22.932     22.934   -0.01      0.45612   0.85255   0.85285  -0.00030
  1   145.448     22.880     22.881   -0.00      0.45163   0.85272   0.85286  -0.00013
105   150.000     22.329     22.328    0.01      0.40606   0.85315   0.85287   0.00027
601   150.000     22.332     22.328    0.02      0.40606   0.85357   0.85287   0.00070
  1   151.553     22.130     22.132   -0.01      0.39051   0.85255   0.85285  -0.00030
106   155.000     21.686     21.682    0.02      0.35599   0.85341   0.85274   0.00067
  1   157.199     21.379     21.383   -0.02      0.33398   0.85201   0.85263  -0.00062
107   160.000     20.991     20.986    0.02      0.30593   0.85311   0.85242   0.00069
  1   163.659     20.428     20.438   -0.05      0.26930   0.85048   0.85205  -0.00157
108   165.000     20.234     20.227    0.03      0.25587   0.85289   0.85188   0.00102
  1   169.326     19.492     19.502   -0.05      0.21256   0.84962   0.85117  -0.00155
109   170.000     19.387     19.382    0.03      0.20581   0.85180   0.85104   0.00076
110   175.000     18.417     18.414    0.01      0.15574   0.85022   0.84981   0.00042
602   175.000     18.420     18.414    0.03      0.15574   0.85080   0.84981   0.00100
  1   175.053     18.390     18.403   -0.07      0.15521   0.84777   0.84979  -0.00203
111   180.000     17.249     17.250   -0.00      0.10568   0.84786   0.84800  -0.00014
603   180.000     17.254     17.250    0.02      0.10568   0.84867   0.84800   0.00067
112   184.000     16.054     16.061   -0.04      0.06563   0.84466   0.84588  -0.00121
604   184.000     16.060     16.061   -0.00      0.06563   0.84575   0.84588  -0.00013
  6   185.030     15.710     15.688    0.14      0.05532   0.84922   0.84517   0.00405
113   186.000     15.286     15.299   -0.08      0.04561   0.84203   0.84442  -0.00240
  6   186.030     15.302     15.286    0.11      0.04530   0.84765   0.84440   0.00325
  6   187.031     14.836     14.826    0.07      0.03528   0.84572   0.84351   0.00221
  5   187.489     14.582     14.589   -0.05      0.03070   0.84158   0.84305  -0.00147
114   188.000     14.284     14.298   -0.10      0.02558   0.83922   0.84248  -0.00327
  6   188.031     14.265     14.279    0.04      0.02527   0.84388   0.84245   0.00143
  6   189.032     13.578     13.578    0.00      0.01525   0.84114   0.84113   0.00002
  5   189.331     13.300     13.315   -0.11      0.01226   0.83640   0.84065  -0.00425
  5   189.707     12.879     12.920   -0.31      0.00849   0.82667   0.83996  -0.01329
  6   190.032     12.474     12.477   -0.02      0.00524   0.83812   0.83924  -0.00111
  5   190.068     12.397     12.418   -0.17      0.00488   0.83082   0.83915  -0.00833
  7   190.070     12.440     12.415    0.20      0.00486   0.84908   0.83914   0.00994
  7   190.170     12.270     12.235    0.28      0.00385   0.85369   0.83887   0.01482
                 NP = 49, RMSPCT =   0.084
```

E=0.361

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

DATE Sept. 18, 1973

Table 6. Comparison of ethane liquid densities.

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          ETHANE SATURATED LIQUID DENSITIES, E = 0.350

            TCRT = 305.330, TTRP = 89.8990

            DCRT =    6.870, DTRP = 21.6800

        7.6173503-001  2.9865351-001 -3.2762394-001
        0.0000000+000  0.0000000+000  0.0000000+000

ID        T,K       MOL/L       CALC     PCNT             X       YX       YC      YDIF
14     91.010      21.639     21.640    -0.00       0.99484  0.72131  0.73343  -0.01212
14    100.020      21.313     21.315    -0.01       0.95302  0.73294  0.73873  -0.00579
14    108.110      21.025     21.024     0.01       0.91547  0.74474  0.74338   0.00136
12    108.150      21.026     21.022     0.02       0.91528  0.74831  0.74341   0.00490
13    110.928      20.915     20.922    -0.03       0.90239  0.73724  0.74498  -0.00774
14    115.050      20.771     20.772    -0.00       0.88325  0.74640  0.74729  -0.00089
12    115.770      20.747     20.746     0.00       0.87991  0.74816  0.74769   0.00047
13    116.483      20.717     20.721    -0.02       0.87660  0.74515  0.74809  -0.00293
13    122.039      20.521     20.519     0.01       0.85081  0.75269  0.75115   0.00154
13    127.594      20.323     20.316     0.03       0.82503  0.75847  0.75415   0.00432
13    133.150      20.128     20.112     0.07       0.79924  0.76479  0.75709   0.00770
15    184.470      18.175     18.138     0.20       0.56101  0.79083  0.78108   0.00975
15    190.000      17.944     17.910     0.19       0.53535  0.79186  0.78325   0.00861
15    200.000      17.516     17.485     0.18       0.48893  0.79408  0.78690   0.00718
15    210.000      17.068     17.042     0.15       0.44251  0.79576  0.79019   0.00557
15    220.000      16.595     16.577     0.11       0.39609  0.79668  0.79304   0.00364
15    230.000      16.093     16.085     0.05       0.34967  0.79707  0.79541   0.00167
15    240.000      15.545     15.557    -0.08       0.30325  0.79496  0.79719  -0.00222
15    250.000      14.957     14.984    -0.18       0.25683  0.79329  0.79826  -0.00497
10    253.150      14.753     14.792    -0.26       0.24221  0.79127  0.79843  -0.00716
10    263.150      14.089     14.136    -0.33       0.19579  0.78970  0.79829  -0.00858
10    273.150      13.342     13.366    -0.33       0.14937  0.78874  0.79687  -0.00813
10    283.150      12.458     12.489    -0.24       0.10296  0.78769  0.79361  -0.00592
10    293.150      11.297     11.314    -0.15       0.05654  0.78358  0.78721  -0.00362
10    298.150      10.499     10.498     0.01       0.03333  0.78193  0.78175   0.00019
10    302.150       9.544      9.543     0.01       0.01476  0.77510  0.77487   0.00022
10    303.150       9.201      9.196     0.05       0.01012  0.77416  0.77239   0.00177
10    304.150       8.737      8.730     0.08       0.00548  0.77227  0.76922   0.00305
10    305.150       7.830      7.820     0.13       0.00084  0.77224  0.76411   0.00813
          NP = 29, RMSPCT =   0.142
```

OGILVIE PRESS, INC., BROOKLYN 17, N. Y. STOCK NO. 450

Table 7. Ethane liquid data not used for least squares.

ID	T,K	MOL/L	CALC	PCNT	X	YX	YC	YDIF
9	100.000	21.371	21.316	0.26	0.95311	0.86067	0.73872	0.12196
9	120.000	20.549	20.593	-0.21	0.86028	0.71692	0.75003	-0.03311
9	140.000	19.777	19.859	-0.41	0.76744	0.72238	0.76064	-0.03826
9	160.000	19.050	19.105	-0.29	0.67460	0.75146	0.77044	-0.01898
9	180.000	18.337	18.320	0.10	0.58176	0.78411	0.77926	0.00484
9	200.000	17.595	17.485	0.63	0.48893	0.81258	0.78690	0.02567
9	220.000	16.755	16.577	1.07	0.39609	0.82969	0.79304	0.03665
9	240.000	15.782	15.557	1.45	0.30325	0.83996	0.79719	0.04277
9	260.000	14.638	14.351	2.00	0.21042	0.85097	0.79845	0.05252
9	280.000	13.183	12.792	3.05	0.11758	0.86915	0.79489	0.07426
9	290.000	12.122	11.729	3.35	0.07116	0.87113	0.78971	0.08143
9	300.000	10.516	10.112	4.00	0.02474	0.88848	0.77899	0.10949
10	305.250	7.600	7.583	0.22	0.00037	0.78096	0.76316	0.01780
11	283.200	12.423	12.484	-0.49	0.10272	0.78179	0.79359	-0.01180
11	288.190	11.895	11.946	-0.43	0.07956	0.78051	0.79092	-0.01041
11	293.180	11.270	11.309	-0.34	0.05640	0.77867	0.78718	-0.00851
11	295.670	10.899	10.934	-0.32	0.04484	0.77672	0.78474	-0.00802
11	298.170	10.472	10.494	-0.21	0.03324	0.77610	0.78172	-0.00562
11	300.660	9.937	9.955	-0.18	0.02168	0.77281	0.77785	-0.00504
11	302.160	9.534	9.540	-0.07	0.01471	0.77282	0.77485	-0.00203
11	303.160	9.190	9.192	-0.02	0.01007	0.77159	0.77236	-0.00078
11	304.150	8.732	8.730	0.02	0.00548	0.76994	0.76922	0.00072
11	304.650	8.397	8.395	0.03	0.00316	0.76825	0.76713	0.00112
11	305.150	7.827	7.820	0.09	0.00084	0.77012	0.76411	0.00601
13	105.372	21.105	21.122	-0.08	0.92818	0.71576	0.74182	-0.02606
13	99.817	21.298	21.323	-0.11	0.95396	0.68284	0.73861	-0.05577
13	94.261	21.490	21.523	-0.15	0.97975	0.56468	0.73535	-0.17068
16	283.200	12.434	12.484	-0.39	0.10272	0.78404	0.79359	-0.00955
16	288.190	11.909	11.946	-0.31	0.07956	0.78335	0.79092	-0.00757
16	293.180	11.290	11.309	-0.17	0.05640	0.78302	0.78718	-0.00416
16	295.670	10.924	10.934	-0.08	0.04484	0.78262	0.78474	-0.00211
16	298.170	10.502	10.494	0.07	0.03324	0.78367	0.78172	0.00195
16	300.660	9.980	9.955	0.25	0.02168	0.78497	0.77785	0.00712
16	302.160	9.578	9.540	0.39	0.01471	0.78669	0.77485	0.01184

Table 8. Calculated oxygen liquid densities

T,K	R,MOL/L	DR/DT	D2R/DT2
54.351	40.830	-0.1377	-0.00019
56.000	40.603	-0.1380	-0.00021
58.000	40.326	-0.1385	-0.00023
60.000	40.049	-0.1390	-0.00026
62.000	39.770	-0.1395	-0.00029
64.000	39.491	-0.1401	-0.00032
66.000	39.210	-0.1408	-0.00035
68.000	38.928	-0.1415	-0.00038
70.000	38.644	-0.1423	-0.00041
72.000	38.358	-0.1432	-0.00045
74.000	38.071	-0.1441	-0.00049
76.000	37.782	-0.1451	-0.00053
78.000	37.491	-0.1462	-0.00057
80.000	37.197	-0.1474	-0.00061
82.000	36.901	-0.1487	-0.00066
84.000	36.602	-0.1500	-0.00071
86.000	36.301	-0.1515	-0.00077
88.000	35.996	-0.1531	-0.00083
90.000	35.688	-0.1548	-0.00089
92.000	35.377	-0.1567	-0.00096
94.000	35.062	-0.1586	-0.00103
96.000	34.742	-0.1608	-0.00111
98.000	34.418	-0.1631	-0.00119
100.000	34.090	-0.1655	-0.00129
102.000	33.756	-0.1682	-0.00139
104.000	33.417	-0.1711	-0.00150
106.000	33.072	-0.1742	-0.00162
108.000	32.720	-0.1776	-0.00176
110.000	32.361	-0.1813	-0.00191
112.000	31.995	-0.1852	-0.00207
114.000	31.620	-0.1896	-0.00226
116.000	31.236	-0.1943	-0.00248
118.000	30.842	-0.1995	-0.00272
120.000	30.438	-0.2052	-0.00300
122.000	30.021	-0.2115	-0.00332
124.000	29.591	-0.2185	-0.00369
126.000	29.147	-0.2263	-0.00413
128.000	28.685	-0.2351	-0.00466
130.000	28.205	-0.2450	-0.00530
132.000	27.704	-0.2564	-0.00608
134.000	27.179	-0.2695	-0.00707
136.000	26.625	-0.2848	-0.00833
138.000	26.037	-0.3031	-0.01000
140.000	25.410	-0.3253	-0.01229
142.000	24.733	-0.3529	-0.01555
144.000	23.993	-0.3886	-0.02051
146.000	23.170	-0.4370	-0.02869
148.000	22.230	-0.5079	-0.04396
150.000	21.108	-0.6253	-0.07893
152.000	19.647	-0.8749	-0.20084
154.000	17.104	-2.1732	-2.34479
154.576	13.630	0.0000	0.00000

Table 9. Calculated fluorine liquid densities.

T,K	R,MOL/L	DR/DT	D2R/DT2
53.481	44.862	-0.1573	-0.00054
54.000	44.781	-0.1576	-0.00055
56.000	44.464	-0.1587	-0.00058
58.000	44.146	-0.1599	-0.00061
60.000	43.825	-0.1612	-0.00065
62.000	43.501	-0.1625	-0.00068
64.000	43.174	-0.1639	-0.00072
66.000	42.845	-0.1654	-0.00076
68.000	42.513	-0.1670	-0.00081
70.000	42.177	-0.1686	-0.00085
72.000	41.838	-0.1704	-0.00090
74.000	41.496	-0.1722	-0.00095
76.000	41.149	-0.1742	-0.00101
78.000	40.799	-0.1763	-0.00107
80.000	40.444	-0.1785	-0.00114
82.000	40.085	-0.1808	-0.00121
84.000	39.720	-0.1833	-0.00129
86.000	39.351	-0.1860	-0.00137
88.000	38.976	-0.1888	-0.00146
90.000	38.596	-0.1918	-0.00156
92.000	38.209	-0.1951	-0.00167
94.000	37.815	-0.1985	-0.00179
96.000	37.415	-0.2022	-0.00192
98.000	37.006	-0.2062	-0.00207
100.000	36.590	-0.2105	-0.00223
102.000	36.164	-0.2151	-0.00242
104.000	35.729	-0.2202	-0.00262
106.000	35.283	-0.2257	-0.00286
108.000	34.826	-0.2316	-0.00313
110.000	34.356	-0.2382	-0.00344
112.000	33.873	-0.2454	-0.00380
114.000	33.374	-0.2534	-0.00422
116.000	32.858	-0.2624	-0.00472
118.000	32.324	-0.2724	-0.00533
120.000	31.768	-0.2838	-0.00606
122.000	31.188	-0.2967	-0.00696
124.000	30.579	-0.3118	-0.00811
126.000	29.939	-0.3294	-0.00959
128.000	29.260	-0.3505	-0.01156
130.000	28.534	-0.3762	-0.01428
132.000	27.751	-0.4084	-0.01821
134.000	26.894	-0.4504	-0.02426
136.000	25.939	-0.5081	-0.03440
138.000	24.843	-0.5939	-0.05377
140.000	23.524	-0.7400	-0.09999
142.000	21.770	-1.0696	-0.27704
144.000	18.328	-3.6894	-7.49794
144.310	15.150	0.0000	0.00000

Table 10. Calculated methane liquid densities

T,K	R,MOL/L	DR/DT	D2R/DT2
90.680	28.147	-0.0825	-0.00031
92.000	28.038	-0.0829	-0.00032
94.000	27.871	-0.0836	-0.00033
96.000	27.704	-0.0842	-0.00035
98.000	27.534	-0.0849	-0.00036
100.000	27.364	-0.0857	-0.00038
102.000	27.192	-0.0865	-0.00040
104.000	27.018	-0.0873	-0.00041
106.000	26.843	-0.0881	-0.00043
108.000	26.665	-0.0890	-0.00045
110.000	26.486	-0.0899	-0.00048
112.000	26.306	-0.0909	-0.00050
114.000	26.123	-0.0919	-0.00052
116.000	25.938	-0.0930	-0.00055
118.000	25.751	-0.0941	-0.00058
120.000	25.561	-0.0953	-0.00061
122.000	25.369	-0.0966	-0.00064
124.000	25.175	-0.0979	-0.00068
126.000	24.978	-0.0993	-0.00072
128.000	24.778	-0.1008	-0.00076
130.000	24.575	-0.1023	-0.00080
132.000	24.368	-0.1040	-0.00085
134.000	24.158	-0.1057	-0.00090
136.000	23.945	-0.1076	-0.00096
138.000	23.728	-0.1096	-0.00103
140.000	23.507	-0.1117	-0.00110
142.000	23.281	-0.1140	-0.00117
144.000	23.051	-0.1164	-0.00126
146.000	22.815	-0.1190	-0.00136
148.000	22.574	-0.1219	-0.00147
150.000	22.328	-0.1249	-0.00159
152.000	22.075	-0.1282	-0.00173
154.000	21.815	-0.1318	-0.00188
156.000	21.547	-0.1358	-0.00207
158.000	21.271	-0.1401	-0.00228
160.000	20.986	-0.1449	-0.00253
162.000	20.691	-0.1503	-0.00282
164.000	20.385	-0.1562	-0.00318
166.000	20.066	-0.1630	-0.00361
168.000	19.732	-0.1707	-0.00414
170.000	19.382	-0.1797	-0.00481
172.000	19.012	-0.1901	-0.00568
174.000	18.620	-0.2026	-0.00683
176.000	18.200	-0.2177	-0.00841
178.000	17.747	-0.2367	-0.01068
180.000	17.250	-0.2612	-0.01415
182.000	16.696	-0.2947	-0.01988
184.000	16.061	-0.3440	-0.03064
186.000	15.299	-0.4261	-0.05538
188.000	14.298	-0.6021	-0.14217
190.000	12.527	-1.5385	-1.72796
190.555	10.200	0.0000	0.00000

Table 11. Calculated ethane liquid densities.

```
         ETHANE SATURATED LIQUID DENSITIES

    T,K      R,MOL/L       DR/DT     D2R/DT2
 89.899      21.680      -0.0360     0.00000
 90.000      21.676      -0.0360     0.00000
 95.000      21.496      -0.0360    -0.00000
100.000      21.316      -0.0360    -0.00001
105.000      21.136      -0.0361    -0.00001
110.000      20.955      -0.0362    -0.00002
115.000      20.774      -0.0363    -0.00002
120.000      20.593      -0.0364    -0.00003
125.000      20.411      -0.0365    -0.00003
130.000      20.228      -0.0367    -0.00004
135.000      20.044      -0.0369    -0.00004
140.000      19.859      -0.0371    -0.00005
145.000      19.673      -0.0374    -0.00006
150.000      19.485      -0.0377    -0.00006
155.000      19.296      -0.0380    -0.00007
160.000      19.105      -0.0384    -0.00008
165.000      18.912      -0.0388    -0.00009
170.000      18.717      -0.0392    -0.00010
175.000      18.520      -0.0398    -0.00011
180.000      18.320      -0.0403    -0.00012
185.000      18.116      -0.0410    -0.00013
190.000      17.910      -0.0417    -0.00015
195.000      17.700      -0.0424    -0.00016
200.000      17.485      -0.0433    -0.00018
205.000      17.266      -0.0443    -0.00020
210.000      17.042      -0.0453    -0.00022
215.000      16.813      -0.0465    -0.00025
220.000      16.577      -0.0478    -0.00028
225.000      16.335      -0.0493    -0.00031
230.000      16.085      -0.0509    -0.00035
235.000      15.826      -0.0527    -0.00039
240.000      15.557      -0.0548    -0.00045
245.000      15.277      -0.0572    -0.00051
250.000      14.984      -0.0600    -0.00059
255.000      14.676      -0.0632    -0.00069
260.000      14.351      -0.0669    -0.00082
265.000      14.005      -0.0715    -0.00099
270.000      13.635      -0.0770    -0.00123
275.000      13.233      -0.0839    -0.00156
280.000      12.792      -0.0929    -0.00208
285.000      12.299      -0.1053    -0.00295
290.000      11.729      -0.1238    -0.00463
295.000      11.040      -0.1554    -0.00871
300.000      10.112      -0.2288    -0.02539
305.000       8.048      -1.2696    -2.44167
305.330       6.870       0.0000     0.00000
```

Table 12. Comparison of oxygen vapor densities.

```
                                            E = 0.382

              TCRT = 154.576, TTRP = 54.3507
              DCRT = 13.630, DTRP = 3.36122-004

          2.7737066-001 -3.3866205-001  7.6907075-001 -1.5761185+000
          9.3987130-001  0.0000000+000  0.0000000+000  0.0000000+000

ID        T,K       MOL/L        CALCD      PCNT           Z       YX        YC       YDIF
99     56.000  5.3300-004  5.3288-004     0.02     0.95458  0.07082  0.07159  -0.00077
99     58.000  8.9930-004  8.9941-004    -0.01     0.90296  0.07289  0.07270   0.00019
99     60.000  1.4640-003  1.4644-003    -0.03     0.85479  0.07505  0.07474   0.00031
99     62.000  2.3057-003  2.3068-003    -0.05     0.80972  0.07792  0.07752   0.00040
99     64.000  3.5233-003  3.5251-003    -0.05     0.76747  0.08123  0.08089   0.00034
99     66.000  5.2367-003  5.2388-003    -0.04     0.72778  0.08497  0.08473   0.00024
99     68.000  7.5880-003  7.5899-003    -0.02     0.69042  0.08906  0.08893   0.00013
99     70.000  1.0742-002  1.0742-002    -0.00     0.65520  0.09343  0.09341   0.00001
99     72.000  1.4885-002  1.4883-002     0.01     0.62194  0.09804  0.09811  -0.00006
99     74.000  2.0227-002  2.0220-002     0.04     0.59048  0.10281  0.10296  -0.00015
99     76.000  2.6996-002  2.6983-002     0.05     0.56067  0.10773  0.10792  -0.00019
99     78.000  3.5441-002  3.5421-002     0.06     0.53239  0.11275  0.11296  -0.00021
99     80.000  4.5831-002  4.5802-002     0.06     0.50552  0.11781  0.11804  -0.00023
99     82.000  5.8449-002  5.8412-002     0.06     0.47996  0.12292  0.12314  -0.00022
99     84.000  7.3595-002  7.3552-002     0.06     0.45562  0.12804  0.12823  -0.00019
99     86.000  9.1589-002  9.1542-002     0.05     0.43242  0.13313  0.13330  -0.00017
99     88.000  1.1276-001  1.1271-001     0.04     0.41026  0.13821  0.13833  -0.00012
99     90.000  1.3745-001  1.3741-001     0.03     0.38910  0.14323  0.14331  -0.00008
99     92.000  1.6603-001  1.6601-001     0.01     0.36885  0.14820  0.14824  -0.00004
99     94.000  1.9887-001  1.9887-001    -0.00     0.34946  0.15311  0.15310   0.00000
99     96.000  2.3637-001  2.3641-001    -0.01     0.33088  0.15794  0.15790   0.00004
99     98.000  2.7894-001  2.7902-001    -0.03     0.31306  0.16270  0.16262   0.00008
99    100.000  3.2702-001  3.2716-001    -0.04     0.29596  0.16738  0.16726   0.00012
99    102.000  3.8108-001  3.8127-001    -0.05     0.27952  0.17196  0.17182   0.00014
99    104.000  4.4162-001  4.4186-001    -0.05     0.26372  0.17645  0.17630   0.00015
99    106.000  5.0914-001  5.0943-001    -0.06     0.24851  0.18086  0.18070   0.00016
99    108.000  5.8421-001  5.8455-001    -0.06     0.23387  0.18518  0.18502   0.00016
99    110.000  6.6747-001  6.6783-001    -0.05     0.21975  0.18940  0.18925   0.00015
99    112.000  7.5953-001  7.5992-001    -0.05     0.20615  0.19355  0.19341   0.00014
99    114.000  8.6121-001  8.6155-001    -0.04     0.19302  0.19759  0.19748   0.00011
99    116.000  9.7325-001  9.7353-001    -0.03     0.18034  0.20156  0.20148   0.00008
99    118.000  1.0965+000  1.0967+000    -0.02     0.16809  0.20545  0.20540   0.00005
99    120.000  1.2321+000  1.2322+000    -0.00     0.15625  0.20926  0.20925   0.00000
99    122.000  1.3812+000  1.3810+000     0.01     0.14480  0.21299  0.21303  -0.00004
99    124.000  1.5450+000  1.5445+000     0.03     0.13372  0.21666  0.21674  -0.00008
99    126.000  1.7250+000  1.7243+000     0.04     0.12299  0.22027  0.22039  -0.00012
99    128.000  1.9230+000  1.9220+000     0.05     0.11259  0.22383  0.22398  -0.00015
99    130.000  2.1411+000  2.1399+000     0.06     0.10252  0.22735  0.22751  -0.00017
99    132.000  2.3819+000  2.3805+000     0.06     0.09275  0.23083  0.23100  -0.00017
99    134.000  2.6483+000  2.6470+000     0.05     0.08327  0.23429  0.23444  -0.00016
99    136.000  2.9444+000  2.9433+000     0.04     0.07407  0.23773  0.23786  -0.00012
99    138.000  3.2750+000  3.2745+000     0.01     0.06514  0.24119  0.24124  -0.00005
99    140.000  3.6468+000  3.6474+000    -0.02     0.05646  0.24468  0.24462   0.00006
99    142.000  4.0692+000  4.0712+000    -0.05     0.04803  0.24819  0.24801   0.00018
99    144.000  4.5552+000  4.5592+000    -0.09     0.03983  0.25176  0.25143   0.00033
99    146.000  5.1261+000  5.1316+000    -0.11     0.03185  0.25536  0.25493   0.00043
99    148.000  5.8177+000  5.8225+000    -0.08     0.02410  0.25892  0.25857   0.00035
99    150.000  6.7056+000  6.6967+000     0.13     0.01654  0.26182  0.26247  -0.00065
99    152.000  7.9239+000  7.9138+000     0.13     0.00919  0.26616  0.26692  -0.00076
99    154.000  1.0225+001  1.0230+001    -0.05     0.00203  0.27367  0.27313   0.00054
              NP = 50, RMSPCT =  0.052
```

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

DATE Sept. 18, 1973

Table 13. Comparison of fluorine vapor densities.

```
                                     E = 0.362

          TCRT = 144.310, TTRP = 53.4811
          DCRT =  15.150, DTRP = 5.67000-004

       2.5715721-001 -2.2706443-001  6.0538644-001 -1.3916332+000
       7.9257188-001  0.0000000+000  0.0000000+000  0.0000000+000

ID       T,K        MOL/L       CALCD      PCNT          Z        YX        YC      YDIF
98    54.000   6.6000-004  6.6001-004  -0.00    0.98473   0.03779   0.03768   0.00010
98    56.000   1.1500-003  1.1518-003  -0.16    0.92853   0.04645   0.04297   0.00348
98    58.000   1.9300-003  1.9272-003   0.14    0.87621   0.04693   0.04877  -0.00184
98    60.000   3.1100-003  3.1038-003   0.20    0.82738   0.05309   0.05493  -0.00184
98    62.000   4.8400-003  4.8291-003   0.23    0.78169   0.05968   0.06135  -0.00167
98    64.000   7.2900-003  7.2821-003   0.11    0.73887   0.06725   0.06792  -0.00067
98    66.000   1.0680-002  1.0675-002   0.05    0.69863   0.07434   0.07459  -0.00026
98    68.000   1.5250-002  1.5253-002  -0.02    0.66077   0.08139   0.08130   0.00009
98    70.000   2.1280-002  2.1293-002  -0.06    0.62507   0.08827   0.08799   0.00028
98    72.000   2.9070-002  2.9105-002  -0.12    0.59135   0.09515   0.09464   0.00051
98    74.000   3.8970-002  3.9029-002  -0.15    0.55945   0.10181   0.10121   0.00060
98    76.000   5.1350-002  5.1434-002  -0.16    0.52923   0.10829   0.10769   0.00060
98    78.000   6.6600-002  6.6713-002  -0.17    0.50057   0.11466   0.11406   0.00060
98    80.000   8.5150-002  8.5291-002  -0.17    0.47333   0.12086   0.12030   0.00056
98    82.000   1.0745-001  1.0761-001  -0.15    0.44742   0.12691   0.12641   0.00050
98    84.000   1.3397-001  1.3416-001  -0.14    0.42275   0.13281   0.13238   0.00044
98    86.000   1.6523-001  1.6541-001  -0.11    0.39923   0.13854   0.13820   0.00034
98    88.000   2.0174-001  2.0191-001  -0.08    0.37677   0.14413   0.14388   0.00025
98    90.000   2.4407-001  2.4420-001  -0.05    0.35532   0.14956   0.14940   0.00015
98    92.000   2.9280-001  2.9286-001  -0.02    0.33479   0.15484   0.15478   0.00006
98    94.000   3.4857-001  3.4852-001   0.01    0.31514   0.15997   0.16001  -0.00004
98    96.000   4.1203-001  4.1184-001   0.05    0.29631   0.16496   0.16509  -0.00013
98    98.000   4.8389-001  4.8352-001   0.08    0.27824   0.16981   0.17003  -0.00021
98   100.000   5.6491-001  5.6432-001   0.10    0.26090   0.17453   0.17482  -0.00029
98   102.000   6.5591-001  6.5507-001   0.13    0.24424   0.17912   0.17947  -0.00035
98   104.000   7.5778-001  7.5667-001   0.15    0.22822   0.18358   0.18398  -0.00040
98   106.000   8.7151-001  8.7012-001   0.16    0.21281   0.18792   0.18836  -0.00044
98   108.000   9.9817-001  9.9651-001   0.17    0.19796   0.19215   0.19261  -0.00046
98   110.000   1.1390+000  1.1371+000   0.17    0.18366   0.19627   0.19673  -0.00046
98   112.000   1.2953+000  1.2932+000   0.16    0.16986   0.20028   0.20072  -0.00044
98   114.000   1.4687+000  1.4666+000   0.15    0.15655   0.20419   0.20460  -0.00041
98   116.000   1.6610+000  1.6590+000   0.12    0.14370   0.20801   0.20836  -0.00035
98   118.000   1.8743+000  1.8725+000   0.09    0.13129   0.21174   0.21200  -0.00027
98   120.000   2.1111+000  2.1099+000   0.06    0.11928   0.21538   0.21554  -0.00016
98   122.000   2.3744+000  2.3741+000   0.01    0.10768   0.21894   0.21898  -0.00004
98   124.000   2.6680+000  2.6690+000  -0.04    0.09644   0.22243   0.22232   0.00011
98   126.000   2.9965+000  2.9992+000  -0.09    0.08556   0.22584   0.22556   0.00027
98   128.000   3.3661+000  3.3709+000  -0.14    0.07503   0.22917   0.22873   0.00045
98   130.000   3.7648+000  3.7921+000  -0.19    0.06481   0.23243   0.23181   0.00062
98   132.000   4.2641+000  4.2739+000  -0.23    0.05491   0.23560   0.23484   0.00076
98   134.000   4.8207+000  4.8319+000  -0.23    0.04530   0.23862   0.23782   0.00081
98   136.000   5.4816+000  5.4905+000  -0.16    0.03598   0.24138   0.24077   0.00061
98   138.000   6.2910+000  6.2909+000   0.00    0.02692   0.24374   0.24375  -0.00000
98   140.000   7.3226+000  7.3133+000   0.13    0.01813   0.24625   0.24683  -0.00058
98   142.000   8.7654+000  8.7644+000   0.24    0.00958   0.24889   0.25023  -0.00133
98   144.000   1.1888+001  1.1893+001  -0.04    0.00127   0.25552   0.25509   0.00044
           NP = 46, RMSPCT =   0.134
```

NATIONAL BUREAU OF STANDARDS, CRYOGENIC ENGINEERING LABORATORY LABORATORY NOTE	PROJECT NO. 2750364	FILE NO. 73-5	PAGE 20
SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine	NAME R.D.Goodwin DATE Sept. 18, 1973		

Table 14. Comparison of methane vapor densities.

```
                                      E = 0.382

          TCRT = 190.555, TTRP = 90.6800
          DCRT =  10.200, DTRP = 1.56787-002

        3.7410143-001 -2.6157309-001  6.7533217-001 -1.0122063+000
        4.3988336-001  0.0000000+000  0.0000000+000  0.0000000+000

ID         T,K       MOL/L          CALCD       PCNT           Z        YX        YC       YDIF
 2      92.000  1.8280-002     1.8280-002       0.00     0.97263   0.21853   0.21874   -0.00021
 2      94.000  2.2860-002     2.2858-002       0.01     0.93261   0.22329   0.22354   -0.00025
 2      96.000  2.8290-002     2.8294-002      -0.01     0.89427   0.22864   0.22828    0.00036
 2      98.000  3.4690-002     3.4691-002      -0.00     0.85749   0.23301   0.23295    0.00006
 2     100.000  4.2160-002     4.2159-002       0.00     0.82218   0.23752   0.23755   -0.00003
 2     102.000  5.0810-002     5.0813-002      -0.01     0.78826   0.24213   0.24207    0.00007
 2     104.000  6.0770-002     6.0772-002      -0.00     0.75564   0.24653   0.24650    0.00003
 2     106.000  7.2160-002     7.2161-002      -0.00     0.72425   0.25086   0.25084    0.00002
 2     108.000  8.5110-002     8.5110-002      -0.00     0.69402   0.25510   0.25510    0.00000
 2     110.000  9.9750-002     9.9753-002      -0.00     0.66490   0.25928   0.25926    0.00002
 2     112.000  1.1623-001     1.1623-001       0.00     0.63681   0.26332   0.26333   -0.00000
 2     114.000  1.3468-001     1.3468-001      -0.00     0.60971   0.26732   0.26730    0.00002
 2     116.000  1.5527-001     1.5527-001       0.00     0.58354   0.27117   0.27119   -0.00002
 2     118.000  1.7814-001     1.7813-001       0.00     0.55826   0.27495   0.27498   -0.00002
 2     120.000  2.0346-001     2.0345-001       0.01     0.53383   0.27864   0.27868   -0.00004
 2     122.000  2.3139-001     2.3138-001       0.00     0.51019   0.28226   0.28228   -0.00003
 2     124.000  2.6212-001     2.6211-001       0.00     0.48732   0.28577   0.28580   -0.00003
 2     126.000  2.9583-001     2.9582-001       0.00     0.46517   0.28921   0.28923   -0.00002
 2     128.000  3.3272-001     3.3271-001       0.00     0.44372   0.29255   0.29257   -0.00002
 2     130.000  3.7299-001     3.7299-001       0.00     0.42292   0.29582   0.29583   -0.00001
 2     132.000  4.1686-001     4.1687-001      -0.00     0.40276   0.29902   0.29900    0.00002
 2     134.000  4.6457-001     4.6461-001      -0.01     0.38320   0.30213   0.30209    0.00004
 2     136.000  5.1638-001     5.1644-001      -0.01     0.36421   0.30515   0.30510    0.00006
 2     138.000  5.7255-001     5.7264-001      -0.02     0.34577   0.30811   0.30803    0.00008
 2     140.000  6.3337-001     6.3351-001      -0.02     0.32786   0.31099   0.31088    0.00011
 2     142.000  6.9916-001     6.9937-001      -0.03     0.31046   0.31380   0.31366    0.00014
 2     144.000  7.7028-001     7.7055-001      -0.04     0.29353   0.31654   0.31637    0.00016
 2     146.000  8.4711-001     8.4745-001      -0.04     0.27708   0.31920   0.31901    0.00019
 2     148.000  9.3007-001     9.3049-001      -0.05     0.26106   0.32179   0.32158    0.00021
 2     150.000  1.0196+000     1.0201+000      -0.05     0.24548   0.32431   0.32409    0.00022
 2     152.000  1.1164+000     1.1169+000      -0.05     0.23030   0.32675   0.32653    0.00022
 2     154.000  1.2209+000     1.2214+000      -0.05     0.21552   0.32912   0.32891    0.00021
 2     156.000  1.3338+000     1.3343+000      -0.04     0.20111   0.33140   0.33123    0.00017
 2     158.000  1.4560+000     1.4563+000      -0.02     0.18707   0.33361   0.33350    0.00011
 2     160.000  1.5884+000     1.5884+000      -0.00     0.17339   0.33571   0.33571    0.00000
 2     162.000  1.7322+000     1.7316+000       0.03     0.16004   0.33772   0.33788   -0.00016
 2     164.000  1.8886+000     1.8870+000       0.08     0.14701   0.33961   0.34000   -0.00039
 2     166.000  2.0593+000     2.0561+000       0.16     0.13430   0.34135   0.34208   -0.00073
 2     168.000  2.2465+000     2.2406+000       0.26     0.12190   0.34291   0.34412   -0.00121
1616   169.067  2.3488+000     2.3463+000       0.11     0.11540   0.34469   0.34520   -0.00051
1614   169.270  2.3687+000     2.3670+000       0.07     0.11417   0.34506   0.34540   -0.00035
 912   169.417  2.3858+000     2.3821+000       0.16     0.11328   0.34480   0.34555   -0.00075
1612   169.468  2.3881+000     2.3873+000       0.03     0.11297   0.34545   0.34560   -0.00015
 910   169.601  2.4054+000     2.4011+000       0.18     0.11217   0.34488   0.34573   -0.00085
 908   169.794  2.4236+000     2.4213+000       0.10     0.11101   0.34547   0.34593   -0.00046
1716   173.088  2.7972+000     2.7964+000       0.03     0.09162   0.34905   0.34920   -0.00015
1714   173.290  2.8203+000     2.8215+000      -0.04     0.09046   0.34961   0.34940    0.00021
```

Table 14 (Continued). Methane vapor densities.

ID	T,K	MOL/L	CALCD	PCNT	Z	YX	YC	YDIF
1712	173.489	2.8457+000	2.8465+000	-0.03	0.08931	0.34973	0.34959	0.00014
1012	173.473	2.8480+000	2.8445+000	0.12	0.08940	0.34896	0.34958	-0.00062
1010	173.675	2.8700+000	2.8701+000	-0.00	0.08824	0.34980	0.34978	0.00002
1008	173.857	2.8935+000	2.8934+000	0.00	0.08720	0.34995	0.34996	-0.00001
1816	177.094	3.3501+000	3.3513+000	-0.03	0.06901	0.35333	0.35315	0.00018
1814	177.292	3.3801+000	3.3822+000	-0.06	0.06792	0.35369	0.35335	0.00034
1114	177.328	3.3863+000	3.3879+000	-0.05	0.06772	0.35364	0.35339	0.00025
1812	177.485	3.4108+000	3.4128+000	-0.06	0.06686	0.35386	0.35354	0.00031
1112	177.509	3.4209+000	3.4166+000	0.12	0.06673	0.35290	0.35357	-0.00067
1110	177.700	3.4602+000	3.4473+000	0.37	0.06568	0.35175	0.35376	-0.00200
1916	181.105	4.0663+000	4.0686+000	-0.06	0.04738	0.35755	0.35722	0.00033
1914	181.304	4.1077+000	4.1101+000	-0.06	0.04633	0.35778	0.35743	0.00034
1213	181.389	4.1269+000	4.1281+000	-0.03	0.04588	0.35769	0.35752	0.00017
1912	181.506	4.1496+000	4.1530+000	-0.08	0.04527	0.35813	0.35765	0.00048
1211	181.589	4.1656+000	4.1708+000	-0.12	0.04483	0.35848	0.35774	0.00074
1209	181.768	4.2042+000	4.2097+000	-0.13	0.04389	0.35870	0.35793	0.00078
1516	183.117	4.5212+000	4.5240+000	-0.06	0.03688	0.35978	0.35940	0.00038
1514	183.322	4.5704+000	4.5754+000	-0.11	0.03582	0.36032	0.35963	0.00069
1512	183.514	4.6189+000	4.6246+000	-0.12	0.03484	0.36063	0.35985	0.00078
1316	184.125	4.7822+000	4.7880+000	-0.12	0.03171	0.36134	0.36055	0.00079
2108	184.087	4.7825+000	4.7775+000	0.10	0.03190	0.35982	0.36051	-0.00068
2107	184.285	4.8263+000	4.8327+000	-0.13	0.03089	0.36161	0.36074	0.00087
1314	184.370	4.8462+000	4.8567+000	-0.22	0.03046	0.36228	0.36084	0.00144
2106	184.471	4.8797+000	4.8857+000	-0.12	0.02994	0.36177	0.36096	0.00081
1312	184.510	4.8876+000	4.8969+000	-0.19	0.02975	0.36228	0.36101	0.00127
6	185.030	5.0380+000	5.0524+000	-0.28	0.02711	0.36359	0.36164	0.00195
6	186.030	5.3840+000	5.3838+000	0.00	0.02208	0.36290	0.36292	-0.00002
2208	186.103	5.4077+000	5.4098+000	-0.04	0.02172	0.36331	0.36302	0.00029
1416	186.129	5.4096+000	5.4192+000	-0.18	0.02159	0.36436	0.36305	0.00131
1414	186.319	5.4795+000	5.4891+000	-0.17	0.02064	0.36461	0.36331	0.00130
2207	186.304	5.4827+000	5.4835+000	-0.01	0.02072	0.36339	0.36329	0.00010
2206	186.501	5.5571+000	5.5581+000	-0.02	0.01974	0.36369	0.36356	0.00013
1412	186.518	5.5591+000	5.5646+000	-0.10	0.01965	0.36434	0.36359	0.00075
6	187.031	5.7860+000	5.7723+000	0.24	0.01711	0.36244	0.36433	-0.00189
6	188.031	6.2750+000	6.2474+000	0.44	0.01219	0.36201	0.36592	-0.00392
2308	188.140	6.2930+000	6.3064+000	-0.21	0.01165	0.36804	0.36612	0.00193
2307	188.343	6.4067+000	6.4218+000	-0.24	0.01066	0.36868	0.36648	0.00219
2306	188.545	6.5278+000	6.5441+000	-0.25	0.00968	0.36926	0.36686	0.00239
6	189.032	6.9180+000	6.8777+000	0.59	0.00732	0.36167	0.36787	-0.00620
5	189.765	7.5510+000	7.5576+000	-0.09	0.00378	0.37093	0.36975	0.00117
6	190.032	7.9600+000	7.9153+000	0.56	0.00250	0.36186	0.37065	-0.00879
5	190.046	7.9350+000	7.9371+000	-0.03	0.00243	0.37113	0.37070	0.00043
7	190.070	8.0000+000	7.9756+000	0.31	0.00232	0.36588	0.37079	-0.00491
7	190.170	8.1700+000	8.1508+000	0.24	0.00184	0.36709	0.37120	-0.00412
7	190.270	8.3600+000	8.3595+000	0.01	0.00136	0.37154	0.37166	-0.00013
5	190.279	8.3920+000	8.3805+000	0.14	0.00132	0.36899	0.37171	-0.00272
7	190.370	8.6200+000	8.6242+000	-0.05	0.00088	0.37333	0.37221	0.00112
7	190.470	9.0000+000	9.0116+000	-0.13	0.00041	0.37689	0.37291	0.00397
5	190.500	9.1610+000	9.1867+000	-0.28	0.00026	0.38333	0.37319	0.01014

NP = 96, RMSPCT = 0.148

Table 15. Comparison of ethane vapor densities.

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        ETHANE SATURATED VAPOR DENSITIES, E = 0.362

          TCRT = 305.330, TTRP = 89.8990
          DCRT =    6.870, DTRP = 1.35114-006

     1.9277432-001  4.1550086-002 -7.8922629-001  3.5766750-001
     1.2454376-001  0.0000000+000  0.0000000+000  0.0000000+000

ID      T,K        MOL/L        CALCD       PCNT          Z        YX         YC        YDIF
 1    90.000   1.3863-006   1.3863-006   0.00     0.99841  -0.07301  -0.07257  -0.00044
 1   100.000   1.3347-005   1.3356-005  -0.07     0.85684  -0.05815  -0.05863   0.00048
 1   110.000   8.1612-005   8.1696-005  -0.10     0.74101  -0.04219  -0.04262   0.00043
 1   120.000   3.5552-004   3.5568-004  -0.04     0.64448  -0.02573  -0.02587   0.00014
 1   130.000   1.1970-003   1.1963-003   0.05     0.56281  -0.00924  -0.00911  -0.00014
 1   140.000   3.3033-003   3.2990-003   0.13     0.49280   0.00698   0.00728  -0.00030
 1   150.000   7.8043-003   7.7918-003   0.16     0.43213   0.02275   0.02309  -0.00034
 1   160.000   1.6308-002   1.6284-002   0.15     0.37904   0.03793   0.03823  -0.00029
 1   170.000   3.0899-002   3.0869-002   0.10     0.33219   0.05247   0.05266  -0.00019
 1   180.000   5.4111-002   5.4094-002   0.03     0.29056   0.06634   0.06639  -0.00006
 1   190.000   8.8911-002   8.8944-002  -0.04     0.25330   0.07952   0.07945   0.00007
 1   200.000   1.3872-001   1.3885-001  -0.09     0.21977   0.09203   0.09186   0.00017
 1   210.000   2.0750-001   2.0777-001  -0.13     0.18943   0.10390   0.10367   0.00024
 1   220.000   2.9992-001   3.0036-001  -0.14     0.16185   0.11517   0.11491   0.00026
 1   230.000   4.2172-001   4.2230-001  -0.14     0.13667   0.12588   0.12563   0.00025
 1   240.000   5.8025-001   5.8088-001  -0.11     0.11359   0.13607   0.13586   0.00021
 1   245.000   6.7626-001   6.7685-001  -0.09     0.10276   0.14098   0.14081   0.00017
 1   250.000   7.8551-001   7.8599-001  -0.06     0.09236   0.14578   0.14566   0.00012
10   253.150   8.6310-001   8.6237-001   0.08     0.08601   0.14848   0.14865  -0.00017
10   263.150   1.1530+000   1.1519+000   0.10     0.06689   0.15771   0.15791  -0.00020
10   273.150   1.5370+000   1.5359+000   0.07     0.04916   0.16665   0.16681  -0.00017
10   283.150   2.0670+000   2.0666+000   0.02     0.03269   0.17533   0.17538  -0.00005
10   293.150   2.8800+000   2.8727+000   0.25     0.01734   0.18285   0.18362  -0.00077
10   298.150   3.5020+000   3.5014+000   0.02     0.01005   0.18755   0.18761  -0.00006
10   302.150   4.3070+000   4.3040+000   0.07     0.00439   0.19036   0.19069  -0.00033
10   303.150   4.6040+000   4.6123+000  -0.18     0.00300   0.19241   0.19143   0.00098
10   304.150   5.0350+000   5.0389+000  -0.08     0.00162   0.19267   0.19214   0.00053
10   305.150   5.9130+000   5.9127+000   0.01     0.00025   0.19268   0.19275  -0.00007
10   305.250   6.1500+000   6.1484+000   0.03     0.00011   0.19233   0.19278  -0.00046
        NP = 29, RMSPCT =  0.104
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PROJECT NO.	FILE NO.	PAGE
2750364	73-5	23

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

DATE Sept. 18, 1973

Table 16. Ethane vapor data not used for least squares.

ID	T,K	MOL/L	CALCD	PCNT	Z	YX	YC	YDIF
1	255.000	9.0997-001	9.1025-001	-0.03	0.08236	0.15046	0.15040	0.00006
1	260.000	1.0522+000	1.0521+000	0.01	0.07275	0.15502	0.15504	-0.00002
1	265.000	1.2154+000	1.2147+000	0.06	0.06351	0.15946	0.15959	-0.00012
1	270.000	1.4041+000	1.4023+000	0.13	0.05460	0.16377	0.16405	-0.00028
1	275.000	1.6245+000	1.6207+000	0.23	0.04602	0.16789	0.16842	-0.00053
1	280.000	1.8861+000	1.8784+000	0.41	0.03775	0.17173	0.17271	-0.00098
1	285.000	2.2047+000	2.1886+000	0.73	0.02977	0.17504	0.17693	-0.00189
1	290.000	2.6107+000	2.5736+000	1.44	0.02206	0.17701	0.18106	-0.00405
6	184.500	6.8910-002	6.8143-002	1.12	0.27329	0.07029	0.07235	-0.00206
6	226.207	3.7705-001	3.7217-001	1.31	0.14596	0.11923	0.12162	-0.00239
6	234.603	4.9353-001	4.9022-001	0.67	0.12581	0.12914	0.13040	-0.00126
6	238.921	5.6437-001	5.6173-001	0.47	0.11599	0.13390	0.13478	-0.00089
6	243.238	6.4280-001	6.4162-001	0.18	0.10652	0.13873	0.13908	-0.00035
6	248.665	7.5717-001	7.5546-001	0.23	0.09509	0.14393	0.14437	-0.00044
6	253.042	8.6348-001	8.5964-001	0.45	0.08623	0.14767	0.14855	-0.00089
6	258.809	1.0219+000	1.0166+000	0.52	0.07501	0.15288	0.15394	-0.00107
6	263.286	1.1611+000	1.1564+000	0.41	0.06664	0.15718	0.15804	-0.00086
6	268.732	1.3571+000	1.3521+000	0.37	0.05683	0.16211	0.16292	-0.00081
6	273.090	1.5403+000	1.5332+000	0.46	0.04926	0.16572	0.16676	-0.00104
6	278.638	1.8108+000	1.8037+000	0.39	0.03997	0.17061	0.17155	-0.00094
6	283.576	2.0862+000	2.0939+000	-0.36	0.03201	0.17666	0.17574	0.00092
6	288.254	2.4115+000	2.4286+000	-0.70	0.02472	0.18155	0.17963	0.00193
11	283.200	2.0685+000	2.0698+000	-0.06	0.03261	0.17558	0.17542	0.00016
11	288.190	2.4160+000	2.4235+000	-0.31	0.02482	0.18042	0.17957	0.00085
11	293.180	2.8716+000	2.8758+000	-0.15	0.01729	0.18409	0.18365	0.00045
11	295.670	3.1543+000	3.1589+000	-0.14	0.01363	0.18612	0.18565	0.00048
11	298.170	3.5002+000	3.5045+000	-0.12	0.01002	0.18807	0.18763	0.00044
11	300.660	3.9408+000	3.9499+000	-0.23	0.00648	0.19052	0.18956	0.00096
11	302.160	4.2943+000	4.3067+000	-0.29	0.00438	0.19208	0.19070	0.00138
11	303.160	4.6053+000	4.6158+000	-0.23	0.00299	0.19269	0.19144	0.00125
11	304.150	5.0203+000	5.0389+000	-0.37	0.00162	0.19464	0.19214	0.00250
11	304.650	5.3276+000	5.3544+000	-0.50	0.00093	0.19659	0.19247	0.00412
11	305.150	5.8663+000	5.9127+000	-0.78	0.00025	0.20313	0.19275	0.01038

Table 17. Calculated oxygen vapor densities.

T,K	R,MOL/L	DR/DT	D2R/DT2
54.351	3.3612-004	9.6727-005	2.4354-005
56.000	5.3288-004	1.4452-004	3.4007-005
58.000	8.9941-004	2.2709-004	4.9253-005
60.000	1.4644-003	3.4449-004	6.8929-005
62.000	2.3068-003	5.0609-004	9.3527-005
64.000	3.5251-003	7.2213-004	1.2342-004
66.000	5.2388-003	1.0035-003	1.5884-004
68.000	7.5899-003	1.3613-003	1.9990-004
70.000	1.0742-002	1.8068-003	2.4655-004
72.000	1.4883-002	2.3511-003	2.9868-004
74.000	2.0220-002	3.0050-003	3.5605-004
76.000	2.6983-002	3.7786-003	4.1840-004
78.000	3.5421-002	4.6817-003	4.8543-004
80.000	4.5802-002	5.7233-003	5.5684-004
82.000	5.8412-002	6.9118-003	6.3239-004
84.000	7.3552-002	8.2554-003	7.1185-004
86.000	9.1542-002	9.7617-003	7.9510-004
88.000	1.1271-001	1.1438-002	8.8208-004
90.000	1.3741-001	1.3293-002	9.7286-004
92.000	1.6601-001	1.5332-002	1.0676-003
94.000	1.9887-001	1.7566-002	1.1666-003
96.000	2.3641-001	2.0002-002	1.2703-003
98.000	2.7902-001	2.2651-002	1.3793-003
100.000	3.2716-001	2.5523-002	1.4944-003
102.000	3.8127-001	2.8633-002	1.6164-003
104.000	4.4186-001	3.1994-002	1.7466-003
106.000	5.0943-001	3.5626-002	1.8865-003
108.000	5.8455-001	3.9548-002	2.0377-003
110.000	6.6783-001	4.3785-002	2.2023-003
112.000	7.5992-001	4.8368-002	2.3830-003
114.000	8.6155-001	5.3330-002	2.5829-003
116.000	9.7353-001	5.8715-002	2.8059-003
118.000	1.0967+000	6.4572-002	3.0569-003
120.000	1.2322+000	7.0965-002	3.3422-003
122.000	1.3810+000	7.7969-002	3.6695-003
124.000	1.5445+000	8.5678-002	4.0493-003
126.000	1.7243+000	9.4210-002	4.4951-003
128.000	1.9220+000	1.0371-001	5.0254-003
130.000	2.1399+000	1.1438-001	5.6657-003
132.000	2.3805+000	1.2647-001	6.4520-003
134.000	2.6470+000	1.4032-001	7.4368-003
136.000	2.9433+000	1.5641-001	8.6997-003
138.000	3.2745+000	1.7539-001	1.0366-002
140.000	3.6474+000	1.9828-001	1.2644-002
142.000	4.0712+000	2.2661-001	1.5903-002
144.000	4.5592+000	2.6300-001	2.0854-002
146.000	5.1316+000	3.1214-001	2.9031-002
148.000	5.8225+000	3.8373-001	4.4334-002
150.000	6.6967+000	5.0204-001	7.9575-002
152.000	7.9138+000	7.5420-001	2.0346-001
154.000	1.0230+001	2.0822+000	2.4109+000
154.576	1.3630+001	0.0000+000	0.0000+000

Table 18. Calculated fluorine vapor densities.

T,K	R,MOL/L	DR/DT	D2R/DT2
53.481	5.6700-004	1.6771-004	4.2852-005
54.000	6.6001-004	1.9119-004	4.7718-005
56.000	1.1518-003	3.0817-004	7.0323-005
58.000	1.9272-003	4.7699-004	9.9683-005
60.000	3.1038-003	7.1188-004	1.3650-004
62.000	4.8291-003	1.0283-003	1.8127-004
64.000	7.2821-003	1.4424-003	2.3426-004
66.000	1.0675-002	1.9709-003	2.9554-004
68.000	1.5253-002	2.6301-003	3.6499-004
70.000	2.1293-002	3.4361-003	4.4236-004
72.000	2.9105-002	4.4046-003	5.2731-004
74.000	3.9029-002	5.5501-003	6.1945-004
76.000	5.1434-002	6.8869-003	7.1844-004
78.000	6.6713-002	8.4282-003	8.2395-004
80.000	8.5291-002	1.0187-002	9.3580-004
82.000	1.0761-001	1.2176-002	1.0539-003
84.000	1.3416-001	1.4407-002	1.1783-003
86.000	1.6541-001	1.6893-002	1.3094-003
88.000	2.0191-001	1.9649-002	1.4475-003
90.000	2.4420-001	2.2689-002	1.5935-003
92.000	2.9286-001	2.6029-002	1.7482-003
94.000	3.4852-001	2.9688-002	1.9129-003
96.000	4.1184-001	3.3688-002	2.0893-003
98.000	4.8352-001	3.8054-002	2.2793-003
100.000	5.6432-001	4.2816-002	2.4854-003
102.000	6.5507-001	4.8009-002	2.7105-003
104.000	7.5667-001	5.3674-002	2.9585-003
106.000	8.7012-001	5.9861-002	3.2339-003
108.000	9.9651-001	6.6631-002	3.5426-003
110.000	1.1371+000	7.4058-002	3.8918-003
112.000	1.2932+000	8.2232-002	4.2910-003
114.000	1.4666+000	9.1264-002	4.7523-003
116.000	1.6590+000	1.0129-001	5.2919-003
118.000	1.8725+000	1.1250-001	5.9315-003
120.000	2.1099+000	1.2511-001	6.7013-003
122.000	2.3741+000	1.3942-001	7.6437-003
124.000	2.6690+000	1.5584-001	8.8210-003
126.000	2.9992+000	1.7492-001	1.0328-002
128.000	3.3709+000	1.9746-001	1.2313-002
130.000	3.7921+000	2.2465-001	1.5026-002
132.000	4.2739+000	2.5834-001	1.8913-002
134.000	4.8319+000	3.0165-001	2.4841-002
136.000	5.4905+000	3.6028-001	3.4720-002
138.000	6.2909+000	4.4628-001	5.3532-002
140.000	7.3133+000	5.9079-001	9.8476-002
142.000	8.7644+000	9.1469-001	2.7251-001
144.000	1.1893+001	3.5620+000	7.7289+000
144.310	1.5150+001	0.0000+000	0.0000+000

Table 19. Calculated methane vapor densities.

T,K	R,MOL/L	DR/DT	D2R/DT2
90.680	1.5679-002	1.8523-003	1.7385-004
92.000	1.8280-002	2.0919-003	1.8937-004
94.000	2.2858-002	2.4952-003	2.1409-004
96.000	2.8294-002	2.9492-003	2.4020-004
98.000	3.4691-002	3.4569-003	2.6763-004
100.000	4.2159-002	4.0206-003	2.9634-004
102.000	5.0813-002	4.6430-003	3.2628-004
104.000	6.0772-002	5.3265-003	3.5744-004
106.000	7.2161-002	6.0736-003	3.8980-004
108.000	8.5110-002	6.8866-003	4.2339-004
110.000	9.9753-002	7.7680-003	4.5823-004
112.000	1.1623-001	8.7204-003	4.9439-004
114.000	1.3468-001	9.7465-003	5.3195-004
116.000	1.5527-001	1.0849-002	5.7100-004
118.000	1.7813-001	1.2032-002	6.1170-004
120.000	2.0345-001	1.3297-002	6.5420-004
122.000	2.3138-001	1.4650-002	6.9870-004
124.000	2.6211-001	1.6093-002	7.4545-004
126.000	2.9582-001	1.7633-002	7.9471-004
128.000	3.3271-001	1.9274-002	8.4681-004
130.000	3.7299-001	2.1023-002	9.0214-004
132.000	4.1687-001	2.2885-002	9.6113-004
134.000	4.6461-001	2.4870-002	1.0243-003
136.000	5.1644-001	2.6986-002	1.0922-003
138.000	5.7264-001	2.9242-002	1.1657-003
140.000	6.3351-001	3.1652-002	1.2454-003
142.000	6.9937-001	3.4229-002	1.3325-003
144.000	7.7055-001	3.6988-002	1.4280-003
146.000	8.4745-001	3.9948-002	1.5335-003
148.000	9.3049-001	4.3130-002	1.6506-003
150.000	1.0201+000	4.6559-002	1.7815-003
152.000	1.1169+000	5.0267-002	1.9288-003
154.000	1.2214+000	5.4288-002	2.0957-003
156.000	1.3343+000	5.8665-002	2.2865-003
158.000	1.4563+000	6.3453-002	2.5065-003
160.000	1.5884+000	6.8715-002	2.7627-003
162.000	1.7316+000	7.4534-002	3.0643-003
164.000	1.8870+000	8.1011-002	3.4240-003
166.000	2.0561+000	8.8280-002	3.8592-003
168.000	2.2408+000	9.6514-002	4.3945-003
170.000	2.4430+000	1.0595-001	5.0661-003
172.000	2.6656+000	1.1691-001	5.9289-003
174.000	2.9119+000	1.2985-001	7.0695-003
176.000	3.1867+000	1.4546-001	8.6322-003
178.000	3.4963+000	1.6482-001	1.0873-002
180.000	3.8497+000	1.8973-001	1.4288-002
182.000	4.2610+000	2.2344-001	1.9949-002
184.000	4.7537+000	2.7274-001	3.0592-002
186.000	5.3730+000	3.5464-001	5.5251-002
188.000	6.2307+000	5.3071-001	1.4281-001
190.000	7.8668+000	1.4868+000	1.7833+000
190.555	1.0200+001	0.0000+000	0.0000+000

Table 20. Calculated ethane vapor densities.

ETHANE SATURATED VAPOR DENSITIES

T,K	R,MOL/L	DR/DT	D2R/DT2
89.899	1.3511-006	3.4418-007	7.9422-008
90.000	1.3863-006	3.5229-007	8.1081-008
95.000	4.5944-006	1.0378-006	2.1037-007
100.000	1.3356-005	2.6924-006	4.8256-007
105.000	3.4683-005	6.2648-006	9.9665-007
110.000	8.1696-005	1.3276-005	1.8818-006
115.000	1.7684-004	2.5955-005	3.2903-006
120.000	3.5568-004	4.7323-005	5.3851-006
125.000	6.7091-004	8.1216-005	8.3256-006
130.000	1.1963-003	1.3223-004	1.2254-005
135.000	2.0304-003	2.0559-004	1.7283-005
140.000	3.2990-003	3.0703-004	2.3493-005
145.000	5.1575-003	4.4257-004	3.0926-005
150.000	7.7918-003	6.1835-004	3.9592-005
155.000	1.1418-002	8.4051-004	4.9474-005
160.000	1.6284-002	1.1151-003	6.0539-005
165.000	2.2666-002	1.4478-003	7.2744-005
170.000	3.0869-002	1.8443-003	8.6050-005
175.000	4.1225-002	2.3101-003	1.0043-004
180.000	5.4094-002	2.8504-003	1.1588-004
185.000	6.9862-002	3.4707-003	1.3243-004
190.000	8.8944-002	4.1767-003	1.5014-004
195.000	1.1178-001	4.9742-003	1.6912-004
200.000	1.3885-001	5.8703-003	1.8956-004
205.000	1.7066-001	6.8727-003	2.1170-004
210.000	2.0777-001	7.9907-003	2.3587-004
215.000	2.5078-001	9.2355-003	2.6252-004
220.000	3.0036-001	1.0621-002	2.9224-004
225.000	3.5725-001	1.2164-002	3.2581-004
230.000	4.2230-001	1.3887-002	3.6425-004
235.000	4.9647-001	1.5817-002	4.0894-004
240.000	5.8088-001	1.7990-002	4.6176-004
245.000	6.7685-001	2.0453-002	5.2532-004
250.000	7.8599-001	2.3267-002	6.0330-004
255.000	9.1025-001	2.6519-002	7.0116-004
260.000	1.0521+000	3.0325-002	8.2712-004
265.000	1.2147+000	3.4858-002	9.9430-004
270.000	1.4023+000	4.0373-002	1.2246-003
275.000	1.6207+000	4.7273-002	1.5572-003
280.000	1.8784+000	5.6239-002	2.0691-003
285.000	2.1886+000	6.8532-002	2.9298-003
290.000	2.5736+000	8.6820-002	4.5876-003
295.000	3.0777+000	1.1813-001	8.6241-003
300.000	3.8180+000	1.9083-001	2.5135-002
305.000	5.6889+000	1.2377+000	2.4827+000
305.330	6.8700+000	0.0000+000	0.0000+000

NATIONAL BUREAU OF STANDARDS, CRYOGENIC ENGINEERING LABORATORY
LABORATORY NOTE

PROJECT NO.	FILE NO.	PAGE
2750364	73-5	28

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

DATE Sept. 18, 1973

10/10/73

```
       PROGRAM LICKFIT
C     REPRESENT ETHANE SATURATED LIQUID DENSITIES.
C     DEFINE X = (TC-T)/TC-TT),  Q = X**1/3,  XE = X**E,  AND -
C     DEFINE  YY = (D-DC)/(DT-DC),  WHEN THE EQN. IS -
C     (YY-X)/(XE-X) = A1 + A2*Q2 + A3*Q3 + . . .
C     DCRT = 6.86, 6.87 POSSIBLY VIA MY VAPORDEN EQN.
C     DTRP = 21.68 ESTIM. VIA REID C. MILLER.
C     ID, (9)TESTER, (10)DOUSLIN, (11)SLIWINSKI, (12)CANFIELD ET AL.,
C     ID, (13)KLOSEK, (14)MILLER, (15)EUBANK, (16)TOMLINSON
       COMMON E,AZ,TTRP,TCRT,DTRP,DCRT, DRDT,D2RDT2, A(6)
       COMMON/999/NP,NF,H(15),Y(200),G(200,15)
       DIMENSION ID(99),T(99),DEN(99), U(99),W(99),XQ(99)
     1 FORMAT(I5, 2F10.0)
     2 FORMAT(1H1 13X 1HE 8X2HAZ 6X4HDCRT 8X2HSS)
     3 FORMAT(5X 4F10.3)
     4 FORMAT(1H1 17X *ETHANE SATURATED LIQUID DENSITIES, E =* F6.3//
      1 20X 6HTCRT =F8.3, 8H, TTRP =F8.4//
      2 20X 6HDCRT =F8.3, 8H, DTRP =F8.4// 2(13X 3E15.7/) /
      3 8X2HID 7X3HT,K 5X5HMOL/L 6X4HCALC 4X4HPCNT
      4 14X 1HX 8X2HYX 8X2HYC 6X4HYDIF )
     5 FORMAT(5X I5, 3F10.3, F8.2, F15.5, 3F10.5)
     6 FORMAT(1H1 16X *ETHANE SATURATED LIQUID DENSITIES* //
      1 17X 3HT,K 3X7HR,MOL/L 5X5HDR/DT 3X7HD2R/DT2 )
     7 FORMAT(10X 2F10.3, F10.4, F10.5)
     9 FORMAT(18X 4HNP =I3, 10H, RMSPCT =F7.3/)
C
C     DO ALL FOUR,  OXYGEN, FLUORINE, METHANE, AND ETHANE.
    10 DO 99 IG=1,4  $  GOTO(11,13,15,17),IG
C     CONSTANTS FOR OXYGEN.
    11 TTRP=54.3507 $ TCRT=154.576 $ TZ=52 $ DT=2 $ NZ=52
    12 DTRP=40.83 $ DCRT=13.63 $ DZ=13.58 $ EZ=0.340  $  GOTO 19
C     CONSTANTS FOR FLUORINE.
    13 TTRP=53.4811 $ TCRT=144.31 $ TZ=50 $ DT=2 $ NZ=48
    14 DTRP=44.6623 $ DCRT=15.15 $ DZ=15.10 $ EZ=0.342 $ GOTO 19
C     CONSTANTS FOR METHANE.
    15 TTRP=90.680 $ TCRT=190.555 $ TZ=88 $ DT=2 $ NZ=52
    16 DTRP=28.147      $ DCRT=10.20 $ DZ=10.05 $ EZ=0.350 $ GOTO 19
C     CONSTANTS FOR ETHANE.
    17 TTRP=89.899 $ TCRT=305.33 $ TZ=80 $ DT=5 $ NZ=46
    18 DTRP=21.68 $ DCRT= 6.87 $ DZ= 6.82 $ EZ=0.349
    19 XN = TCRT-TTRP  $  YN = DTRP-DCRT
C     READ NP DATA FOR LEAST SQUARES.
C     READ L.A.WEBER S  OXYGEN VOLUMES, CC/MOL.
    20 DO 27 J=1,99  $  READ 1, ID(J),T(J),DEN(J)  $  IF(ID(J)) 21,28
    21 IF(ID(J)-15) 23,22
    22 CONTINUE
    23 IF(ID(J)-99) 25,24
    24 DEN(J) = 1000/DEN(J)
    25 U(J) = X = (TCRT-T(J))/XN  $  Q = CUBERTF(X)  $  DO 26 K=2,6
    26 G(J,K) = Q**K  $  G(J,1) = 1
    27 W(J) = (DEN(J)-DCRT)/YN
    28 NPP = NP = J-1  $  NF = 3  $  E = 0.36
C     EXPLORE E, AZ, AND DCRT.
    29 AZ = NF  $  SSK = 1.0E+010
    30 DO 49 IE=1,21  $  E = EZ + 0.001*IE
```

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      LICKFIT                                                 10/10/73

C     SET UP THE LEAST SQUARES ARRAYS.
   36 DO 40 J=1,NP  $  X = U(J)  $  XQ(J) = XE = X**E
   37 Y(J) = (W(J)-X)/(XE-X)
   40 CONTINUE $ CALL EGENFT $ SS=0 $ DO 43 J=1,NP $ YC=0 $ DO 41 K=1,NF
   41 YC = YC + H(K)*G(J,K)  $  X = U(J)  $  XE = XQ(J)
   42 DC = DCRT + (X + (XE-X)*YC)*YN
   43 SS = SS + (DEN(J)/DC-1)**2  $  SS = 100*SQRTF(SS/NP)
   44 IF(SS.LT.SSK) 45,48
   45 SSK=SS $ EK=E $ AZK=AZ $ DK=DCRT
   46 DO 47 K=1,6
   47 A(K) = H(K)
   48 CONTINUE
   49 CONTINUE
   50 E=EK $ AZ=AZK $ DCRT=DK  $  YN = DTRP - DCRT
C     USE SAVED CONSTANTS FOR DEVIATIONS.
   60 PRINT 4, E,TCRT,TTRP,DCRT,DTRP,(A(K),K=1,6)  $  SS = 0
   61 DO 70 J=1,NPP  $  X = U(J)  $  XE = X**E  $  XEX = XE-X
   62 YC = 0  $  DO 63 K=1,NF
   63 YC = YC + A(K)*G(J,K)
   64 YS = X + XEX*YC  $  DC = DCRT + YN*YS
   65 YX = (W(J)-X)/XEX  $  YD = YX-YC
   66 PCT = 100*(DEN(J)/DC-1)  $  SS = SS + PCT**2
   67 PRINT 5, ID(J),T(J),DEN(J), DC,PCT, X,YX,YC,YD
   68 IF(J-NP) 70,69
   69 SS = SQRTF(SS/NP)  $  PRINT 9, NP, SS
   70 CONTINUE
C     PRINT UNIFORM TABLE FOR PUBLICATION.
   71 PRINT 6  $  DO 80 J=1,NZ  $  IF(J-1) 73,72
   72 TT = TTRP  $  GO TO 76
   73 IF(J-NZ) 75,74
   74 TT = TCRT  $  GO TO 76
   75 TT = TZ + DT*J
   76 R = DENLIQF(TT)
   80 PRINT 7, TT,R,DRDT,D2RDT2
   99 CONTINUE
C     DO OTHER ETHANE DATA WITH EXISTING COEFFICIENTS.
  100 PRINT 4, E,TCRT,TTRP,DCRT,DTRP,(A(K),K=1,6)  $  SS = 0
  101 DO 110 J=1,99  $  READ 1, IDD,TT,DN  $  IF(IDD) 102,999
  102 X=(TCRT-TT)/XN $ Q=CUBERTF(X) $ XE=X**E $ XEX=XE-X
  103 YC = A(1)  $  DO 104 K=2,NF
  104 YC = YC + A(K)*Q**K
  105 DC = DCRT + YN*(X+XEX*YC)  $  PCT = 100*(DN/DC-1)
  106 YY = (DN-DCRT)/YN  $  YX = (YY-X)/XEX  $  YD = YX-YC
  110 PRINT 5, IDD,TT,DN, DC,PCT, X,YX,YC,YD
  999 STOP  $  END
```

10/10/73

```
      PROGRAM VAPORFIT
C    REPRESENT ETHANE SATURATED VAPOR DENSITIES.
C    THIS FORM IS CONSTRAINED AT THE TRIPLE POINT, AND
C    DEFINE X(T) AS FOR THE VAPOR PRESSURE EQUATION -
C    Z = (1-X) = (TC/T-1)/(TC/TT-1),  ZE = Z**E, Q = Z**1/3,  AND -
C    DEFINE YY = LN(DC/D)/LN(DC/DT), AND THE DEPENDENT VARIABLE -
C    Y(Z,YY) = (YY-Z)/(ZE-Z),  WHEN THE L.S. EQN. IS -
C    Y(Z,YY) = A1 + A2*Q2 + A3*Q3 + A4*Q4 + . . .
C    ID., (1)VIRIAL/V.P., (6)PORTER, (10)DOUSLIN, (11)SLIWINSKI.
      COMMON E,AL, TTRP,TCRT, DTRP,DCRT, DRDT,D2RDT2, A(9)
      COMMON/999/NP,NF,H(15),Y(200),G(200,15)
      DIMENSION ID(99),T(99),DEN(99), U(99),W(99), ZQ(99)
    1 FORMAT(I5, F10.0, E15.5)
    2 FORMAT(1H1 18X 1HE 8X2HAL 6X4HDCRT 8X2HSS)
    3 FORMAT(10X 4F10.3)
    4 FORMAT(1H1 17X *ETHANE SATURATED VAPOR DENSITIES, E =* F6.3//
     1 20X   6HTCRT =F8.3, 8H, TTRP =F8.4/
     2 20X   6HDCRT =F8.3, 8H, DTRP =E12.5// 2(13X 4E15.7/) /
     2 8X2HID 7X3HT,K 8X5HMOL/L 8X5HCALCD 4X4HPCNT
     3 12X 1HZ 8X2HYX 8X2HYC 6X4HYDIF )
    5 FORMAT(5X I5, F10.3, 2E13.4, F8.2, F13.5, 3F10.5)
    6 FORMAT(I5, 2F10.0)
    7 FORMAT(1H1 16X *ETHANE SATURATED VAPOR DENSITIES* //
     1 17X 3HT,K 6X7HR,MOL/L 8X5HDR/DT 6X7HD2R/DT2 )
    8 FORMAT(10X F10.3, 3E13.4)
    9 FORMAT(18X 4HNP =I3, 10H, RMSPCT =F7.3/)
   61 FORMAT(1H1 7X2HID 7X3HT,K 8X5HMOL/L 8X5HCALCD 4X4HPCNT
     1 12X 1HZ 8X2HYX 8X2HYC 6X4HYDIF )
C
C    DO ALL FOUR, OXYGEN, FLUORINE, METHANE, ETHANE.
   10 DO 81 IG=1,4  $  GOTO(11,13,15,17),IG
C    CONSTANTS FOR OXYGEN.
   11 TTRP=54.3507 $ TCRT=154.576 $ TZ=52 $ DT=2 $ NZ=52
   12 DTRP=3.36122E-4 $ DCRT=13.63 $ DZ=13.58 $ EZ=0.360 $ GOTO 19
C    CONSTANTS FOR FLUORINE.
   13 TTRP=53.4811 $ TCRT=144.31 $ TZ=50 $ DT=2 $ NZ=48
   14 DTRP=5.670E-4 $ DCRT=15.15 $ DZ=15.10 $ EZ=0.340   $  GOTO 19
C    CONSTANTS FOR METHANE.
   15 TTRP=90.680 $ TCRT=190.555 $ TZ=88 $ DT=2 $ NZ=52
   16 DTRP=0.01567865 $ DCRT=10.20 $ DZ=10.05 $ EZ=0.360 $ GOTO 19
C    CONSTANTS FOR ETHANE.
C    OMIT 24, AND FIX DTRP.
   17 TTRP=89.899 $ TCRT=305.33 $ TZ=80 $ DT=5 $ NZ=46
   18 DTRP=       1.35114E-6 $ DCRT=6.87 $ DZ=6.84 $ EZ=0.340
   19 ZN = TCRT/TTRP-1  $  YN = LOGF(DCRT/DTRP)
C    READ OUR ID(1) DATA MIXED WITH DOUSLIN.
C    INCREASE OUR DEN BY 0.15 PCT TO AGREE WITH DOUSLIN.
   20 DO 27 J=1,200  $  IF(IG-4) 22,21
   21 READ 1, ID(J),T(J),DEN(J)  $  IF(ID(J)) 23,28
   22 READ 6, ID(J),T(J),DEN(J)  $  IF(ID(J)) 25,28
   23 IF(ID(J)-1) 25,24
   24 CONTINUE
   25 U(J) = Z = (TCRT/T(J)-1)/ZN  $  Q = CUBERTF(Z)  $  DO 26 K=2,7
   26 G(J,K) = Q**K  $  G(J,1) = 1
   27 W(J) = LOGF(DCRT/DEN(J))/YN
```

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      VAPORFIT                                                  10/10/73

   28 NP = J-1  $  AL = NF = 5  $  E = 0.360
C     EXPLORE DCRT, AND EXPONENT E.
   33 SSK = 1.0E+010
   34 DO 48 IE=1,21  $  E = EZ + 0.002*IE
C     SET UP THE ARRAYS FOR LEAST SQUARES.
   36 DO 39 J=1,NP  $  Z = U(J)  $  ZQ(J) = ZE = Z**E
   37 Y(J) = (W(J)-Z)/(ZE-Z)
   39 CONTINUE  $  CALL EGENFT  $  SS = 0
C     NOW GET THE RMS DEVIATION.
   40 DO 44 J=1,NP  $  YC = 0  $  DO 41 K=1,NF
   41 YC = YC + H(K)*G(J,K)
   42 Z = U(J)  $  YS = Z + (ZQ(J)-Z)*YC
   43 DC = DCRT*EXPF(-YN*YS)
   44 SS = SS + (DC/DEN(J)-1)**2  $  SS = 100*SQRTF(SS/NP)
   45 IF(SS.LT.SSK) 46,48
   46 SSK=SS $ EK=E $ ALK=AL $ DK=DCRT  $  DO 47 K=1,9
   47 A(K) = H(K)
   48 CONTINUE
   49 E=EK $ AL=ALK $ DCRT=DK  $  YN = LOGF(DK/DTRP)
C     USE SAVED CONSTANTS FOR DEVIATIONS.
   50 PRINT 4, E,TCRT,TTRP,DCRT,DTRP,(A(K),K=1,8)  $  SS = 0
   51 DO 59 J=1,NP  $  Z = U(J)  $  ZE = Z**E  $  ZEZ = ZE - Z
   52 YC = 0  $  DO 53 K=1,NF
   53 YC = YC + A(K)*G(J,K)
   54 YS = Z + ZEZ*YC  $  DC = DCRT*EXPF(-YN*YS)
   55 YX = (W(J)-Z)/ZEZ  $  YD = YX - YC
   56 PCT = 100*(DEN(J)/DC-1)  $  SS = SS + PCT**2
   57 IF(IG.EQ.3.AND.J.EQ.48) 58,59
   58 PRINT 61
   59 PRINT 5, ID(J),T(J),DEN(J), DC,PCT, Z,YX,YC,YD
   60 SS = SQRTF(SS/NP)  $  PRINT 9, NP, SS
C     PRINT UNIFORM TABLE FOR PUBLICATION.
   71 PRINT 7  $  DO 80 J=1,NZ  $  IF(J-1) 73,72
   72 TT = TTRP  $  GO TO 76
   73 IF(J-NZ) 75,74
   74 TT = TCRT  $  GO TO 76
   75 TT = TZ + DT*J
   76 R = DENGASF(TT)
   80 PRINT 8, TT,R, DRDT, D2RDT2
   81 CONTINUE  $  PRINT 61
C     DO OTHER ETHANE DATA WITH EXISTING COEFFICIENTS.
   82 DO 88 J=1,99  $  READ 6, IDD,TT,DN  $  IF(IDD) 83,99
   83 Z = (TCRT/TT-1)/ZN  $  ZE = Z**E  $  ZEZ = ZE - Z
   84 Q = CUBERTF(Z)  $  YC = A(1)  $  DO 85 K=2,NF
   85 YC = YC + A(K)*Q**K
   86 YY = LOGF(DCRT/DN)/YN  $  YX = (YY-Z)/ZEZ  $  YD = YX-YC
   87 DC = DCRT*EXPF(-YN*(Z+ZEZ*YC))  $  PCT = 100*(DN/DC-1)
   88 PRINT 5, IDD,TT,DN, DC,PCT, Z,YX,YC,YD
   99 STOP  $  END
```

SUBJECT The Orthobaric Densities of Ethane, Methane, Oxygen and Fluorine

NAME R.D.Goodwin

DATE Sept. 18, 1973

```
                                                    10/10/73

      FUNCTION DENLIQF(T)
C     ETHANE SATURATED LIQUID DENSITIES, MOL/L.
C     Y = A1 + A2*Q2 + A3*Q3 + . . . ,  YN = DTRP-DCRT,
C     DEN = DCRT + YN*(X + (XE-X)*Y).
      COMMON E,AZ,TTRP,TCRT,DTRP,DCRT, DRDT,D2RDT2, A(6)
    1 FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT. * / )
    2 IF(TCRT-T) 3,4,5
    3 PRINT 1   $   STOP
    4 DENLIQF=DCRT  $  DRDT=D2RDT2=0  $  RETURN
    5 XN=TCRT-TTRP $ YN=DTRP-DCRT $ X=(TCRT-T)/XN $ DXDT=-1/XN
    6 XE = X**E  $  XE1 = E*XE/X  $  XE2 = (E-1)*XE1/X
    7 W = CUBERTF(X)  $  W1 = W/3/X  $  W2 = -2*W1/3/X
    8 Q = XE-X  $  Q1 = XE1 - 1  $  Q2 = XE2
    9 NF = AZ  $  Y = A(1)  $  Y1 = Y2 = 0  $  DO 11 K=2,NF
   10 Y = Y + A(K)*W**K  $  Y1 = Y1 + K*A(K)*W**(K-1)
   11 Y2 = Y2 + K*(K-1)*A(K)*W**(K-2)
   12 Y2 = Y1*W2 + Y2*W1**2  $  Y1 = Y1*W1
   13 DENLIQF = DCRT + (X + Q*Y)*YN
   14 DRDT = (1 + Q*Y1 + Q1*Y)*YN*DXDT
   15 D2RDT2 = (Q*Y2 + 2*Q1*Y1 + Q2*Y)*YN*DXDT**2  $  RETURN  $  END
```

```
                                                    10/10/73

      FUNCTION DENGASF(T)
C     ETHANE SATURATED VAPOR DENSITIES, MOL/L.
C     Y = A1 + A2*Q2 + A3*Q3 + . . ,  NF = AL,  YN = LN(DCRT/DTRP),
C     U = Z + (ZE-Z)*Y,   DEN = DCRT*EXP(-YN*U).
C     NOTE THAT Z = 0 ONLY AT T = TCRT, WHICH IS EXCLUDED.
      COMMON E,AL, TTRP,TCRT, DTRP,DCRT, DRDT,D2RDT2, A(9)
    1 FORMAT(1H0 9X *DENGASF = 0, T EXCEEDS TCRT. * / )
    2 IF(TCRT-T) 3,4,5
    3 PRINT 1  $  STOP
    4 DENGASF = DCRT  $  DRDT = D2RDT2 = 0  $  RETURN
    5 ZN=TCRT/TTRP-1  $  YN=LOGF(DCRT/DTRP) $  Z=(TCRT/T-1)/ZN
    6 DZDT = -TCRT/ZN/T**2  $  D2ZDT2 = -2*DZDT/T
    7 ZE = Z**E  $  ZE1 = E*ZE/Z  $  ZE2 = (E-1)*ZE1/Z
    8 X = ZE-Z  $  X1 = ZE1 - 1  $  X2 = ZE2
    9 Q = CUBERTF(Z)  $  Q1 = Q/3/Z  $  Q2 = -2*Q1/3/Z
   10 NF = AL  $  Y = A(1)  $  Y1 = Y2 = 0  $  DO 13 K=2,NF
   11 Y = Y + A(K)*Q**K
   12 Y1 = Y1 + K*A(K)*Q**(K-1)
   13 Y2 = Y2 + K*(K-1)*A(K)*Q**(K-2)
   14 Y2 = Y1*Q2 + Y2*Q1**2  $  Y1 = Y1*Q1
   15 U = Z + X*Y  $  UA = 1 + X*Y1 + X1*Y  $  U1 = UA*DZDT
   16 U2 = UA*D2ZDT2 + (X*Y2 + 2*X1*Y1 + X2*Y)*DZDT**2
   17 XP = EXPF(-YN*U)  $  DENGASF = F = DCRT*XP  $  YU = -YN*U1
   18 DRDT = YU*F  $  D2RDT2 = (YU*YU-YN*U2)*F  $  RETURN  $  END
```

APPENDIX M

Cryogenics Division–NBS Institute for Basic Standards
LABORATORY NOTE

COST CENTER	FILE NO	PAGE
2750364	73-6	

SUBJECT Liquid-Vapor Saturation (Orthobaric) Temperatures of Ethane and Methane

NAME R.D. Goodwin

DATE Nov. 28, 1973

1. Introduction.

The present, new investigation has been necessary to accommodate the extreme range of ethane saturated vapor densities (a factor of 10^7). Our previous work on ethane appears in Lab. Notes 73-2, 3, 4, 5.

Analytical description of the two-phase, liquid-vapor equilibrium (temperature-density relationship) is needed for our new equation of state which originates on this locus (NBS IR 73-342). In particular, the forms used below give the important property that all derivatives are zero at the critical point.

In the following we split the range, using different functions according $\rho \lessgtr \rho_c$. In each case the dependent variable is

$$Y(T) = (T_c/T - 1)/(T_c/T_t - 1) \tag{1}$$

The symbols used here appear in a LIST.

2. The Saturated Vapor Temperatures.

The analytical formulation is

$$Y(T) = U(\sigma) \cdot [1 + A_0 \cdot \ell n(\sigma/\sigma_g) + W(\sigma)] \tag{2}$$

where

$$U(\sigma) = \exp[\alpha \cdot (u_g - u)], \tag{2-a}$$

and

$$W(\sigma) = \sum_{i=1}^{n} A_i \cdot (q^i - q_g^i). \tag{2-b}$$

The notation is $q = \sigma^{1/3}$, $q_g = \sigma_g^{1/3}$, and $u_g = 1/|\sigma_g - 1|$.

This equation is constrained at the vapor triple point.

Fixed-point constants are given by table 1, and coefficients by table 2. The comparisons of results for ethane and for methane are in tables 3,5. Deviations necessarily are systematic because the "data" are smoothed analytically (Lab. Note 73-5). We believe all deviations to be well within the real accuracy of the data.

3. The Saturated Liquid Temperatures.

The analytical formulation is

$$\ell n(Y) = \beta \cdot (u_t - u) + W(\sigma) \tag{3}$$

where

$$W(\sigma) = \sum_{i=1}^{n} B_i \cdot (x^i - x_t^i). \tag{3-a}$$

Cryogenics Division–NBS Institute for Basic Standards LABORATORY NOTE	COST CENTER 2750364	FILE NO 73-6	PAGE 2

SUBJECT
Liquid-Vapor Saturation (Orthobaric) Temperatures of Ethane and Methane

NAME R. D. Goodwin
DATE Nov. 28, 1973

The notation is $x_t \equiv |\sigma_t - 1|$, $u_t \equiv 1/x_t$.

This equation is constrained at the liquid triple point.

The comparisons of results for ethane and for methane are in tables 4, 6. Computer programs are attached.

LIST OF SYMBOLS

d,	density, mol/ℓ,	DEN
d_c ,	critical-point density,	DCRT
d_g ,	vapor triple-point density,	DGAT
d_t ,	liquid triple-point density,	DTRP
q,	$\sigma^{1/3}$, $q_g \equiv \sigma_g^{1/3}$	
ρ,	d/d_t , density reduced at liquid triple point	
σ,	d/d_c , density reduced at the critical point	
σ_g ,	d_g / d_c , reduced triple-point vapor density	
σ_t ,	d_t / d_c , reduced triple-point liquid density	
T,	$T_s(\rho)$, the saturation temperature	
T_c ,	critical-point temperature,	TCRT
T_t ,	triple-point temperature,	TTRP
u,	$1/x$, $u_g \equiv 1/x_g$, $u_t \equiv 1/x_t$	
x,	$\lvert\sigma - 1\rvert$, $x_g \equiv \lvert\sigma_g - 1\rvert$, $x_t \equiv \lvert\sigma_t - 1\rvert$	

Table 1. The fixed-point constants

	Ethane	Methane
T_t, K	89.899	90.680
T_c , K	305.330	190.555
d_c , mol/ℓ	6.87	10.20
d_t , liquid	21.68	28.147
d_g , vapor	$1.35114 . 10^{-6}$	$1.567\,865 . 10^{-2}$

Table 2. Coefficients for the equations

		Ethane	Methane
Vapor	α	3/2	1/2
	A_0	-0.0610 6983	-0.1596 5159
	A_1	-0.5510 7806	-0.6669 5380
	A_2	1.8906 0757	1.0242 2995
	A_3	-4.8476 0684	-0.5885 7993
	A_4	8.5887 8625	0.2042 8358
	A_5	-8.3103 1296	-
	A_6	3.3001 3887	-
rms, %	d	0.111	0.043
	T	0.009	0.004
Liquid	β	1/3	1/3
	B_1	9.1071 7170	8.5837 7917
	B_2	-7.9603 9387	-7.0525 4699
	B_3	4.8472 6284	4.1610 2443
	B_4	-1.5919 0104	-1.3691 9291
	B_5	0.2253 7899	0.2067 1342
rms, %	d	0.004	0.006
	T	0.016	0.006

Cryogenics Division-NBS Institute for Basic Standards LABORATORY NOTE	COST CENTER 2750364	FILE NO 73-6	PAGE 4
SUBJECT Table 3. Ethane Saturated Vapor Temperatures	NAME R. D. Goodwin DATE Nov. 28 1973		

```
NF =  7, AL =  1.500, PE =  0.000, DGAT =  1.35114-006

TTRP = 89.899, TCRT = 305.330, DTRP = 21.680, DCRT = 6.870

 -0.06106983     -0.55107806      1.89060757     -4.84760654
  8.58878625     -8.31031296      3.30013887      0.00000000
  0.00000000      0.00000000      0.00000000      0.00000000

    MOL/L           CALC        PCNT       T,K       CALC      PCNT      DTS/DC
1.35114-006     1.35114-006     0.00     89.899     89.899     0.00    2.915+006
1.38631-006     1.38619-006    -0.01     90.000     90.000     0.00    2.848+006
4.59443-006     4.58134-006    -0.28     95.000     95.013     0.01    9.651+005
1.33561-005     1.33129-005    -0.32    100.000    100.016     0.02    3.714+005
3.46826-005     3.46067-005    -0.22    105.000    105.012     0.01    1.594+005
8.16960-005     8.16454-005    -0.06    110.000    110.004     0.00    7.518+004
1.76844-004     1.76987-004     0.08    115.000    114.995    -0.00    3.346+004
3.55631-004     3.56292-004     0.17    120.000    119.987    -0.01    2.111+004
6.70938-004     6.72259-004     0.20    125.000    124.983    -0.01    1.231+004
1.19634-003     1.19845-003     0.18    130.000    129.984    -0.01    7.567+003
2.03041-003     2.03275-003     0.12    135.000    134.989    -0.01    4.870+003
3.29903-003     3.30029-003     0.04    140.000    139.996    -0.00    3.262+003
5.15754-003     5.15568-003    -0.04    145.000    145.004     0.00    2.263+003
7.79177-003     7.78449-003    -0.09    150.000    150.012     0.01    1.619+003
1.14183-002     1.14040-002    -0.13    155.000    155.017     0.01    1.191+003
1.62842-002     1.62628-002    -0.13    160.000    160.019     0.01    8.969+002
2.26660-002     2.26402-002    -0.11    165.000    165.018     0.01    6.903+002
3.08686-002     3.08446-002    -0.08    170.000    170.013     0.01    5.415+002
4.12247-002     4.12114-002    -0.03    175.000    175.006     0.00    4.322+002
5.40939-002     5.41016-002     0.01    180.000    179.997    -0.00    3.502+002
6.98623-002     6.99003-002     0.05    185.000    184.989    -0.01    2.877+002
8.89439-002     8.90172-002     0.08    190.000    189.982    -0.01    2.392+002
1.11782-001     1.11888-001     0.10    195.000    194.979    -0.01    2.009+002
1.38850-001     1.38978-001     0.09    200.000    199.978    -0.01    1.704+002
1.70662-001     1.70787-001     0.07    205.000    204.982    -0.01    1.457+002
2.07770-001     2.07862-001     0.04    210.000    209.988    -0.01    1.253+002
2.50780-001     2.50803-001     0.01    215.000    214.997    -0.00    1.085+002
3.00359-001     3.00280-001    -0.03    220.000    220.007     0.00    9.434+001
3.57253-001     3.57050-001    -0.06    225.000    225.017     0.01    8.234+001
4.22301-001     4.21977-001    -0.08    230.000    230.023     0.01    7.208+001
4.96469-001     4.96061-001    -0.08    235.000    235.026     0.01    6.322+001
5.80877-001     5.80460-001    -0.07    240.000    240.023     0.01    5.553+001
6.76852-001     6.76541-001    -0.05    245.000    245.015     0.01    4.879+001
7.85990-001     7.85922-001    -0.01    250.000    250.003     0.00    4.286+001
9.10251-001     9.10553-001     0.03    255.000    254.989    -0.00    3.760+001
1.05210+000     1.05283+000     0.07    260.000    259.976    -0.01    3.291+001
1.21471+000     1.21579+000     0.09    265.000    264.969    -0.01    2.867+001
1.40231+000     1.40343+000     0.08    270.000    269.972    -0.01    2.482+001
1.62073+000     1.62131+000     0.04    275.000    274.988    -0.00    2.124+001
1.87845+000     1.87773+000    -0.04    280.000    280.013     0.00    1.788+001
2.18860+000     2.18618+000    -0.11    285.000    285.035     0.01    1.463+001
2.57357+000     2.57061+000    -0.11    290.000    290.032     0.01    1.146+001
3.07773+000     3.08011+000     0.08    295.000    294.980    -0.01    8.351+000
3.81803+000     3.82168+000     0.10    300.000    299.980    -0.01    5.426+000

NP = 44, DNRMSPCT = 0.111, TSRMSPCT = 0.009
```

Table 4. Ethane Saturated Liquid Temperatures

```
         NF =  5, AL =  0.000, BE =  0.333, OGAT =  1.35114-006

         TTRP = 89.899, TCRT = 305.330, DTRP = 21.680, DCRT = 6.870

            9.10717170       -7.96039387       4.84726284      -1.59190104
            0.22537899        0.00000000       0.00000000       0.00000000
            0.00000000        0.00000000       0.00000000       0.00000000

        MOL/L             CALC      PCNT        T,K       CALC      PCNT      DTS/DD
  2.16800+001      2.16800+001      0.00     89.899     89.899      0.00  -2.753+001
  2.16764+001      2.16763+001     -0.00     90.000     89.999     -0.00  -2.753+001
  2.14963+001      2.14951+001     -0.01     95.000     94.967     -0.04  -2.764+001
  2.13162+001      2.13145+001     -0.01    100.000     99.952     -0.05  -2.771+001
  2.11359+001      2.11341+001     -0.01    105.000    104.951     -0.05  -2.773+001
  2.09553+001      2.09538+001     -0.01    110.000    109.958     -0.04  -2.771+001
  2.07743+001      2.07732+001     -0.01    115.000    114.969     -0.03  -2.766+001
  2.05928+001      2.05921+001     -0.00    120.000    119.983     -0.01  -2.758+001
  2.04106+001      2.04105+001     -0.00    125.000    124.997     -0.00  -2.746+001
  2.02276+001      2.02280+001      0.00    130.000    130.010      0.01  -2.733+001
  2.00438+001      2.00445+001      0.00    135.000    135.020      0.01  -2.717+001
  1.98588+001      1.98598+001      0.01    140.000    140.027      0.02  -2.698+001
  1.96727+001      1.96739+001      0.01    145.000    145.031      0.02  -2.678+001
  1.94852+001      1.94864+001      0.01    150.000    150.032      0.02  -2.655+001
  1.92961+001      1.92972+001      0.01    155.000    155.031      0.02  -2.631+001
  1.91052+001      1.91062+001      0.01    160.000    160.027      0.02  -2.604+001
  1.89123+001      1.89132+001      0.00    165.000    165.021      0.01  -2.575+001
  1.87173+001      1.87178+001      0.00    170.000    170.014      0.01  -2.544+001
  1.85198+001      1.85201+001      0.00    175.000    175.006      0.00  -2.511+001
  1.83196+001      1.83195+001     -0.00    180.000    179.999     -0.00  -2.476+001
  1.81164+001      1.81160+001     -0.00    185.000    184.992     -0.00  -2.438+001
  1.79098+001      1.79092+001     -0.00    190.000    189.986     -0.01  -2.397+001
  1.76996+001      1.76987+001     -0.00    195.000    194.981     -0.01  -2.354+001
  1.74852+001      1.74843+001     -0.01    200.000    199.978     -0.01  -2.308+001
  1.72664+001      1.72653+001     -0.01    205.000    204.977     -0.01  -2.260+001
  1.70425+001      1.70415+001     -0.01    210.000    209.978     -0.01  -2.208+001
  1.68130+001      1.68121+001     -0.01    215.000    214.981     -0.01  -2.153+001
  1.65774+001      1.65767+001     -0.00    220.000    219.985     -0.01  -2.094+001
  1.63348+001      1.63344+001     -0.00    225.000    224.990     -0.00  -2.033+001
  1.60845+001      1.60843+001     -0.00    230.000    229.996     -0.00  -1.967+001
  1.58255+001      1.58256+001      0.00    235.000    235.002      0.00  -1.898+001
  1.55567+001      1.55571+001      0.00    240.000    240.007      0.00  -1.825+001
  1.52767+001      1.52773+001      0.00    245.000    245.011      0.00  -1.749+001
  1.49838+001      1.49846+001      0.01    250.000    250.013      0.01  -1.668+001
  1.46761+001      1.46770+001      0.01    255.000    255.014      0.01  -1.582+001
  1.43511+001      1.43518+001      0.01    260.000    260.012      0.00  -1.493+001
  1.40054+001      1.40059+001      0.00    265.000    265.008      0.00  -1.398+001
  1.36348+001      1.36350+001      0.00    270.000    270.002      0.00  -1.298+001
  1.32333+001      1.32331+001     -0.00    275.000    274.997     -0.00  -1.191+001
  1.27923+001      1.27917+001     -0.00    280.000    279.994     -0.00  -1.076+001
  1.22985+001      1.22978+001     -0.01    285.000    284.993     -0.00  -9.500+000
  1.17293+001      1.17290+001     -0.00    290.000    289.997     -0.00  -8.090+000
  1.10398+001      1.10403+001      0.00    295.000    295.003      0.00  -6.441+000
  1.01117+001      1.01117+001      0.00    300.000    300.000     -0.00  -4.358+000

NP = 44, DNRMSPCT = 0.004, TSRMSPCT = 0.016
```

Table 5. Methane Saturated Vapor Temperatures

```
      NF =   5, AL =  0.500. BE =  0.000, DGAT =  1.56787-002

      TTRP = 90.680, TCRT = 190.555, DTRP = 28.147, DCRT =10.200

       -0.15965159      -0.56695380       1.02422995      -0.58857933
        0.20428356       0.00000000       0.00000000       0.00000000
        0.00000000       0.00000000       0.00000000       0.00000000

        MOL/L            CALC        PCNT       T,K       CALC      PCNT      DTS/DD
  1.56786-002     1.56786-002       0.00     90.680     90.680      0.00    5.391+002
  1.82791-002     1.82630-002       0.02     92.000     91.998     -0.00    4.775+002
  2.28579-002     2.28668-002       0.04     94.000     93.996     -0.00    4.005+002
  2.82943-002     2.83066-002       0.04     96.000     95.996     -0.00    3.390+002
  3.46926-002     3.47064-002       0.04     98.000     97.996     -0.00    2.893+002
  4.21625-002     4.21756-002       0.03    100.000     99.997     -0.00    2.488+002
  5.08186-002     5.08288-002       0.02    102.000    101.998     -0.00    2.154+002
  6.07803-002     6.07855-002       0.01    104.000    103.999     -0.00    1.878+002
  7.21719-002     7.21702-002      -0.00    106.000    106.000      0.00    1.647+002
  8.51224-002     8.51123-002      -0.01    108.000    108.001      0.00    1.453+002
  9.97656-002     9.97466-002      -0.02    110.000    110.002      0.00    1.288+002
  1.16241-001     1.16213-001      -0.02    112.000    112.003      0.00    1.147+002
  1.34692-001     1.34655-001      -0.03    114.000    114.004      0.00    1.026+002
  1.55269-001     1.55226-001      -0.03    116.000    116.004      0.00    9.221+001
  1.78128-001     1.78080-001      -0.03    118.000    118.004      0.00    8.314+001
  2.03431-001     2.03383-001      -0.02    120.000    120.004      0.00    7.522+001
  2.31346-001     2.31304-001      -0.02    122.000    122.003      0.00    6.827+001
  2.62058-001     2.62022-001      -0.01    124.000    124.002      0.00    6.215+001
  2.95748-001     2.95725-001      -0.01    126.000    126.001      0.00    5.672+001
  3.32616-001     3.32611-001      -0.00    128.000    128.000      0.00    5.189+001
  3.72870-001     3.72889-001       0.01    130.000    129.999     -0.00    4.757+001
  4.16733-001     4.16780-001       0.01    132.000    131.998     -0.00    4.370+001
  4.64444-001     4.64520-001       0.02    134.000    133.997     -0.00    4.021+001
  5.16255-001     5.16362-001       0.02    136.000    135.996     -0.00    3.706+001
  5.72441-001     5.72579-001       0.02    138.000    137.995     -0.00    3.420+001
  6.33297-001     6.33462-001       0.03    140.000    139.995     -0.00    3.159+001
  6.99144-001     6.99331-001       0.03    142.000    141.995     -0.00    2.921+001
  7.70334-001     7.70534-001       0.03    144.000    143.995     -0.00    2.704+001
  8.47251-001     8.47451-001       0.02    146.000    145.995     -0.00    2.503+001
  9.30320-001     9.30504-001       0.02    148.000    147.996     -0.00    2.319+001
  1.02001+000     1.02016+000       0.01    150.000    149.997     -0.00    2.148+001
  1.11685+000     1.11694+000       0.01    152.000    151.998     -0.00    1.989+001
  1.22143+000     1.22144+000       0.00    154.000    154.000     -0.00    1.842+001
  1.33441+000     1.33433+000      -0.01    156.000    156.001      0.00    1.705+001
  1.45656+000     1.45636+000      -0.01    158.000    158.003      0.00    1.576+001
  1.58877+000     1.58843+000      -0.02    160.000    160.005      0.00    1.455+001
  1.73204+000     1.73156+000      -0.03    162.000    162.007      0.00    1.341+001
  1.88759+000     1.88697+000      -0.03    164.000    164.008      0.00    1.234+001
  2.05685+000     2.05610+000      -0.04    166.000    166.008      0.01    1.132+001
  2.24155+000     2.24073+000      -0.04    168.000    168.008      0.01    1.036+001
  2.44381+000     2.44300+000      -0.03    170.000    170.008      0.00    9.433+000
  2.66631+000     2.66564+000      -0.03    172.000    172.006      0.00    8.548+000
  2.91249+000     2.91214+000      -0.01    174.000    174.003      0.00    7.696+000
  3.18691+000     3.18711+000       0.01    176.000    175.999     -0.00    6.671+000
  3.49581+000     3.49685+000       0.03    178.000    177.994     -0.00    6.066+000
  3.84823+000     3.85039+000       0.06    180.000    179.989     -0.01    5.275+000
  4.25806+000     4.26143+000       0.08    182.000    181.985     -0.01    4.488+000
  4.74867+000     4.75265+000       0.08    184.000    183.985     -0.01    3.690+000
  5.36526+000     5.36679+000       0.03    186.000    185.996     -0.00    2.858+000
  6.22000+000     6.20573+000      -0.23    188.000    188.028      0.01    1.935+000

NP = 50, DNRMSPCT = 0.043, TSRMSPCT = 0.004
```

Table 6. Methane Saturated Liquid Temperatures

```
        NF =  5, AL =  0.000, BE =  0.333, DGAT =  1.56787-002

        TTRP = 90.680, TCRT = 190.555, DTRP = 28.147, DCRT =10.200

           8.58377917     -7.05254599       4.16102443     -1.36319291
           0.20671342      0.00000000       0.00000000      0.00000000

       MOL/L              CALC       PCNT          T,K       CALC      PCNT      DTS/DD
  2.81470+001      2.81470+001       0.00       90.680     90.680      0.00   -1.208+001
  2.80378+001      2.80375+001      -0.00       92.000     91.996     -0.00   -1.203+001
  2.78714+001      2.78706+001      -0.00       94.000     93.991     -0.01   -1.194+001
  2.77036+001      2.77026+001      -0.00       96.000     95.988     -0.01   -1.186+001
  2.75344+001      2.75332+001      -0.00       98.000     97.986     -0.01   -1.176+001
  2.73638+001      2.73625+001      -0.00      100.000     99.985     -0.01   -1.167+001
  2.71916+001      2.71904+001      -0.00      102.000    101.986     -0.01   -1.157+001
  2.70179+001      2.70167+001      -0.00      104.000    103.987     -0.01   -1.147+001
  2.68425+001      2.68415+001      -0.00      106.000    105.988     -0.01   -1.136+001
  2.66654+001      2.66645+001      -0.00      108.000    107.990     -0.01   -1.125+001
  2.64865+001      2.64857+001      -0.00      110.000    109.992     -0.01   -1.113+001
  2.63056+001      2.63051+001      -0.00      112.000    111.994     -0.01   -1.101+001
  2.61228+001      2.61224+001      -0.00      114.000    113.996     -0.00   -1.089+001
  2.59379+001      2.59377+001      -0.00      116.000    115.998     -0.00   -1.076+001
  2.57507+001      2.57507+001       0.00      118.000    118.000      0.00   -1.063+001
  2.55612+001      2.55615+001       0.00      120.000    120.002      0.00   -1.050+001
  2.53693+001      2.53697+001       0.00      122.000    122.004      0.00   -1.036+001
  2.51749+001      2.51754+001       0.00      124.000    124.006      0.00   -1.022+001
  2.49777+001      2.49784+001       0.00      126.000    126.007      0.01   -1.008+001
  2.47776+001      2.47784+001       0.00      128.000    128.008      0.01   -9.928+000
  2.45745+001      2.45754+001       0.00      130.000    130.009      0.01   -9.775+000
  2.43682+001      2.43692+001       0.00      132.000    132.009      0.01   -9.618+000
  2.41585+001      2.41595+001       0.00      134.000    134.009      0.01   -9.457+000
  2.39452+001      2.39462+001       0.00      136.000    136.009      0.01   -9.292+000
  2.37280+001      2.37290+001       0.00      138.000    138.009      0.01   -9.122+000
  2.35067+001      2.35076+001       0.00      140.000    140.008      0.01   -8.948+000
  2.32810+001      2.32818+001       0.00      142.000    142.007      0.01   -8.768+000
  2.30506+001      2.30513+001       0.00      144.000    144.006      0.00   -8.584+000
  2.28152+001      2.28158+001       0.00      146.000    146.005      0.00   -8.395+000
  2.25744+001      2.25748+001       0.00      148.000    148.003      0.00   -8.200+000
  2.23276+001      2.23278+001       0.00      150.000    150.002      0.00   -7.999+000
  2.20746+001      2.20745+001      -0.00      152.000    152.000     -0.00   -7.793+000
  2.18146+001      2.18143+001      -0.00      154.000    153.998     -0.00   -7.579+000
  2.15471+001      2.15466+001      -0.00      156.000    155.996     -0.00   -7.359+000
  2.12713+001      2.12705+001      -0.00      158.000    157.995     -0.00   -7.132+000
  2.09863+001      2.09853+001      -0.00      160.000    159.993     -0.00   -6.896+000
  2.06912+001      2.06901+001      -0.01      162.000    161.992     -0.00   -6.652+000
  2.03849+001      2.03835+001      -0.01      164.000    163.991     -0.01   -6.399+000
  2.00658+001      2.00643+001      -0.01      166.000    165.991     -0.01   -6.135+000
  1.97322+001      1.97307+001      -0.01      168.000    167.992     -0.00   -5.859+000
  1.93820+001      1.93807+001      -0.01      170.000    169.993     -0.00   -5.570+000
  1.90125+001      1.90114+001      -0.01      172.000    171.994     -0.00   -5.265+000
  1.86201+001      1.86195+001      -0.00      174.000    173.997     -0.00   -4.943+000
  1.82004+001      1.82004+001       0.00      176.000    176.000     -0.00   -4.600+000
  1.77467+001      1.77475+001       0.00      178.000    178.003      0.00   -4.232+000
  1.72499+001      1.72516+001       0.01      180.000    180.006      0.00   -3.833+000
  1.66958+001      1.66983+001       0.01      182.000    182.008      0.00   -3.394+000
  1.60606+001      1.60632+001       0.02      184.000    184.008      0.00   -2.903+000
  1.52986+001      1.52997+001       0.01      186.000    186.003      0.00   -2.338+000
  1.42978+001      1.42937+001      -0.03      188.000    187.993     -0.00   -1.652+000
  1.25270+001      1.25276+001       0.00      190.000    190.000      0.00   -6.700-001

NP = 51, DNRMSPCT = 0.006, TSRMSPCT = 0.006
```

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Appendix I. The Computer Programs

```
      PROGRAM TSATFIT
C     DESCRIBE ETHANE SATN. TEMPS.,  TSAT(DEN).
C     DEFINE R=D/DTRP, S=D/DCRT, ST=DTRP/DCRT,  AND -
C     YY(TSAT) = (TCRT/T-1)/(TCRT/TTRP-1),  AND -
C
      COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSDR, A(15),B(15)
      COMMON/999/NP,NF,H(15),Y(200),G(200,15)
      DIMENSION  T(99),DEN(99),YY(99),F(15)
      DIMENSION UL(99)
    2 FORMAT(1H1 30X *ETHANE SATURATION TEMPERATURES* //
     1 16X4HNF =I3, 6H, AL =F7.3, 6H, BE =F7.3, 8H, DGAT =E13.5//
     1 16X 6HTTRP =F7.3, 8H, TCRT =F8.3, 8H, DTRP =F7.3,
     2 8H, DCRT =F6.3// 3(12X 4F16.8/ ) /
     315X5HMOL/L 11X4HCALC 5X4HPCNT 8X3HT,K 6X4HCALC 5X4HPCNT6X6HDTS/DD)
    3 FORMAT(1H1 14X 5HMOL/L 11X4HCALC 5X4HPCNT
     3 8X3HT,K 6X4HCALC 5X4HPCNT 6X6HDTS/DD )
    4 FORMAT(5X 2E15.5, F9.2, F11.3, F10.3, F9.2, E12.3)
    5 FORMAT(13X 2HNF 13X2HAL 13X2HBE 8X2HSS)
    6 FORMAT(10X I5, 2E15.5, F10.3)
    9 FORMAT(1H0 6X 4HNP =I3, 12H, DNRMSPCT =F6.3, 12H, TSRMSPCT =F6.3)
   11 TTRP=89.899 $ TCRT=305.33 $ YN = TCRT/TTRP-1
   12 DTRP=21.68  $  DCRT=6.87  $  DGAT=1.35114E-6
   13 ST=DGAT/DCRT $ VT=1/(1-ST) $ QT=CUBERTF(ST)
C
C     SATD. VAPOR TEMPS. CONSTRAINED AT T.P. BY SUBTRACTION  -
C     EQUATION,  YY = U(S)*(1+W(S)),    U = EXP(AL*(VT-V)),
C     V = 1/ABS(S-1),    Q = S**(1/3),   AND -
C     W = A1*LN(S/ST) + A2*(Q-QT) + A3*(Q2-QT2) + . . .
C     GENERATE THE SATD. VAPOR DATA.
   25 DO 29 J=1,44  $  IF(J-1) 27,26
   26 T(J) = TTRP  $  GO TO 28
   27 T(J) = 80 + 5*J
   28 DEN(J) = DENGASF(T(J))
   29 YY(J) = (TCRT/T(J)-1)/YN   $   NP = 44
C     PRINT FOR NF,  GET AL BY TRIAL.
   30 AL = 1.50
   31 DO 69 NF=4,10 $  NG = NF  $  SSK = 1.0E+100
   32 DO 40 J=1,NP  $  S=DEN(J)/DCRT $ Q=CUBERTF(S) $ V=1/(1-S)
   33 U = EXPF(AL*(VT-V))  $  G(J,1) = U*LOGF(S/ST)
   35 DO 36 K=2,NF  $  N = K-1
   36 G(J,K) = U*(Q**N - QT**N)
   40 Y(J) = YY(J) - U
   49 CALL EGENFT  $  DO 50 K=1,NF
   50 A(K) = H(K)  $  SD = SS = 0
   51 DO 52 J=1,NP  $  TC = TSATF(DEN(J))
   52 SS = SS + (TC/T(J)-1)**2  $  SS = 100*SQRTF(SS/NP)
   53 IF(SS.LT.SSK) 54,56
   54 SSK=SS $ NGK=NG $ ALK=AL $ BEK=BE  $  DO 55 K=1,NF
   55 F(K) = A(K)
   56 CONTINUE
   57 CONTINUE $ NG=NGK $ AL=ALK $ BE=BEK  $  DO 58 K=1,NF
   58 A(K) = F(K)  $  SS = SD = 0
```

Appendix I. (continued)

```
 C     PRINT CONSTANTS AND DEVIATIONS.
   60 PRINT 2, NG,AL,BE,DGAT. TTRP,TCRT,DTRP,DCRT, (A(K),K=1,12)
   61 DO 67 J=1,NP  $  D=DEN(J)  $  X=T(J)  $  DC=FINDSATF(0,X)
```

```
        TSATFIT                                              11/28/73

    62 DPCT = 100*(DC/D-1)  $  SD = SD + DPCT*DPCT
    64 TC = TSATF(D)  $  DTSDD = DTSDR/DTRP
    65 TPCT = 100*(TC/X-1)  $  SS = SS + TPCT*TPCT
    67 PRINT 4, D,DC,DPCT, X,TC,TPCT, DTSDD
    68 SD=SQRTF(SD/NP) $ SS=SQRTF(SS/NP) $ PRINT 9, NP, SD, SS
    69 CONTINUE  $   AL = 0
  C
  C    SATD. LIQUID TEMPS. CONSTRAINED AT THE T.P. BY SUBTRACTION, -
  C    EQN.,  LN(YY) = W(S),  WHERE  X=ABS(S-1),  XT=ABS(ST-1), AND -
  C    W(S) = BE*(1/XT-1/X) + B1*(X-XT) + B2*(X2-XT2) + . . .
  C    GENERATE LIQUID DATA.
    70 DO 74 J=1,44  $  IF(J-1) 72,71
    71 T(J) = TTRP  $  GO TO 73
    72 T(J) = 80 + 5*J
    73 DEN(J) = DENLIQF(T(J))
    74 YY(J) = LOGF((TCRT/T(J)-1)/YN)
    75 NP = 44  $  NG = NF = 5  $  XT = DTRP/DCRT - 1
  C    SET UP FIXED LEAST SQUARES FUNCTIONS.
    80 DO 85 J=1,NP  $  S = DEN(J)/DCRT  $  X = ABSF(S-1)
    81 UL(J) = 1/XT - 1/X  $  DO 82 K=1,NF  $  N = K
    82 G(J,K) = X**N - XT**N
    85 CONTINUE
  C    FIND NF, BE BY TRIAL.
    90 BE = 1.0/3.0  $  DO 91 J=1,NP
    91 Y(J) = YY(J) - BE*UL(J)  $  CALL EGENFT  $  DO 92 K=1,NF
    92 B(K) = H(K)  $  SD = SS = 0
  C    PRINT LIQUID DEVIATIONS.
   100 PRINT 2, NG,AL,BE,DGAT, TTRP,TCRT,DTRP,DCRT, (B(K),K=1,12)
   101 DO 105 J=1,NP  $  D=DEN(J)  $  X=T(J)  $  DC = FINDSATF(1,X)
   102 DPCT = 100*(DC/D-1)  $  SD = SD + DPCT**2
   103 TC = TSATF(D)  $  DTSDD = DTSDR/DTRP
   104 TPCT = 100*(TC/X-1)  $  SS = SS + TPCT**2
   105 PRINT 4, D,DC,DPCT, X,TC,TPCT, DTSDD
   106 SD = SQRTF(SD/NP)  $  SS = SQRTF(SS/NP)
   107 PRINT 9, NP, SD,SS
   110 CONTINUE
   999 STOP  $   END
```

Appendix I. (continued)

11/28/73

```
      FUNCTION TSATF(DEN)
      COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSDR, A(15),B(15)
    1 R=DEN/DTRP $ S=DEN/DCRT $ QS = S-1 $ DSDR=DTRP/DCRT $ IF(QS) 2,30
    2 X = ABSF(QS)  $  X1 = DSDR*QS/X  $  YN = TCRT/TTRP - 1
    3 V = 1/X  $  V1 = -DSDR/QS/X   $   IF(QS) 4,30,15
C    SATD. VAPOR TEMPS. CONSTRAINED AT T.P. BY SUBTRACTION  -
C    EQUATION.  YY = U(S)*(1+W(S)),    U = EXP(AL*(VT-V)),
C    V = 1/ABS(S-1),    Q = S**(1/3),  AND -
C    W = A1*LN(S/ST) + A2*(Q-QT) + A3*(Q2-QT2) + . . .
    4 ST=DGAT/DCRT $ VT=1/(1-ST) $ QT=CUBERTF(ST)
    5 U = EXPF(AL*(VT-V))  $  U1 = -AL*V1*U
    6 Q = CUBERTF(S)  $  Q1 = Q*DSDR/3/S
    7 W = 1 + A(1)*LOGF(S/ST)  $  W1 = A(1)*DSDR/S
    8 DO 10 K=2,NG  $  N = K-1
    9 W = W + A(K)*(Q**N - QT**N)
   10 W1 = W1 + N*A(K)*Q1*Q**(N-1)
   12 F = U*W  $  F1 = U*W1 + U1*W  $  Q = 1 + YN*F
   14 TSATF = TCRT/Q  $  DTSDR = -YN*F1*TSATF/Q   $   RETURN
C     SATD. LIQUID TEMPS. CONSTRAINED AT THE T.P. BY SUBTRACTION, -
C     EQN.,  LN(YY) = W(S),  WHERE  X=ABS(S-1),  XT=ABS(ST-1), AND -
C     W(S) = BE*(1/XT-1/X) + B1*(X-XT) + B2*(X2-XT2) + . . .
   15 XT = DSDR-1  $  W = BE*(1/XT-V)  $  W1 = -BE*V1
   17 DO 19 K=1,NG   $   N = K
   18 W = W + B(K)*(X**N - XT**N)
   19 W1 = W1 + B(K)*N*X1*X**(N-1)
   20 F = EXPF(W)  $  F1 = W1*F  $  Q = 1 + YN*F
   22 TSATF = TCRT/Q  $  DTSDR = -YN*F1*TSATF/Q   $   RETURN
   30 TSATF = TCRT  $  DTSDR = 0  $  RETURN   $   END


       FUNCTION DENGASF(T)
C     ETHANE SATURATED VAPOR DENSITIES, MOL/L.
C     Y = A1 + A2*Q2 + A3*Q3 + . . ,   NF = AL,  YN = LN(DCRT/DTRP),
C     U = Z + (ZE-Z)*Y,    DEN = DCRT*EXP(-YN*U).
       DIMENSION A(5)
       DATA (TTRP=89.899),(TCRT=305.33),(E=0.362)
       DATA (DCRT=6.87),(DTRP=1.35114E-6)
       DATA(A = 0.19277431, 0.04155009, -0.78922629,
      1 0.35746750, 0.12454376)
     1 FORMAT(1H0 9X *DENGASF = 0, T EXCEEDS TCRT. * / )
     2 IF(TCRT-T) 3,4,5
     3 PRINT 1  $  STOP
     4 DENGASF = DCRT  $  DRDT = D2RDT2 = 0  $  RETURN
     5 ZN=TCRT/TTRP-1  $  YN=LOGF(DCRT/DTRP) $  Z=(TCRT/T-1)/ZN
     6 DZDT = -TCRT/ZN/T/T  $  ZE = Z**E  $  ZE1 = E*ZE/Z
     8 X = ZE-Z  $  X1 = ZE1-1  $  Q = CUBERTF(Z)  $  Q1 = Q/3/Z
    10 Y = A(1)  $  Y1 = 0  $  DO 13 K=2,5
    11 Y = Y + A(K)*Q**K
    12 Y1 = Y1 + K*A(K)*Q**(K-1)
    13 CONTINUE  $  Y1 = Y1*Q1
    15 U = Z + X*Y  $  UA = 1 + X*Y1 + X1*Y  $  U1 = UA*DZDT
    16 XP = EXPF(-YN*U)  $  DENGASF = F = DCRT*XP
    17 DRDT = -YN*U1*F    $    RETURN   $   END
```

Appendix I. (continued)

```
                                                          11/28/73
        FUNCTION FINDSATF(M,T)
  C    THIS FINDSATF ADJUSTED FOF ETHANE.
  C    ITERATE DEN TO MINIMIZE (T-TS) VIA TSATF(DEN).
  C     1 = 0 FOR VAPOR,   M = 1 FCR LIQUID.
        COMMON NG,AL,BE,TTRP,TCRT, DGAT,DTRP,DCRT, DTSDR, A(15),B(15)
        DATA (DGT=1.0E-6),(DLT=23.0)
      1 FORMAT(1H0 9X *FINDSATF = 0,  FAILS TO CONVERGE.* / )
      2 FORMAT(1H0 9X *FINDSATF = 0,  T EXCEEDS TCRT.* / )
      3 IF(T-TCRT) 4,22,23
      4 IF(M.EQ.0) 5,6
      5 D = DENGASF(T)   $  GO TO 7
      6 D = DENLIQF(T)
      7 DO 20 J=1,50 $ DT=T-TSATF(D) $ IF(ABSF(DT/T)-1.0E-6) 21,21,8
      8 DTDD = DTSDR/DTRP   $  IF(DTDD.EQ.0.0) 22,9
      9 DD = DT/DTDD   $  IF(ABSF(DD/D)-1.0E-6) 21,21,10
     10 D = D + DD   $  IF(M.EQ.0) 11,15
     11 IF(D.GT.DGT) 13,12
     12 D = DGT   $  GO TO 20
     13 IF(D.LT.DCRT) 20,14
     14 D = DCRT - 0.02   $  GO TO 20
     15 IF(D.GT.DLT) 16,17
     16 D = DLT   $  GO TO 20
     17 IF(D.GT.DCRT) 20,18
     18 D = DCRT + 0.02
     20 CONTINUE   $  FINDSATF = 0   $  PRINT 1   $  RETURN
     21 FINDSATF = D   $   RETURN
     22 FINDSATF = DCRT   $  RETURN
     23 FINDSATF = 0   $  PRINT 2   $  RETURN   $  END
```

```
                                                          11/28/73

       FUNCTION DENLIQF(T)
 C    ETHANE SATURATED LIQUID DENSITIES, MOL/L.
 C    Y = A1 + A2*Q2 + A3*Q3 + . . . ,   YN = DTRP-DCRT,
 C    DEN = DCRT + YN*(X + (XE-X)*Y).
       DATA (TCRT=305.33),(TTRP=89.899),(DCRT=6.87),(DTRP=21.68),(E=0.35)
       DATA (A=0.76173503),(B=0.29865351),(C=-0.32762394)
     1 FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT. * / )
     2 IF(TCRT-T) 3,4,5
     3 PRINT 1   $   STOP
     4 DENLIQF=DCRT   $  DRDT=D2FDT2=0   $  RETURN
     5 XN=TCRT-TTRP $ YN=DTRP-DCPT $ X=(TCRT-T)/XN $ DXDT=-1/XN
     6 XE = X**E   $  XE1 = E*XE/X   $  W = CUBERTF(X)   $  W1 = W/3/X
     8 Q = XE-X   $  Q1 = XF1-1
     9 WW = W*W   $  Y = A + B*WW + C*X
    10 Y1 = 2*B*W + 3*C*WW
    11 Y1 = Y1*W1
    13 DENLIQF = DCRT + (X + Q*Y)*YN
    14 DRDT = (1 + Q*Y1 + Q1*Y)*YN*DXDT   $   RETURN   $  END
```

Appendix I. (continued) 11/28/73

```
      FUNCTION DENGASF(T)
C     METHANE SAT. VAPOR DEN, MOL/L, VIA VAPORFIT, 11/19/73.
C     Y = A1 + A2*Q2 + A3*Q3 + . . ,  NF = AL,  YN = LN(DCRT/DTRP),
C     U = Z + (ZE-Z)*Y,   DEN = DCRT*EXP(-YN*U).
      DIMENSION A(5)
      DATA (TTRP=90.68),(TCRT=190.555),(E=0.388)
      DATA (DCRT=10.2),(DTRP=0.01567865)
      DATA(A = 0.3925579, -0.4976888, 1.3200516,
     1 -1.6817790, 0.6848609)
    1 FORMAT(1H0 9X *DENGASF = 0, T EXCEEDS TCRT. * / )
    2 IF(TCRT-T) 3,4,5
    3 PRINT 1  $  STOP
    4 DENGASF = DCRT  $  DRDT = D2RDT2 = 0  $  RETURN
    5 ZN=TCRT/TTRP-1  $  YN=LOGF(DCRT/DTRP) $  Z=(TCRT/T-1)/ZN
    6 DZDT = -TCRT/ZN/T/T  $  ZE = Z**E  $  ZE1 = E*ZE/Z
    8 X = ZE-Z  $  X1 = ZE1-1  $  Q = CUBERTF(Z)  $  Q1 = Q/3/Z
   10 Y = A(1)  $  Y1 = 0  $  DO 13 K=2,5
   11 Y = Y + A(K)*Q**K
   12 Y1 = Y1 + K*A(K)*Q**(K-1)
   13 CONTINUE  $  Y1 = Y1*Q1
   15 U = Z + X*Y  $  UA = 1 + X*Y1 + X1*Y  $  U1 = UA*DZDT
   16 XP = EXPF(-YN*U)  $  DENGASF = F = DCRT*XP
   17 DRDT = -YN*U1*F    $    RETURN   $   END
```

```
      FUNCTION DENLIQF(T)
C     METHANE SATD. LIQUID DEN, MOL/L, VIA LAB. NOTE 73-5.
C     Y = A1 + A2*Q2 + A3*Q3 + . . . ,  YN = DTRP-DCRT,
C     DEN = DCRT + YN*(X + (XE-X)*Y).
      DATA (TTRP=90.68),(TCRT=190.555),(E=0.361)
      DATA (DCRT=10.2),(DTRP=28.147)
      DATA (A=0.83709103),(B=0.08416127),(C=-0.07478575)
    1 FORMAT(1H0 9X *DENLIQF = 0, T EXCEEDS TCRT. * / )
    2 IF(TCRT-T) 3,4,5
    3 PRINT 1   $   STOP
    4 DENLIQF=DCRT  $  DRDT=D2RDT2=0  $  RETURN
    5 XN=TCRT-TTRP $ YN=DTRP-DCRT $ X=(TCRT-T)/XN $ DXDT=-1/XN
    6 XE = X**E  $  XE1 = E*XE/X  $  W = CUBERTF(X)  $  W1 = W/3/X
    8 Q = XE-X  $  Q1 = XE1-1
    9 WW = W*W  $  Y = A + B*WW + C*X
   10 Y1 = 2*3*W + 3*C*WW
   11 Y1 = Y1*W1
   13 DENLIQF = DCRT + (X + Q*Y)*YN
   14 DRDT = (1 + Q*Y1 + Q1*Y)*YN*DXDT   $   RETURN  $  END
```

APPENDIX N

LOW-TEMPERATURE ELASTIC PROPERTIES OF ALUMINUM 5083-0 AND FOUR FERRITIC NICKEL STEELS†

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ABSTRACT

The low-temperature elastic properties have been determined for five commercial alloys that have possible structural applications at cryogenic temperatures. The alloys are 5083-0 aluminum and four ferritic steels: 3.5, 5, 6, and 9 percent nickel. An ultrasonic (10 MHz) pulse-superposition method was used to measure longitudinal and transverse wave velocities. Using the velocities and the mass density as input, the following moduli were calculated: longitudinal modulus, Young's (tensile) modulus, shear (rigidity) modulus, bulk modulus (reciprocal compressibility), and Poisson's ratio. Measurements were made semi-continuously from 300 K to 4 K. The composition dependence of iron-nickel alloys is reviewed comprehensively up to 12 percent nickel. Debye temperatures were calculated from the elastic constants. A discussion is given of the temperature dependences of the elastic constants, differential relationships among the elastic constants, and the possible relationships between elastic and plastic properties.

Key Words: Aluminum alloy; bulk modulus; compressibility; Debye temperature; elastic constant; nickel steels; Poisson's ratio; shear modulus; sound velocity; Young's modulus.

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* NRC-NBS Postdoctoral Research Associate, 1973-4.

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INTRODUCTION

The recent expansion of cryogenic technology to extensive use of liquefied gases has created new materials problems. In particular, detailed knowledge and understanding of the mechanical properties of common metals and alloys are required. The temperature range of interest is from room temperature to near absolute zero. For engineering, the most important mechanical properties in cryogenic applications are strength (sometimes strength-to-density ratio) and toughness (resistance to low-temperature embrittlement). In this paper, the elastic properties of several common alloys are reported between 300 and 4 K. These properties--Young's modulus, shear modulus, etc.--are essential engineering design parameters, are useful parameters in alloy development, are fundamental data for fracture analysis and theories of solid-solution strengthening, figure prominently in dislocation-model descriptions of mechanical properties, and can be related empirically to a variety of phenomena associated with plastic deformation. Gilman[1] has maintained that "the most important mechanical characteristic of a crystal is its elastic modulus." The elastic moduli of polycrystalline aggregates are also paramount.

It is well known[2] that the major contributions of the addition of small amounts of nickel to steel are: (1) hardening of the ferritic alpha phase; (2) retarding the bainite and pearlite transformations; (3) lowering the γ-α transition temperature, which enables nickel steels to be hardened by quenching at lower temperatures; and (4) resistance to embrittlement at low temperatures. Thus, nickel steels are well suited for cryogenic applications.

Three and one-half percent nickel steel is a weldable low-carbon steel

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useful at temperatures down to about -100°C. Its possible applications include the containment at atmospheric pressure of liquid ethylene and other liquefied gases of higher boiling points, such as ethane, acetylene, carbon dioxide, and propane. Five percent nickel steel is useful at temperatures down to about -120°C in its quenched-and-tempered state and down to lower temperatures in its austenitized, temperized, reversion-annealed state; and nine percent nickel steel is useful down to liquid nitrogen temperatures (-196°C). This alloy may contain as much as 15 percent austenite and could be used for the containment of liquefied oxygen, argon, and nitrogen.

Aluminum alloys also are particularly useful for low-temperature applications, since at cryogenic temperatures their strength increases without loss of ductility. In particular, the 5000 series alloys contain magnesium as the major alloying constituent; magnesium is very effective as a hardener. Alloys in this series possess good welding characteristics and good resistance to corrosion in marine atmosphere.

The low-temperature elastic properties are reported here for five commercial alloys that have possible structural applications at cryogenic temperatures. These alloys are 5083 aluminum and four ferritic steels: 3.5, 5, 6, and 9 percent nickel. An ultrasonic (10 MHz) pulse-superposition method was used to measure longitudinal and transverse wave velocities. Using the velocities and the mass density as input, the following moduli were calculated: longitudinal modulus, Young's (tensile) modulus, shear (rigidity) modulus, bulk modulus (reciprocal compressibility), and Poisson's ratio. Measurements were made semi-continuously from 300 K to 4 K.

These data have been compared to previously reported results and used to calculate the elastic Debye temperatures. Also, the elastic moduli have been used to deduce information on some of the plastic properties of the materials.

Most engineering alloys selected for cryogenic use have close-packed crystal structures; these include austenitic steels and alloys of aluminum, copper, nickel, and titanium. Commercial purity body-centered cubic alloys tend to have high ductile-to-brittle transition temperatures, that is, a high notch sensitivity. The nickel steels reported on here are a notable exception to the general exclusion of body-centered alloys from cryogenic structures.

EXPERIMENTAL

The alloy specimens were obtained from commercial sources in the form of plates. The nickel steels were used as-received (quenched and tempered in the cases of the 3.5 and 9.0 percent nickel specimens, and austenitized, temperized, and reversion annealed in the cases of the 5 and 6 percent nickel specimens). The 5083 aluminum was annealed at 413°C for 30 min. at a pressure of 5×10^{-6} torr and cooled in the furnace. Cylindrical specimens 5/8-in. (1.6-cm) in diameter and 3/8-in. (1.0-cm) long were prepared by grinding. Opposite faces were flat and parallel within 100×10^{-6} in. (2.5 μm). Chemical compositions (obtained from mill analyses), hardness numbers, and mass densities are given in Table 1. Hardness was determined by standard metallurgical methods. Mass density was determined by Archimedes' method using distilled water as a standard.

Quartz transducers (10 MHz) were bonded to the specimens with phenyl salicylate for room-temperature measurements and with a stopcock grease for lower temperatures. The specimen holder is shown in Fig. 1. The holder was placed in the ullage of a helium dewar and lowered stepwise to achieve cooling. Temperatures were monitored with a chromel-constantan thermocouple contacting the specimen.

Ultrasonic sound-wave velocities, both longitudinal and transverse, were determined by a pulse-superposition technique.[3-5] High-frequency pulses (nominally 10 MHz) were gated from a continuous carrier in such a way that they were all phase coherent. Each pulse, when applied to the quartz transducer, generated an echo train in the specimen. The repetition rate of the pulses was adjusted so that each pulse was superposed on the second echo of each preceding pulse. Thus, the transit time of a sound wave in the specimen is directly related to the repetition rate of the pulses. Denoting the carrier frequency by f, the repetition rate is then f/n, where n is an integer. Typical values of n, which are determined from the frequency-divider setting, were 70-200 for these experiments. It follows that the round-trip transit time t in the specimen is simply

$$t = n/(2f) \; . \tag{1}$$

Ultrasonic velocities v are given by

$$v = 2\ell/t , \tag{2}$$

where ℓ is the specimen length. A block diagram of the experimental apparatus is shown in Fig. 2.

In practice the pulse-superposition method proceeded as follows. The carrier frequency f was adjusted as closely as possible to the resonant frequency of the quartz transducer (nominally 10 MHz). The frequency-divider setting n was then varied until each pulse was approximately superposed on the second echo from each preceding pulse. The carrier frequency was then readjusted until a maximum constructive interference condition was obtained. A change in the environmental conditions of the specimen caused a change in the transit time, and thus in the interference condition. As the environment changed, superposition was maintained by adjusting the carrier frequency. The divider setting was kept constant for a given experiment. Thus, the experimentally measured quantity was $\Delta f/f$. It is easily shown that

$$\Delta t/t = -\Delta f/f, \tag{3}$$

and that

$$\Delta v/v = \Delta f/f + \Delta\ell/\ell. \tag{4}$$

Since an elastic modulus C is related to the velocity v and mass density ρ by

$$C = \rho v^2 , \tag{5}$$

it follows that

$$\Delta C/C = \Delta\rho/\rho + 2\Delta v/v. \tag{6}$$

Since $\Delta\rho/\rho = -3\Delta\ell/\ell$, one then obtains

$$\Delta C/C = 2\Delta f/f - \Delta\ell/\ell. \tag{7}$$

Changes of elastic moduli due to temperature effects were determined. The measured quantities were thus $\frac{1}{f}\frac{\Delta f}{\Delta T}$, where T is absolute temperature. Since the thermal expansion coefficient α is defined as

$$\alpha = \frac{1}{\ell}\frac{\Delta\ell}{\Delta T}, \tag{8}$$

it follows that

$$\frac{1}{C}\frac{\Delta C}{\Delta T} = 2\left(\frac{1}{f}\frac{\Delta f}{\Delta T}\right) - \alpha. \tag{9}$$

At room temperature, elastic moduli typically change linearly with temperature. The temperature coefficient $(1/C)\,(dC/dT)$ is then significant, since it gives the relative modulus change with temperature. Room-temperature values of the temperature coefficients are reported in this paper.

It is usually found that the thermal-expansion contribution to $(1/C)\,(dC/dT)$ is less than 10% of the velocity contribution, that is, $|\alpha| \leqslant \cdot\ 2\,|(1/f)\,(df/dT)|$. Thus, errors in the thermal expansion coefficient will not lead to significant errors in the temperature coefficients of the elastic moduli.

Except for determining room-temperature values of $(1/C)\,(dC/dT)$, effects of thermal expansion are neglected in this paper. Typically an elastic modulus changes by only 5-10% over the temperature range 4-300K, and neglect of thermal expansion leads to an error of at most 0.5% in the low-temperature value of the elastic modulus. Such errors are well within experimental accuracy. Thus, when elastic-moduli — temperature curves were fit to a semi-theoretical function, as discussed below, thermal expansion was neglected.

Relative velocity changes as small as 10^{-5} could be detected; however, absolute errors in the measured moduli are estimated to be about 1-2 percent. Thus, since the individual data points are normalized to the room-temperature value, the overall curve could be shifted by 1 or 2 percent because of systematic error.

RESULTS

From the longitudinal and transverse ultrasonic velocities, v_ℓ and v_t, the respective elastic moduli are given by:

$$C_\ell = \rho v_\ell^2 , \qquad (10)$$

and

$$C_t = \rho v_t^2 , \qquad (11)$$

where ρ is the mass density.

While polycrystalline aggregates (quasi-isotropic solids) have only two independent elastic constants, several constants are commonly used for various applications. The four most common are the bulk modulus B, Young's modulus E, the shear modulus G, and Poisson's ratio ν. These constants can be calculated from C_ℓ and C_t by the relationships

$$E = 3C_t \, (C_\ell - \tfrac{4}{3} C_t) \; / \; (C_\ell - C_t), \qquad (12)$$

$$B = C_\ell - \tfrac{4}{3} C_t, \qquad (13)$$

$$\nu = \tfrac{1}{2} (C_\ell - 2C_t) \; / \; (C_\ell - C_t), \qquad (14)$$

and

$$G = C_t. \qquad (15)$$

Rather than calculate the temperature dependence of these four elastic constants point by point from the experimental moduli, C_ℓ and C_t can be fit to a semi-theoretical relationship suggested by Varshni[6]:

$$C = C^o - s/(e^{t/T} - 1), \qquad (16)$$

where C^o, s, and t are adjustable parameters and T is the temperature. The value of C at T = O K is C^o, and -s/t is the high-temperature limit of dC/dT. By invoking an Einstein oscillator model of solids, it can be shown (in the absence of electronic effects) that t is the Einstein characteristic temperature. The elastic constants can then be calculated from the moduli using Eqs. 12-15.

A. 5083 Aluminum

Longitudinal (C_ℓ) and transverse (C_t = G) moduli are shown in Figs. 3 and 4. Room-temperature values of the elastic constants are given in Table 2 and room-temperature values of the temperature coefficients of the elastic constants are given in Table 3. Values of commercially pure aluminum (1100 aluminum) are included for comparison.

Curves in Figs. 3 and 4 are plots of Eq. 16 determined by an unweighted least-squares fit of the data. Average percentage differences between measured and curve values are 0.03% and 0.10% for the longitudinal and transverse moduli, respectively. Parameters C°, s, and t are given in Table 4.

The elastic constants were calculated from the moduli shown in Figs. 3 and 4 by Eqs.12-14. The constants E, B, and ν are shown in Figs. 5-7.

B. Ferritic Nickel Steels

Longitudinal and transverse moduli for the four nickel steels are shown in Figs. 8 and 9. Two of the nickel steels, 5 and 6 percent nickel, exhibit maxima at low temperatures. These maxima may be caused by magnetic transitions. The occurrence of these maxima, however, necessitated fitting the low-temperature data to a different function. The Varshni function (Eq. 16) was fit to the data from room temperature to the maximum. The dashed curve represents a continuation of the Varshni function. From O K to the maximum, a polynomial of the form

$$C = C_o + A\tau^2 + B\tau^3 + D\tau^4 \qquad (17)$$

was used to fit the data, where C_o, A, B, and D are adjustable parameters and $\tau = T/T_{max}$, where T is the temperature and T_{max} is the temperature at which the maximum occurs. Since this function has no physical significance, the parameters are not reported. However, the function does satify the requirement that the slope go to zero as T approaches zero. Also it was required that the slope go to zero as T approaches T_{max}.

Room-temperature values of the elastic constants are given in Table 2, and room-temperature values of the temperature coefficients of the elastic constants are given in Table 3. Average percentage differences between measured and curve values vary between 0.01% and 0.04% for the longitudinal moduli and 0.02% to 0.04% for the transverse moduli. The constants E, B, and ν are shown in Figs. 10-12.

C. Elastic Debye Temperatures

It is of interest to calculate the elastic Debye temperature θ for the alloys. This fundamental parameter is important in the lattice properties of solids and is related to the elastic wave velocities by[7]

$$\theta = K\langle v \rangle , \tag{18}$$

where

$$K = \frac{h}{k}\left(\frac{3N\rho}{4\pi A}\right)^{1/3} \tag{19}$$

Here h is Planck's constant, k is Boltzmann's constant, N is Avogadro's constant, ρ is the mass density, and A is the atomic weight. The average velocity is given by

$$v = \left(\frac{v_{\ell}^{-3} + 2v_t^{-3}}{3}\right)^{-1/3} \tag{20}$$

The Debye temperatures for the nickel steels and 5083 aluminum at T = 0 K are given in Table 5. The Debye temperatures of iron and commercially pure aluminum are included for comparison.

DISCUSSION

The elastic properties of 5083 aluminum behave regularly with respect to temperature. The elastic moduli (C_{ℓ}, C_t = G, B, E) decrease with increasing temperature, show a relative flatness at low temperatures, achieve zero slope at T = 0K, and approach linear behavior at high temperatures. Poisson's ratio also behaves regularly, having a positive temperature coefficient.

As mentioned earlier, however, the moduli of two of the nickel steels (5 and 6 percent nickel) behave anomalously at low temperatures. The moduli first increase with increasing temperature, then decrease approaching linear behavior. Both C_{ℓ} and C_t exhibit a maximum at approximately the same temperature. The 6 percent alloy was checked on both heating and cooling, and no hysteresis seemed to be associated with the anomaly. This behavior is similar to that of some stainless steels,[8] which undergo paramagnetic to antiferromagnetic transitions at low temperatures. Possibly, the anomalies are caused by some magnetic transition.

It is emphasized that the data reported here are dynamic (adiabatic) rather than static (isothermal) and apply to rapid, rather than slow loading. In most cases the differences between adiabatic and isothermal elastic constants are small, less than one percent. Conversion formulas are given by Landau and Lifshitz,[9] for example.

Of the many possible engineering elastic constants (five - C_ℓ, E, G, B, and ν - are discussed herein), only two are independent. Both isotropic and quasi-isotropic solids are characterized elastically by two constants. Thus, n-2 independent relationships must exist among n variables. By differentiation, several quite useful relationships can be obtained. These include:

$$\frac{dC_\ell}{C_\ell} = \frac{1}{B + \frac{4}{3}G} \left(dB + \frac{4}{3}\, dG\right), \tag{21}$$

$$\frac{dE}{E} = \frac{G}{G + 3B} \cdot \frac{dB}{B} + \frac{3B}{G + 3B} \cdot \frac{dG}{G} \tag{22}$$

$$\frac{dB}{B} = \frac{dE}{E} + \frac{2}{1-2\nu}\, d\nu\,, \tag{23}$$

$$\frac{dG}{G} = \frac{dB}{B} - \frac{3}{(1+\nu)(1-2\nu)}\, d\nu, \tag{24}$$

and

$$\frac{d\nu}{\nu} = \frac{E}{E-2G} \cdot \left(\frac{dE}{E} - \frac{dG}{G}\right) \tag{25}$$

If $\nu \approx \frac{1}{3}$, which is a typical value for most metals and alloys, then these equations simplify to

$$\frac{dC_\ell}{C_\ell} \approx \frac{2}{3}\frac{dB}{B} + \frac{1}{3}\frac{dG}{G}, \tag{26}$$

$$\frac{dE}{E} \approx \frac{dB}{9B} + \frac{8}{9}\cdot\frac{dG}{G}, \tag{27}$$

$$\frac{dB}{B} \approx \frac{dE}{E} + 2\frac{d\nu}{\nu}, \tag{28}$$

$$\frac{dG}{G} \approx \frac{dB}{B} - \frac{9}{4}\cdot\frac{d\nu}{\nu}, \tag{29}$$

and

$$\frac{d\nu}{\nu} \approx 4\left(\frac{dE}{E} - \frac{dG}{G}\right) \approx \frac{4}{9}\left(\frac{dB}{B} - \frac{dG}{G}\right) \tag{30}$$

These relationships contain some surprising and useful information. For example: Young's modulus is eight times more sensitive to shear than to dilatation; Poisson's ratio depends equally, but oppositely, on shear and dilatation, and only on the B/G ratio; the longitudinal modulus is twice as sensitive to dilatation as to shear, etc.

Furthermore, these relationships can be used to predict a wide variety of effects when only partial information is available. Equations (26)-(30) can be expressed generally as

$$\frac{dX}{X} \approx a\frac{dY}{Y} + b\frac{dZ}{Z}, \tag{31}$$

where X, Y, and Z are elastic constants and a and b are numerical coefficients. Much more powerful relationships result by introducing another variable V:

$$\frac{1}{X}\frac{dX}{dV} \approx \frac{a}{Y}\frac{dY}{dV} + \frac{b}{Z}\frac{dZ}{dV}, \tag{32}$$

where V represents any independent variable such as temperature, pressure, or composition. As a useful example, these relationships will now be used to discuss the effects of nickel on the elastic properties of iron.

The existing data[10-28] on the room-temperature elastic constants of nickel-steels are presented in Figs. 13-16. Data for pure iron, obtained by a

Voigt-Reuss-Hill-arithmetic average of single-crystal data[29] are also included. The data were least-squares fitted to a straight line, the slope of which is included in the figures. The data of Speich, Schwoeble, and Leslie was omitted from the least-squares fit for the bulk modulus and Poisson's ratio.

If, in Eq. (32), V represents composition, the change with composition in one elastic constant can be found from the measured changes with composition in two others. For example, considerably more data exists for Young's modulus and the shear modulus of nickel steels than for Poisson's ratio. Using Eq. (21), however, the compositional dependence of ν can be found from E and G data:

$$\frac{1}{\nu}\frac{d\nu}{dV} \approx 4\left(\frac{1}{E}\frac{dE}{dV} - \frac{1}{G}\frac{dG}{dV}\right), \qquad (33)$$

or

$$\frac{d\nu}{dV} \approx \frac{4}{3}\left(\frac{1}{2}\frac{dE}{dV} - \frac{1}{.8}\frac{dG}{dV}\right), \qquad (34)$$

since $\nu \approx \frac{1}{3}$, $E \approx 2$ (x 10^{11} N/m^2) and $G \approx .8$ (x 10^{11} N/m^2) for iron. Using the slopes given in Figs. 13 and 14 as values for dE/dV and dG/dV, $d\nu/dV \approx 6.7 \times 10^{-4}$. The slope given in Fig. 16 is $\sim 7 \times 10^{-4}$. Similarly, if the G and B data are used in Eq. 27 (with $B \approx 1.6 \times 10^{11}$ N/m^2), then $dE/dV \approx -2.19 \times 10^9$ N/m^2, in very good agreement with the measured value of -2.22×10^9 N/m^2. In fact, using the E and G data to calculate the compositional dependence of B and ν justifies excluding the Speich et al. data from the linear least-squares fit for the compositional dependence of B and ν.

The Debye temperatures of the nickel steels are lower than the Debye temperatures of either iron or nickel[24, 29] This is expected since the elastic constants, and thus the sound velocities, decrease drastically with the addition of nickel to iron. In fact, the largest known alloying effects on elastic constants may occur for iron-nickel alloys.[28] This effect is not completely understood, but may in part be caused by magnetic interactions.

Finally, the relationship between elastic and plastic properties is discussed briefly, and the possible use of elastic data for predicting plastic properties is indicated. The importance of this is two-fold. First, for cryogenic engineering applications the most important properties of metals are strength and toughness. Second, the possible relationships between elastic and plastic properties seem to be generally unappreciated.

Usually, elastic and plastic behavior are considered separately. For example, in a typical stress-strain experiment the elastic and plastic regions can be separated by an elastic limit, a proportional limit, or sometimes a yield point. While these concepts differ from each other and are not always well-defined and reproducible experimentally, they serve to define a stress level that if exceeded results in permanent, plastic, irreversible mechanical deformation.

The most obvious link between elastic and plastic properties is provided by a dislocation model of microplastic mechanical behavior. All students of dislocation theory know that the mathematical equations describing phenomena such as slip, yielding, bending, cleavage, etc. from a dislocation viewpoint almost always contain elastic constants as material parameters. In an isotropic elasticity model these constants are Young's modulus, the shear modulus, and Poisson's ratio. Isotropy is, of course, an idealization since all real materials are anisotropic in some way.

Despite its potentially high impact, surprisingly little work on elastic-plastic relationships has been published. The advantages that might accrue from such work include: (a) the ability to relate plasticity more intimately to interatomic forces; (b) the possibility of correlating plastic properties with other parameters via the elastic constants — for example atomic number, melting temperature, or Debye theta; and (c) a possibly higher degree of correlation among plastic properties themselves. Some correlations — for example, between Young's modulus and yield stress, or between microhardness and the shear modulus — are already well known.[1]

The most thorough study of the elastic-plastic relationship was made by Pugh.[32] Other studies have been made by Hasselman[33] and by Crutchley and Reid[34] Pugh made the following suggestions: (1) at temperatures less than one third of its melting point, a material's resistance to plastic deformation is proportional to Gb, where G is the shear modulus, and b is the magnitude of the Burgers vector; (2) fracture strength is proportional to Ba, where B is the bulk modulus, and a is the lattice parameter; (3) ductility increases with B/G, the ratio of the bulk modulus to the shear modulus. Since Poisson's ratio ν is an increasing monotonic function of B/G, ductility should also increase with Poisson's ratio; most data support his suggestion -- lead ($\nu = 0.40$), aluminum ($\nu = 0.37$), copper ($\nu = 0.34$), chromium ($\nu = 0.25$), beryllium ($\nu = 0.04$) as examples. Since Poisson's ratio changes only very slowly with alloying, mechanical deformation, etc., it does not provide as sensitive an index of ductility as would be desired. On the other hand, small changes in Poisson's ratio may correspond to large changes in ductility. A possible large influence of ν on the plastic anisotropy of b.c.c. metals was discussed by Crutchley, Reid, and Webster.[35] In terms of the iron-nickel alloys reported on here, the following inferences would be drawn from the room-temperature elastic data: (1) the plastic resistance decreases with increasing nickel content; (2) the fracture strength decreases slightly with increasing nickel content; and (3) the ductility, as measured by B/G increases slightly with increasing nickel content. The experimental study by Jolley[36] contradicts the first two assertions while affirming the third. The poor correlation in this case between elastic and plastic properties suggests either that the particular dislocation models used by Pugh[32] are too simple or that alloying nickel into iron changes somehow the behavior of dislocations in the alloy. For example, atomic ordering could cause localized effects on dislocations that would not be revealed by macroscopic elastic constants.

This leads naturally to another topic, which is especially important in the cryogenic application of iron-nickel alloys -- the ductile - brittle transition. The elastic data in Figs. 8-12 show no irregularities near temperatures where the ductile-brittle transitions occur. This is expected since acoustic waves sample a macroscopic volume of a specimen, and the modulus defect due to dislocations is quite small. Assuming the ductile-brittle transition results from immobilizing dislocations, then measurement of ultrasonic attenuation would be a better approach than measurement of ultrasonic velocities, if in these alloys dislocations contribute significantly to the attenuation.

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Table 1. Compositions and Properties of Alloys

Alloy	Chemical Composition, Mill Analyses (wt. pct.)											Hardness (DPH No., 1 kg Load)	Mass Density at 294 K (g/cm^3)
	Fe	C	Mn	P	S	Si	Ni	Cr	Mo	Aℓ	N		
Fe-3.5 Ni	Bal	.10	.46	.015	.013	.20	3.62	--	--	--	--	174	7.858
Fe-5 Ni	Bal	.13	.45	.025	.025	.275	5.00	--	.275	.085	.020	233	7.821
Fe-6 Ni	Bal	.06	1.12	.005	.004	.24	5.66	.63	.18	--	--	246	7.821
Fe-9 Ni	Bal	.06	.56	.007	.003	.27	9.25	--	--	--	--	260	7.841
	Aℓ	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	V	Ni		
Aℓ 5083	Bal	.08	.19	04	.63	4.75	.13	.04	.01	.007	.003	78	2.666

Table 2. Room Temperature Values of Elastic Constants (10^{11} N/m^2 except ν (dimensionless))

Alloy	E	G	B	ν
Aℓ 5083	0.716	0.269	0.716	0.333
Aℓ 1100*	0.695	0.259	0.724	0.340
Fe-3.5 Ni	2.038	0.791	1.600	0.288
Fe-5 Ni	1.984	0.770	1.559	0.288
Fe-6 Ni	2.024	0.790	1.543	0.281
Fe-9 Ni	1.951	0.754	1.562	0.292
Fe **	2.05	0.81	1.664	0.282

* Calculated from data taken by the authors.

** Reference 31.

Table 3. Logarithmic Temperature Derivatives of Elastic Constants at Room Temperature (10^{-4} K^{-1})

Alloy	$\frac{1}{B}\frac{dB}{dT}$	$\frac{1}{E}\frac{dE}{dT}$	$\frac{1}{G}\frac{dG}{dT}$	$\frac{1}{\nu}\frac{d\nu}{dT}$
Aℓ 5083	-2.15	-6.29	-6.81	2.08
Aℓ 1100*	-2.24	-5.25	-5.60	1.41
Fe - 3.5 Ni	-1.56	-2.82	-3.02	0.93
Fe - 5 Ni	-1.53	-3.32	-3.61	1.32
Fe - 6 Ni	-1.42	-3.21	-3.52	1.40
Fe - 9 Ni	-1.25	-2.77	-3.01	1.08
Fe **	-0.90	-2.11	-2.31	0.95

* Calculated from data taken by the authors.

** Calculated from data in Reference 24 using a Voigt-Reuss-Hill average.

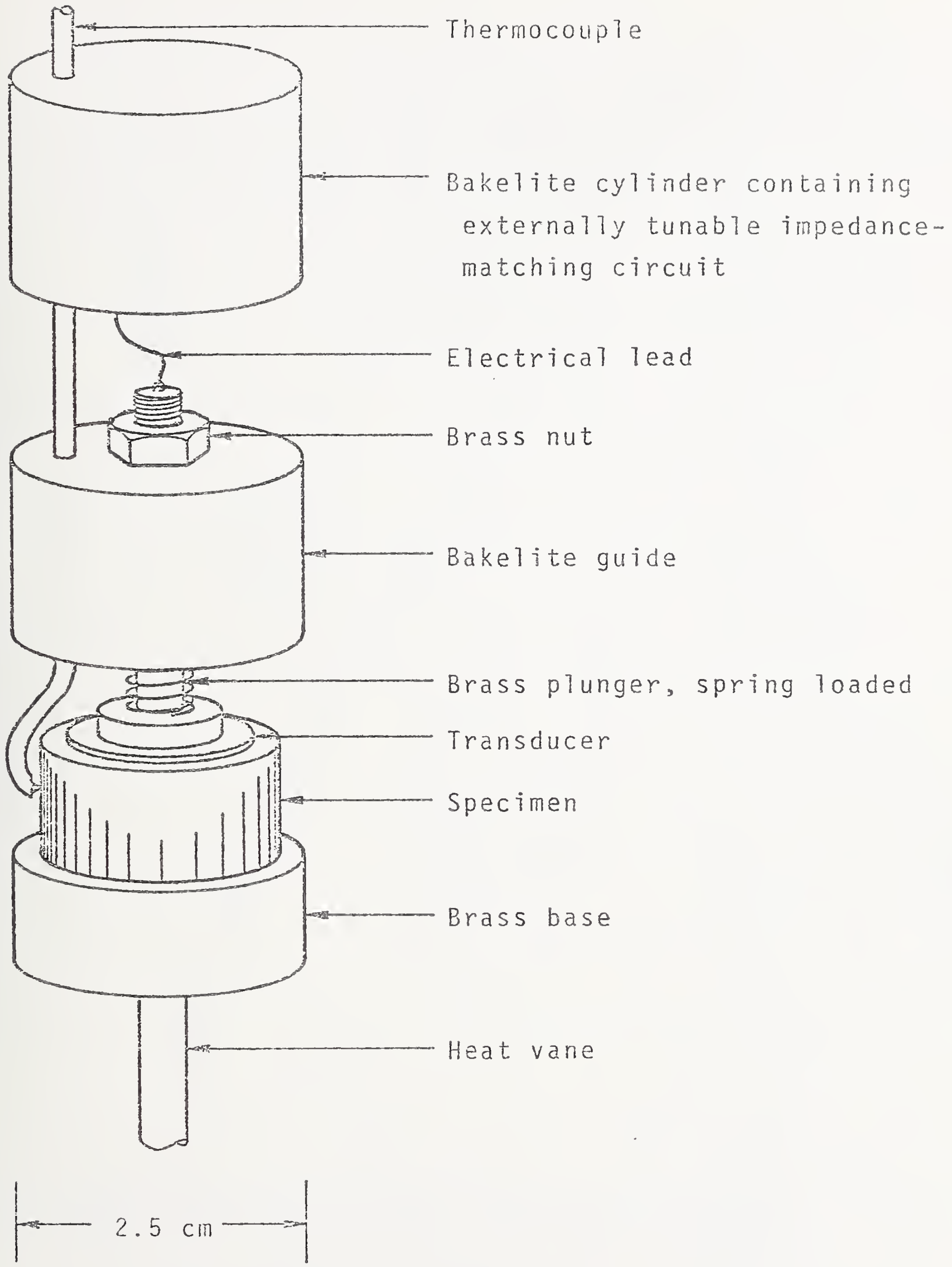
Table 4. Parameters in Equation 3

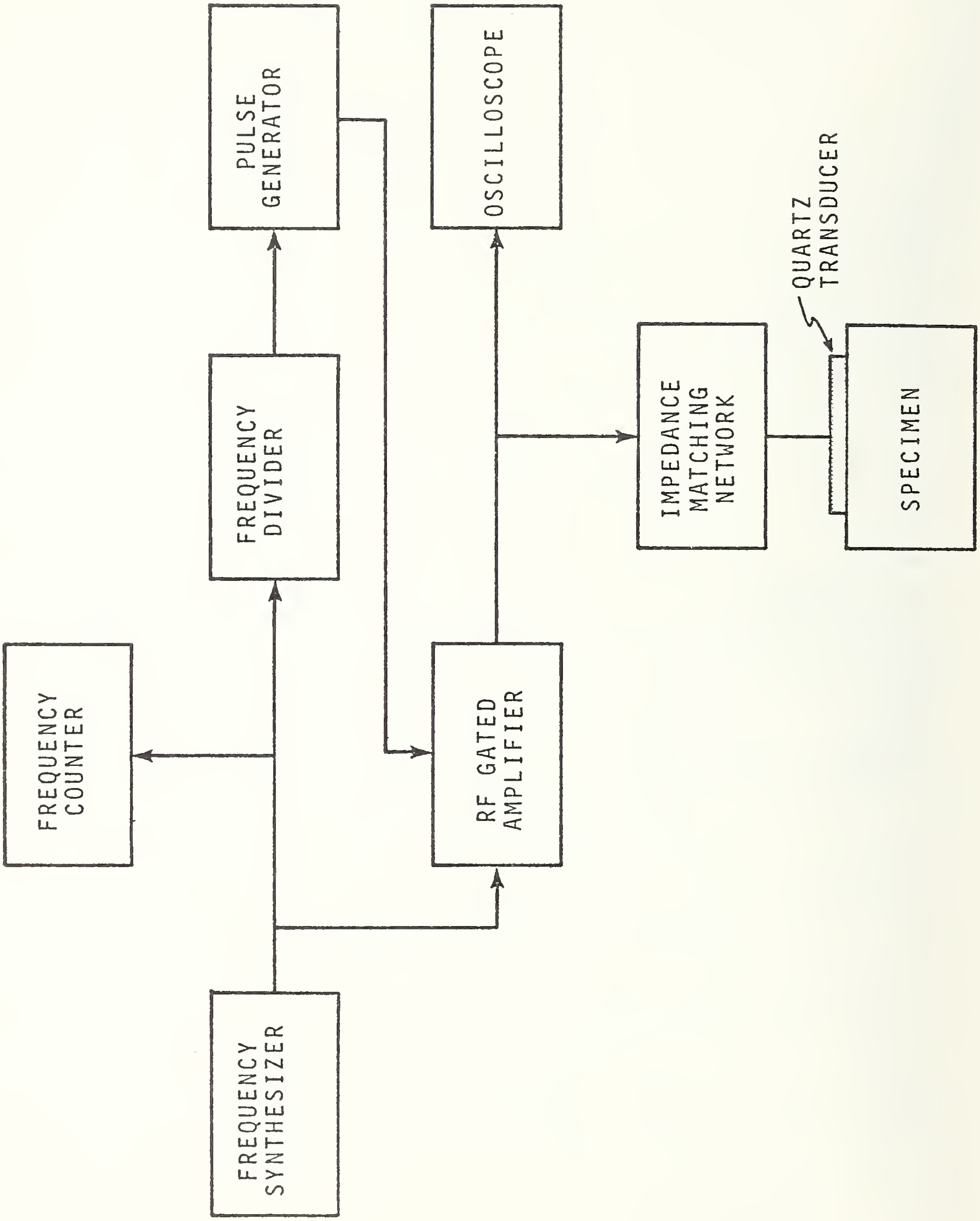
Alloy	Mode	C^o (10^{11} N/m^2)	s (10^{11} N/m^2)	t (K)
Aℓ5083	ρv_ℓ^2	1.151	0.093	235.3
	ρv_t^2	0.307	0.038	206.7
Fe - 3.5 Ni	ρv_ℓ^2	2.763	0.140	246.7
	ρv_t^2	0.840	0.053	218.7
Fe - 5 Ni	ρv_ℓ^2	2.687	0.230	353.8
	ρv_t^2	0.819	0.104	345.8
Fe - 6 Ni	ρv_ℓ^2	2.692	0.244	380.5
	ρv_t^2	0.835	0.125	398.7
Fe - 9 Ni	ρv_ℓ^2	2.663	0.126	252.7
	ρv_t^2	0.799	0.057	246.0

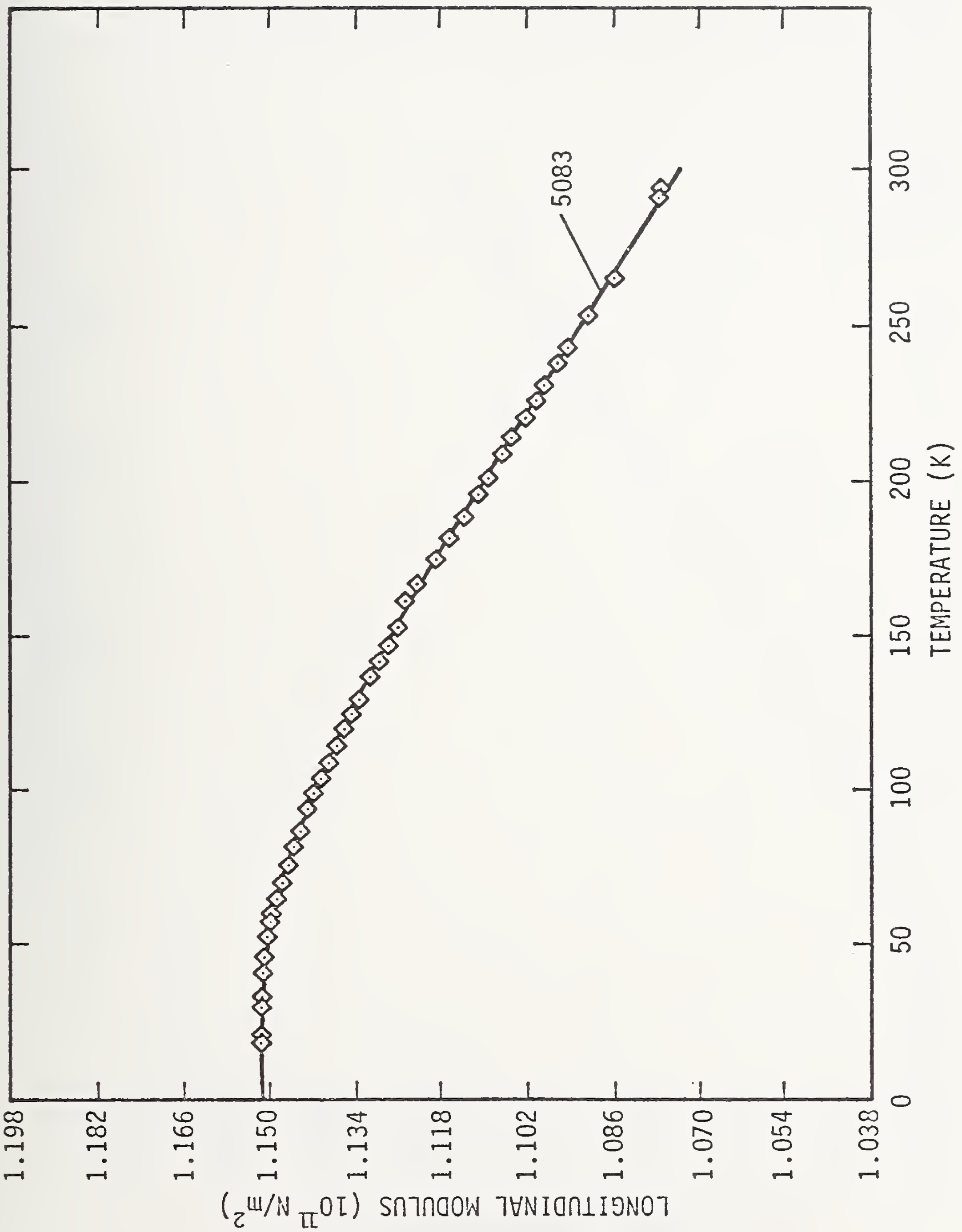
Table 5. Elastic Debye Temperatures at T = O K

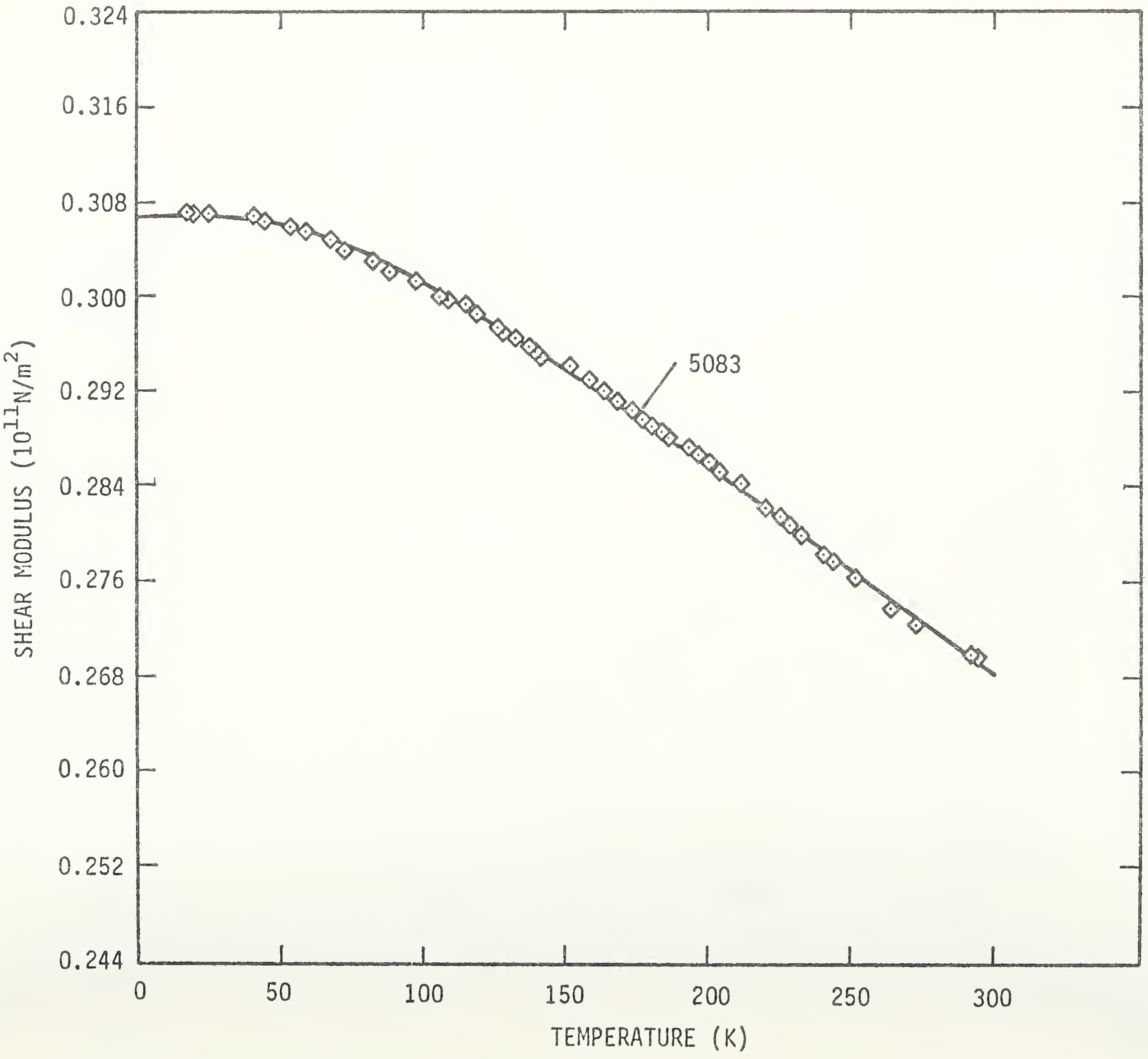
Alloy	θ (K)
Aℓ 5083	414.8
Aℓ 1100	405.4
Fe - 3.5 Ni	463.7
Fe - 5 Ni	459.0
Fe - 6 Ni	463.4
Fe - 9 Ni	453.0
Fe *	477

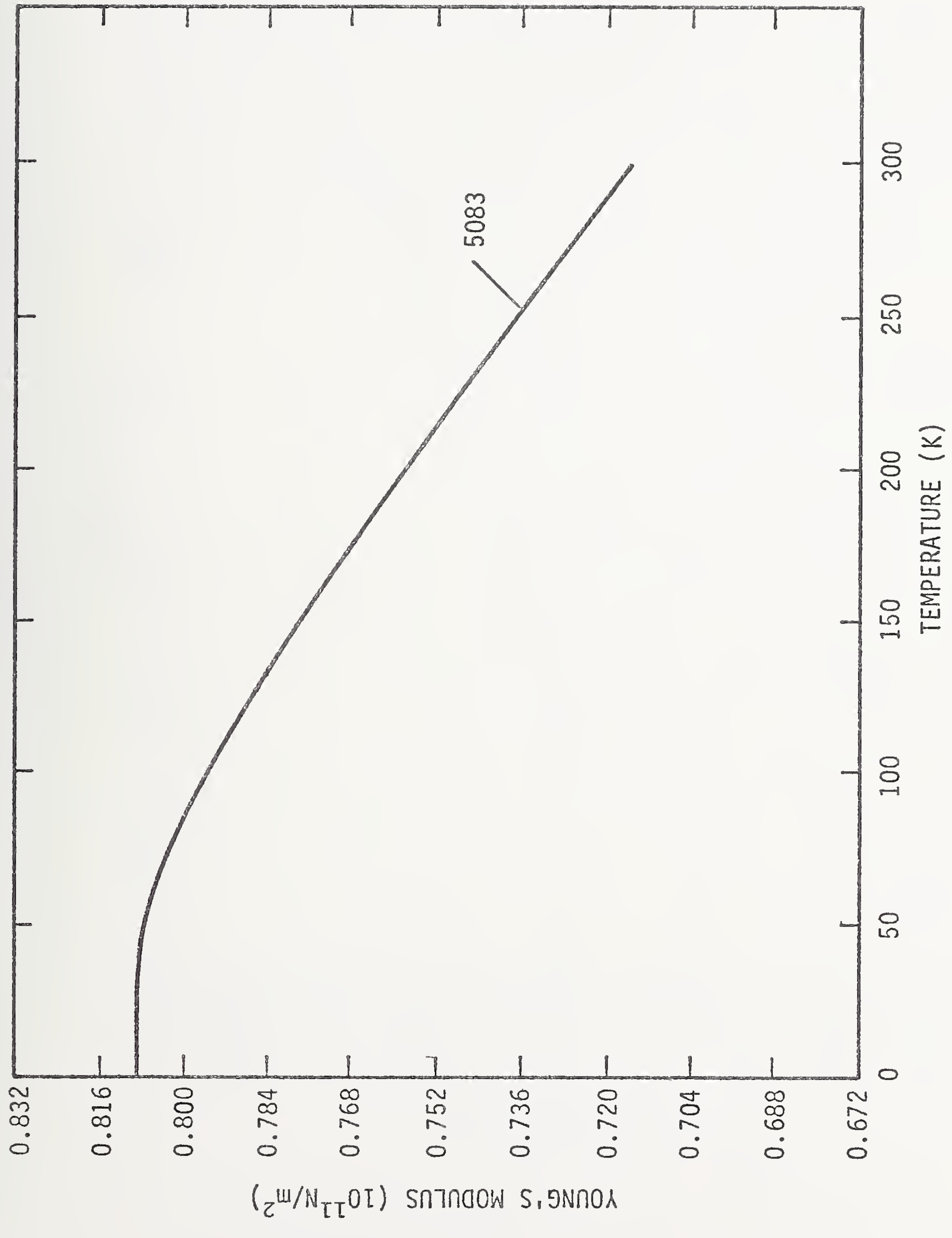
* Reference 24.


Thermocouple
Bakelite cylinder containing externally tunable impedance-matching circuit
Electrical lead
Brass nut
Bakelite guide
Brass plunger, spring loaded
Transducer
Specimen
Brass base
Heat vane
2.5 cm

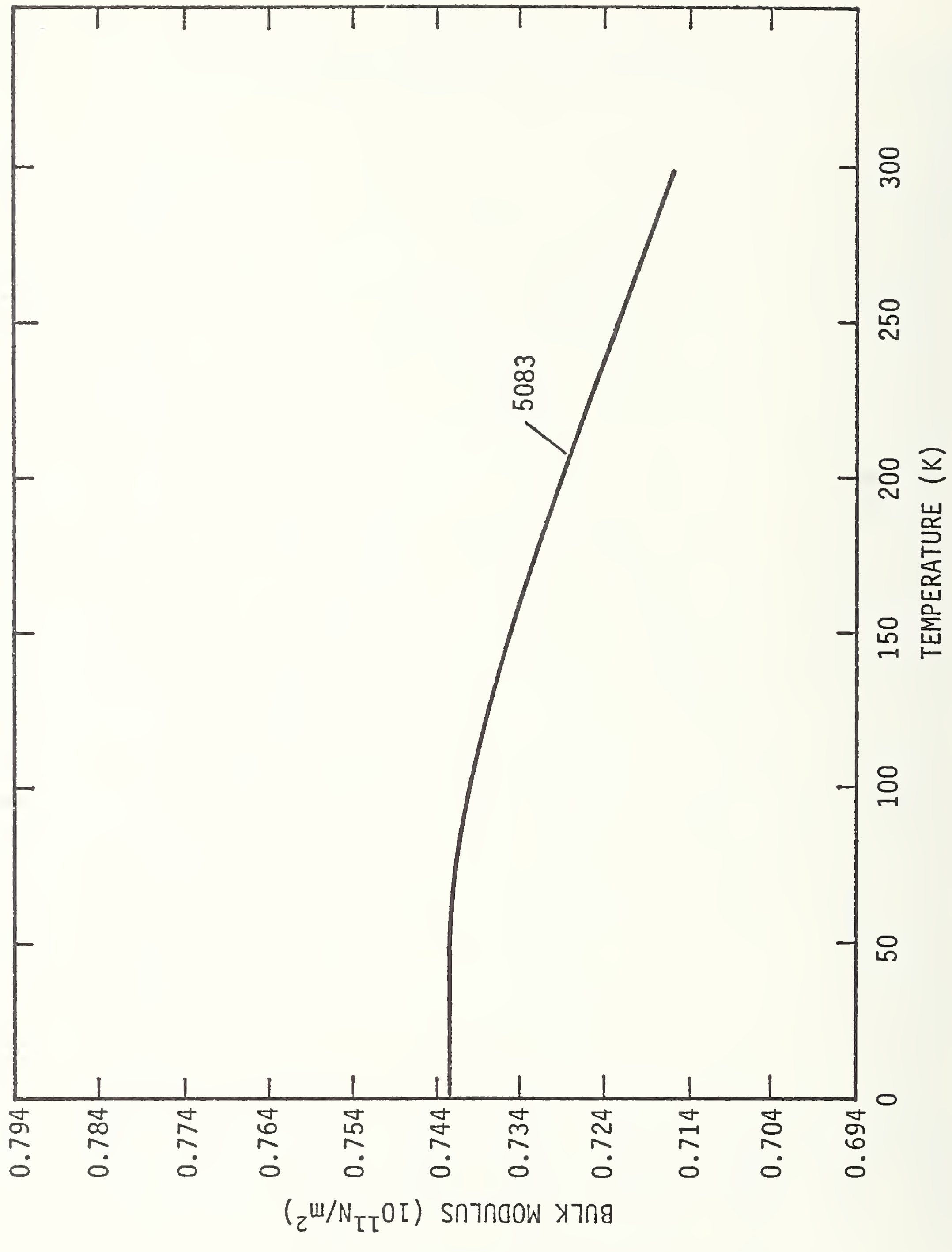

FREQUENCY SYNTHESIZER
FREQUENCY COUNTER
FREQUENCY DIVIDER
PULSE GENERATOR
RF GATED AMPLIFIER
OSCILLOSCOPE
IMPEDANCE MATCHING NETWORK
QUARTZ TRANSDUCER
SPECIMEN

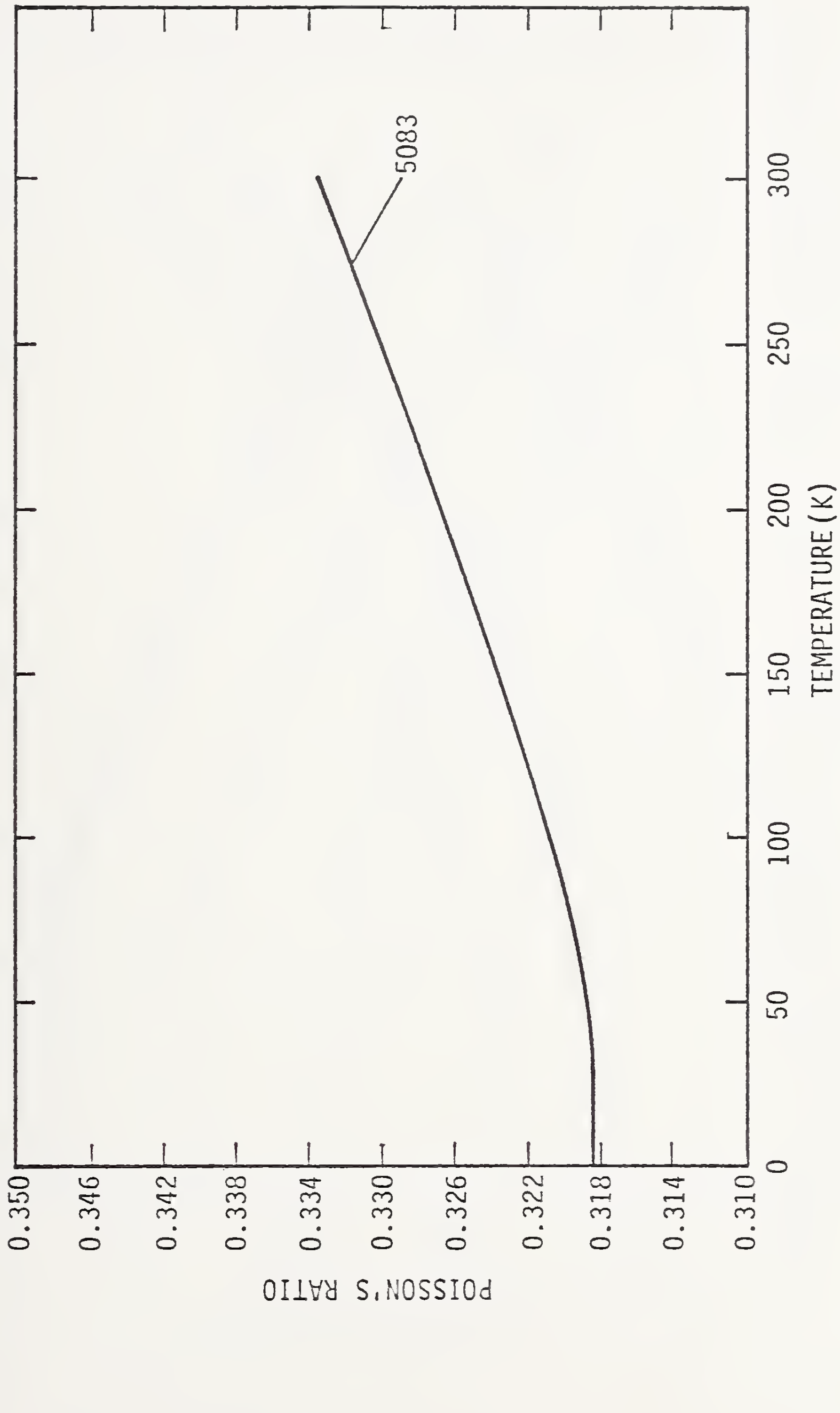

LONGITUDINAL MODULUS (10^{11} N/m^2)
1.198
1.182
1.166
1.150
1.134
1.118
1.102
1.086
1.070
1.054
1.038
TEMPERATURE (K)
0
50
100
150
200
250
300
5083

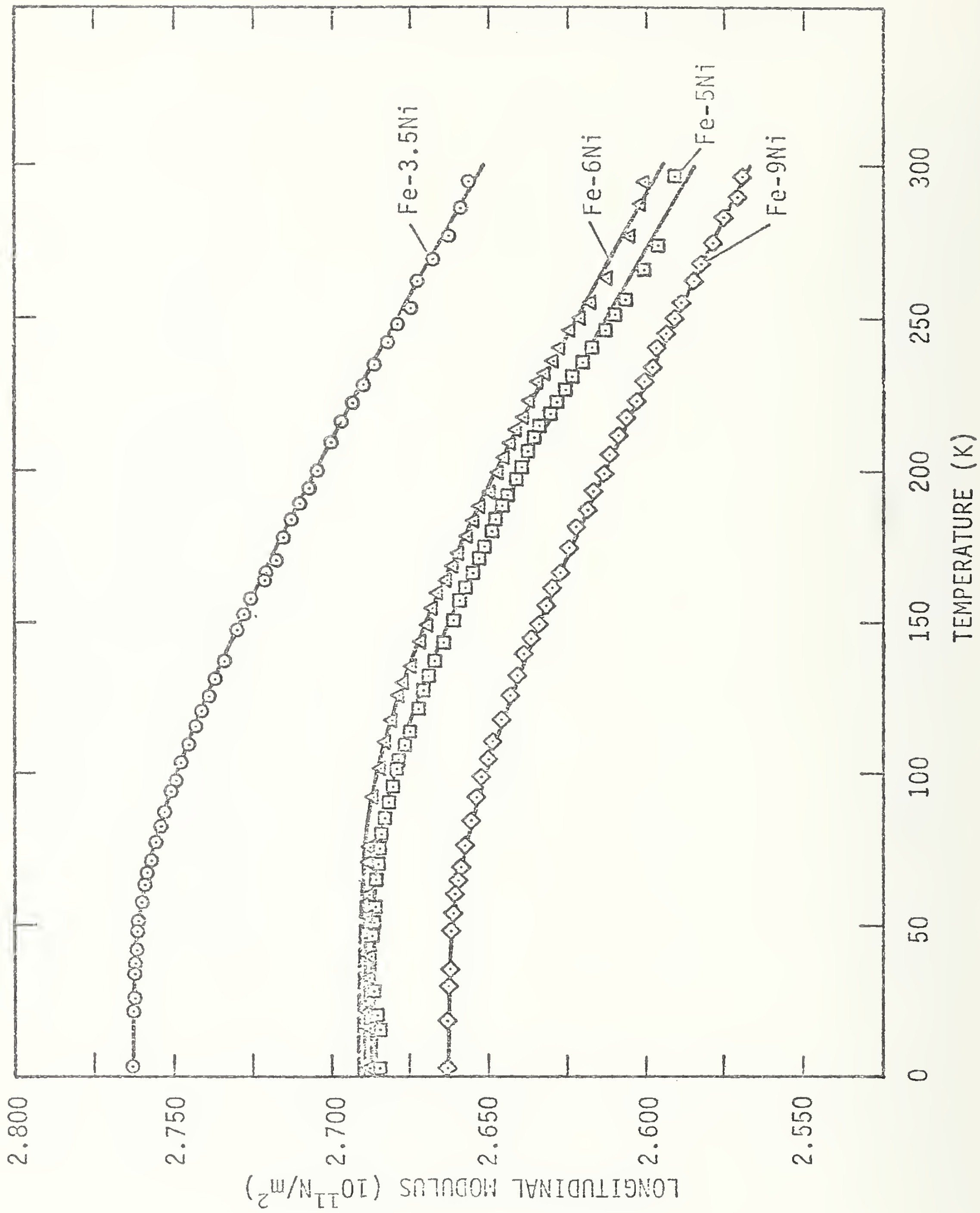

0.324
0.316
0.308
0.300
0.292
0.284
0.276
0.268
0.260
0.252
0.244
SHEAR MODULUS (10^{11}N/m^2)
0
50
100
150
200
250
300
TEMPERATURE (K)
5083

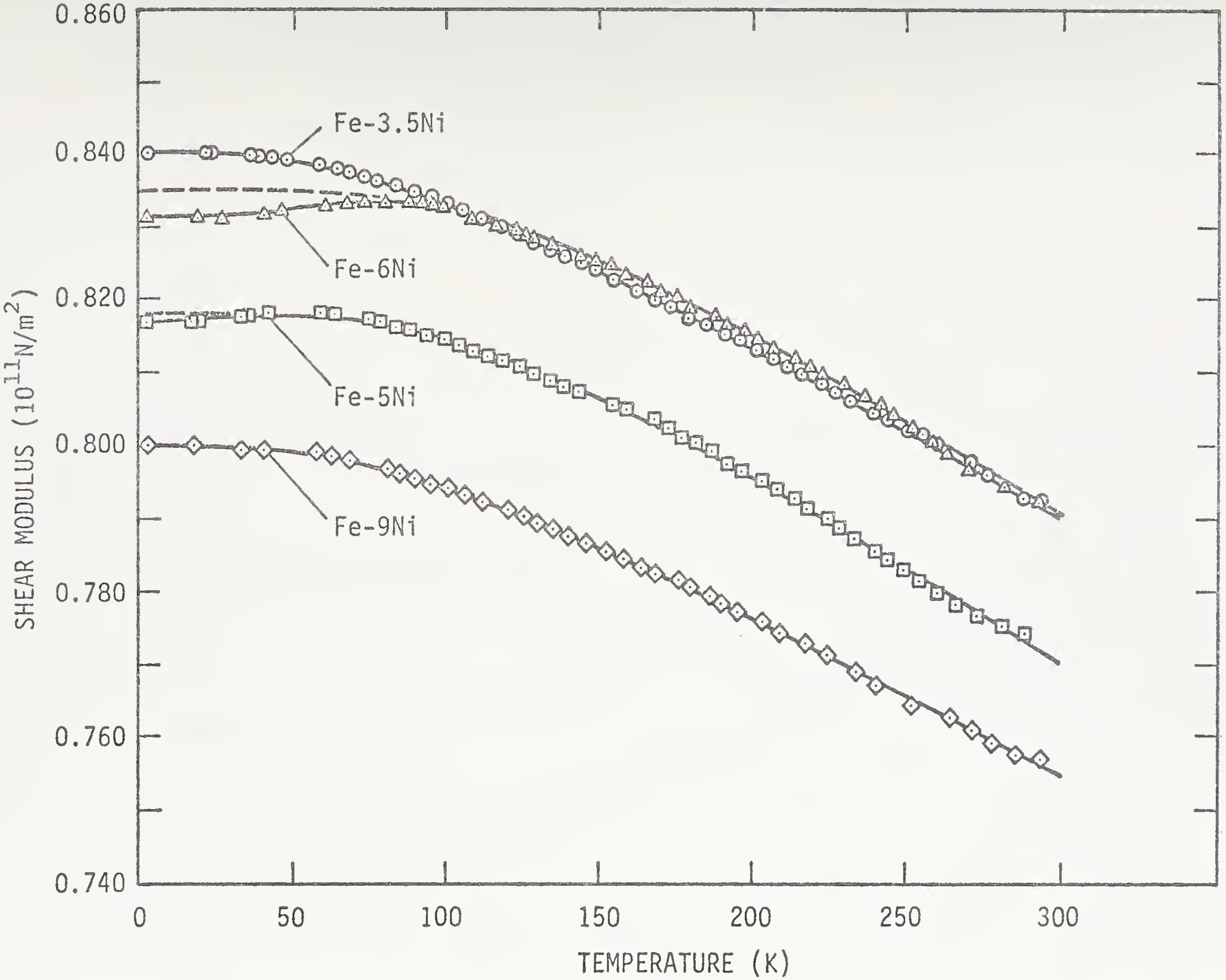


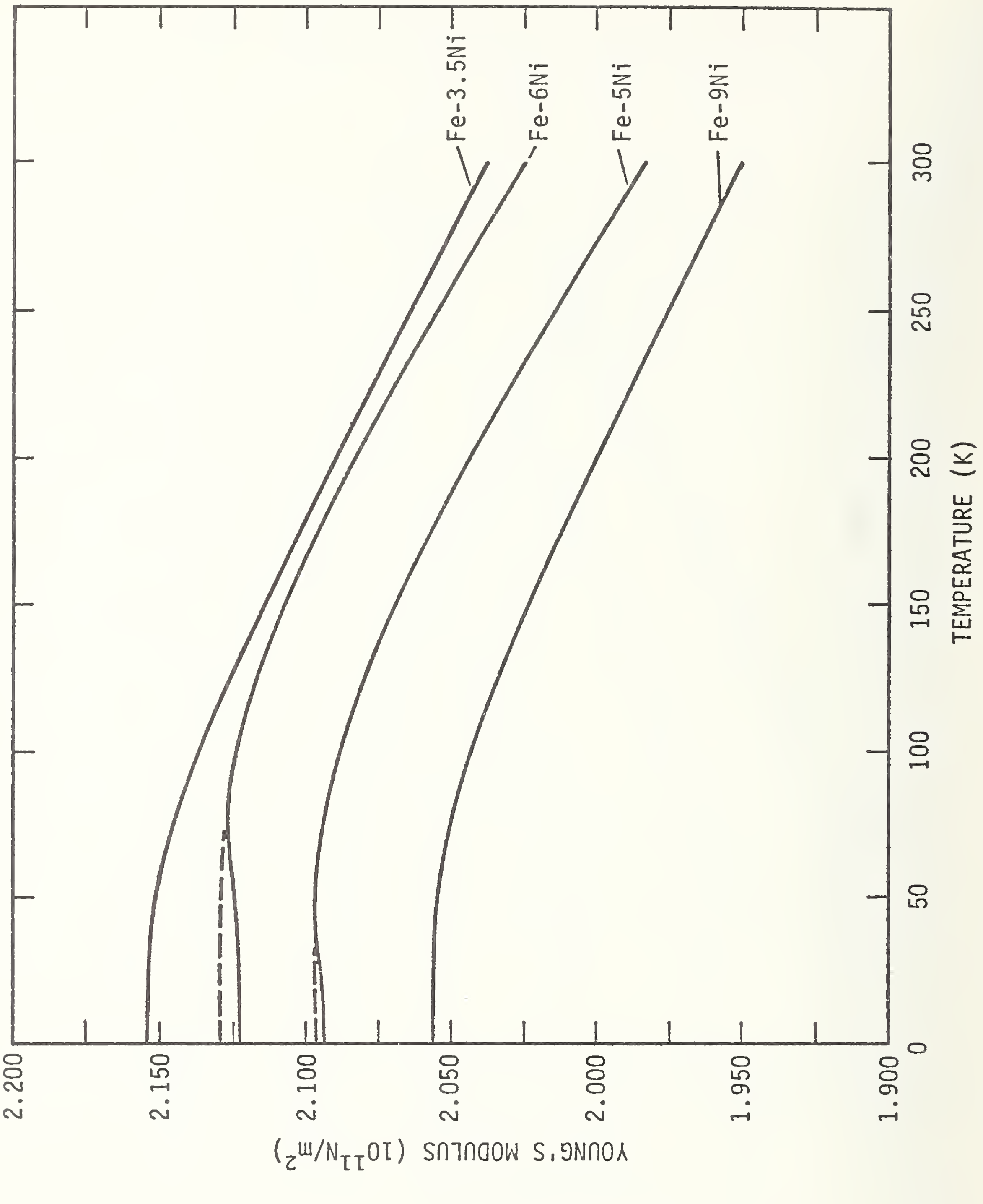
5083
TEMPERATURE (K)
0
50
100
150
200
250
300
YOUNG'S MODULUS ($10^{11}N/m^2$)
0.832
0.816
0.800
0.784
0.768
0.752
0.736
0.720
0.704
0.688
0.672

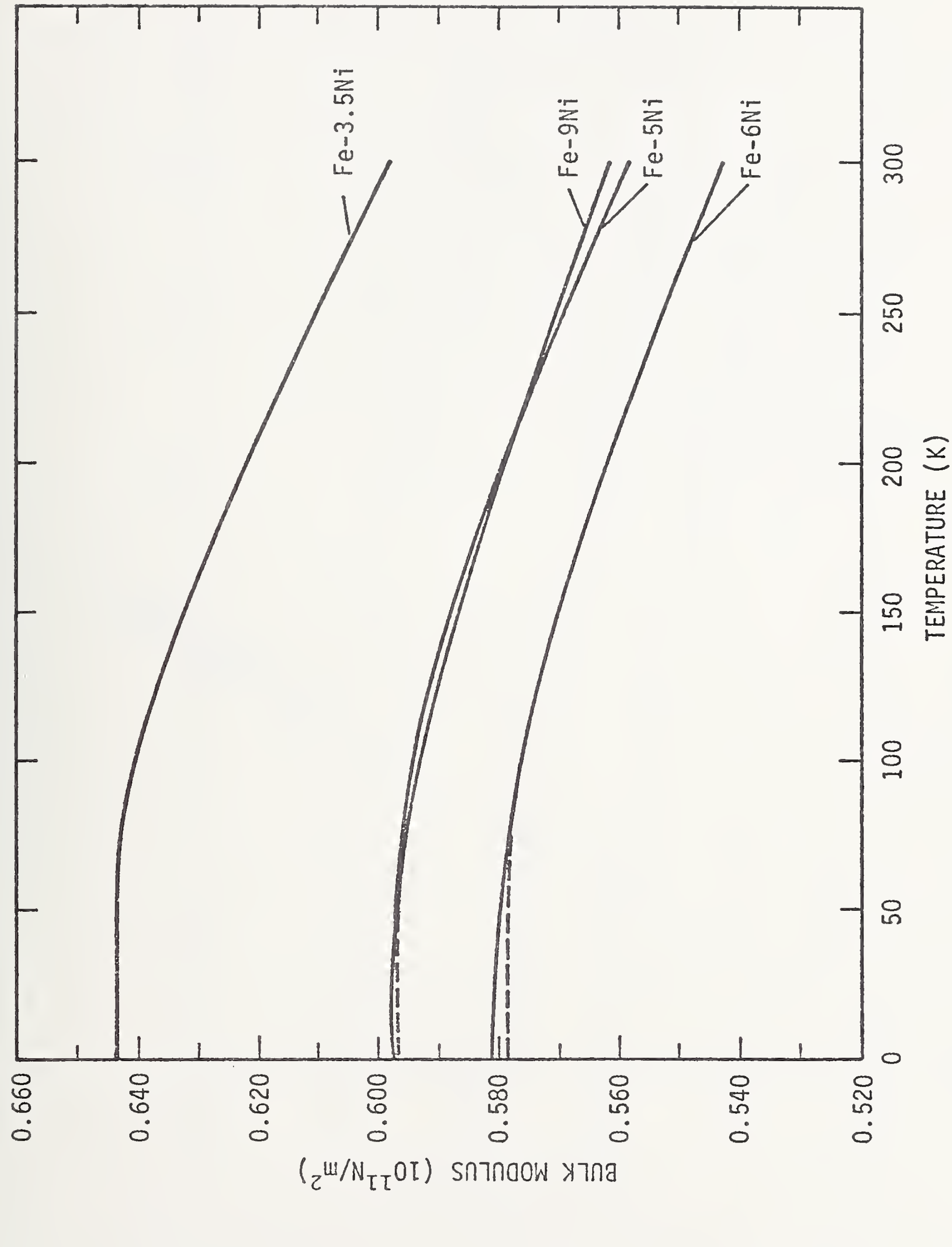

BULK MODULUS (10^{11}N/m^2)
0.794
0.784
0.774
0.764
0.754
0.744
0.734
0.724
0.714
0.704
0.694
TEMPERATURE (K)
0
50
100
150
200
250
300
5083

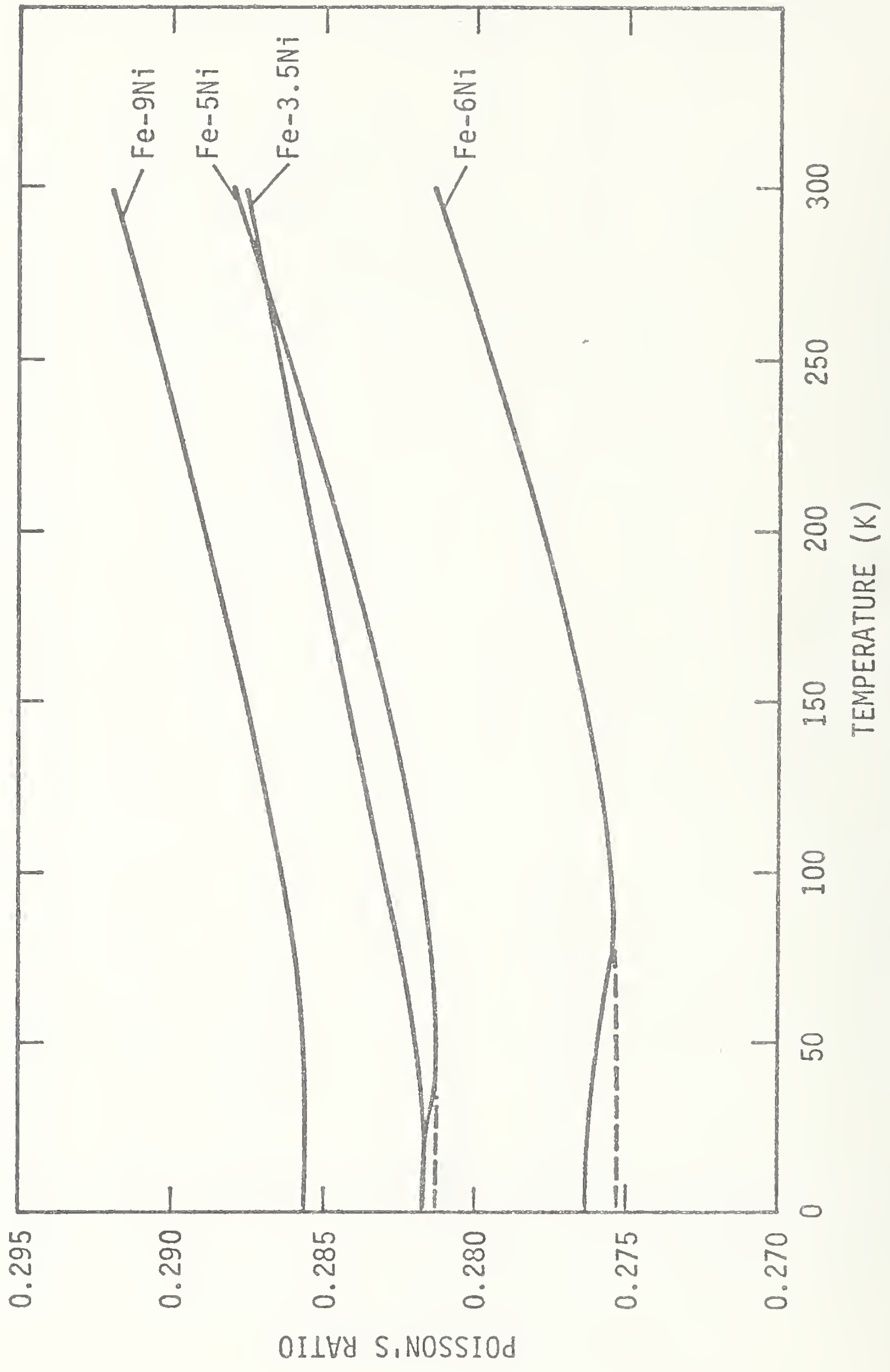

POISSON'S RATIO
0.350
0.346
0.342
0.338
0.334
0.330
0.326
0.322
0.318
0.314
0.310
TEMPERATURE (K)
0
50
100
150
200
250
300
5083

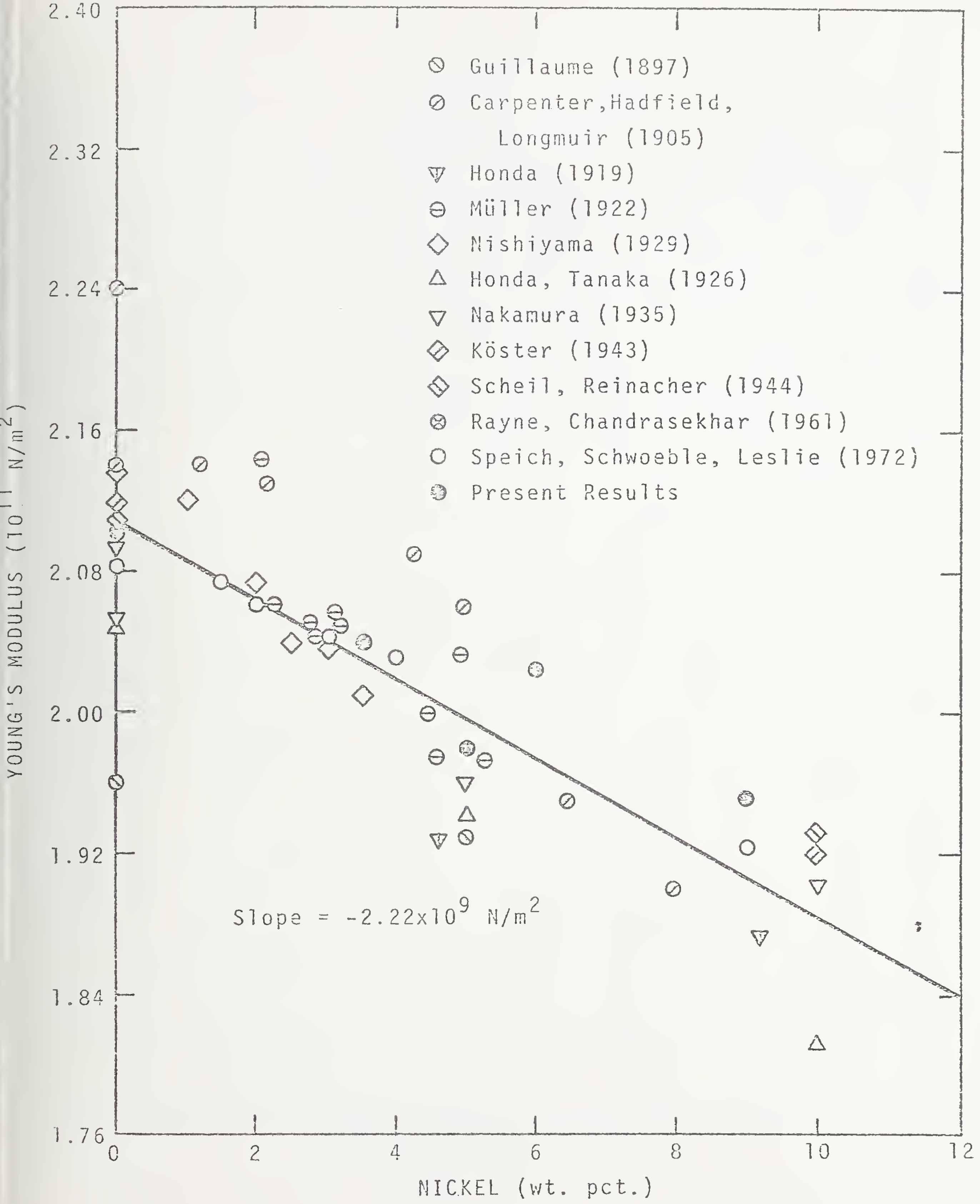

LONGITUDINAL MODULUS (10^{11}N/m^2)
2.800
2.750
2.700
2.650
2.600
2.550
TEMPERATURE (K)
0
50
100
150
200
250
300
Fe-3.5Ni
Fe-6Ni
Fe-5Ni
Fe-9Ni

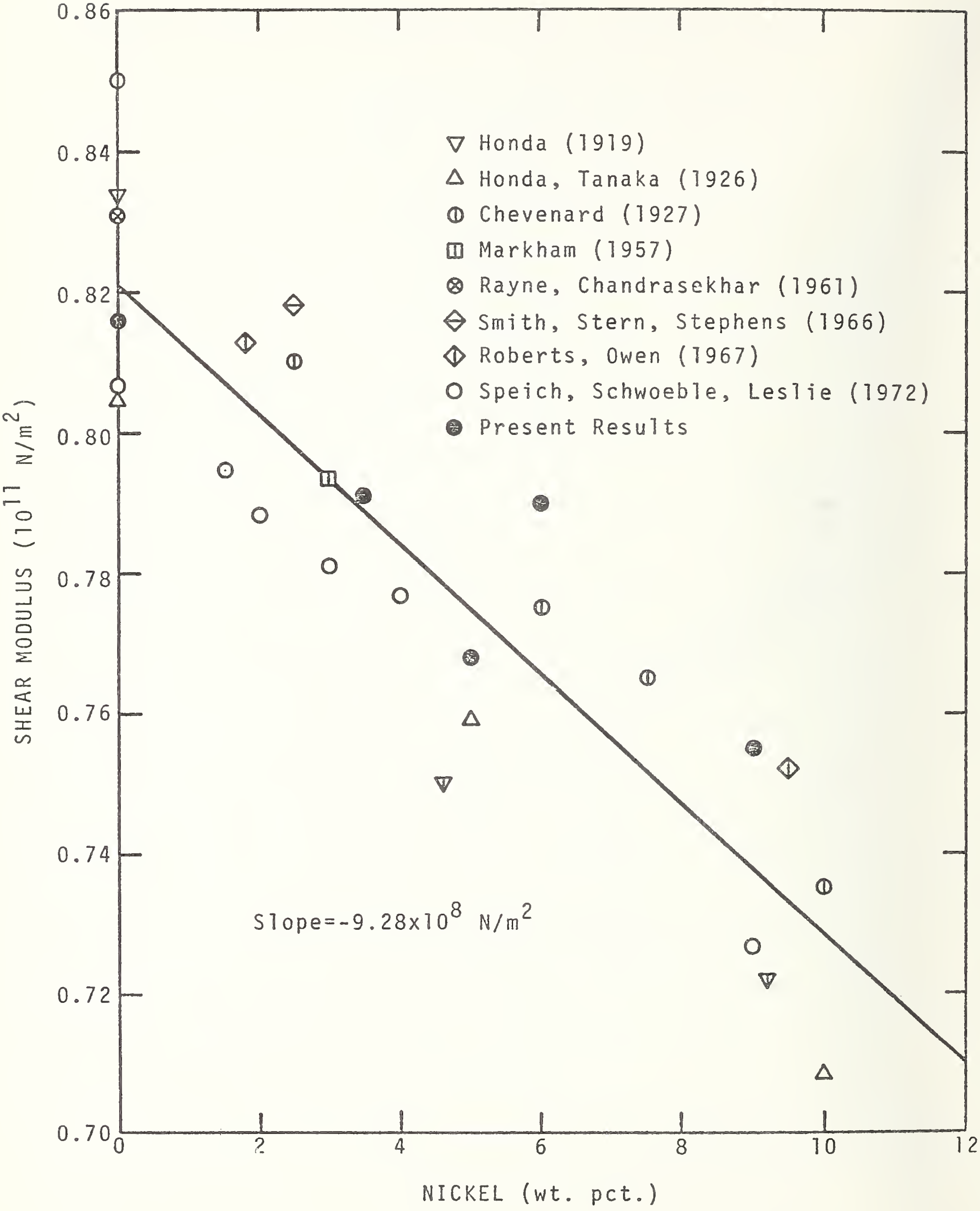

0.860
0.840
0.820
0.800
0.780
0.760
0.740
SHEAR MODULUS (10^{11}N/m^2)
0
50
100
150
200
250
300
TEMPERATURE (K)
Fe-3.5Ni
Fe-6Ni
Fe-5Ni
Fe-9Ni

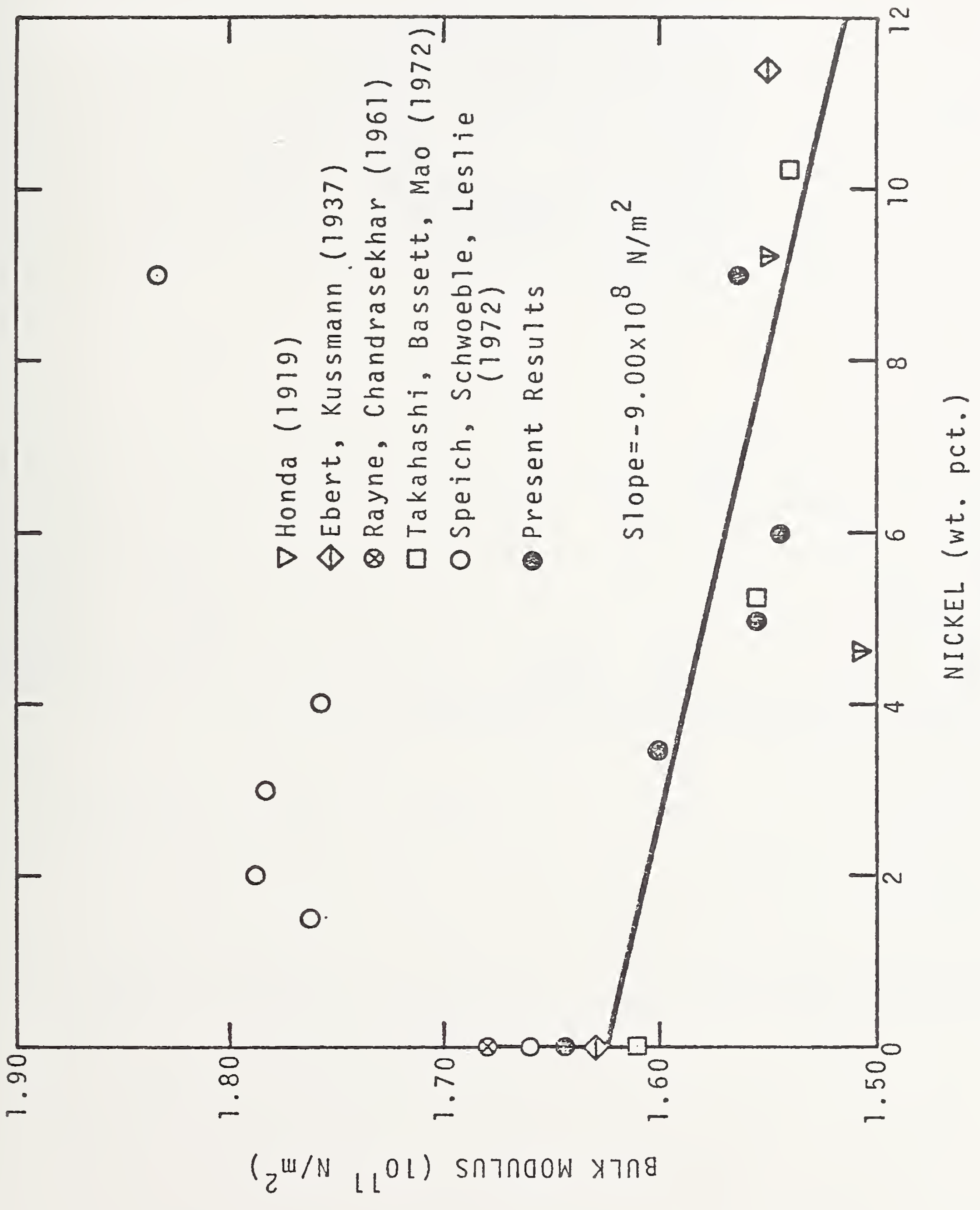

Fe-3.5Ni
Fe-6Ni
Fe-5Ni
Fe-9Ni
YOUNG'S MODULUS (10^{11}N/m^2)
2.200
2.150
2.100
2.050
2.000
1.950
1.900
TEMPERATURE (K)
0
50
100
150
200
250
300

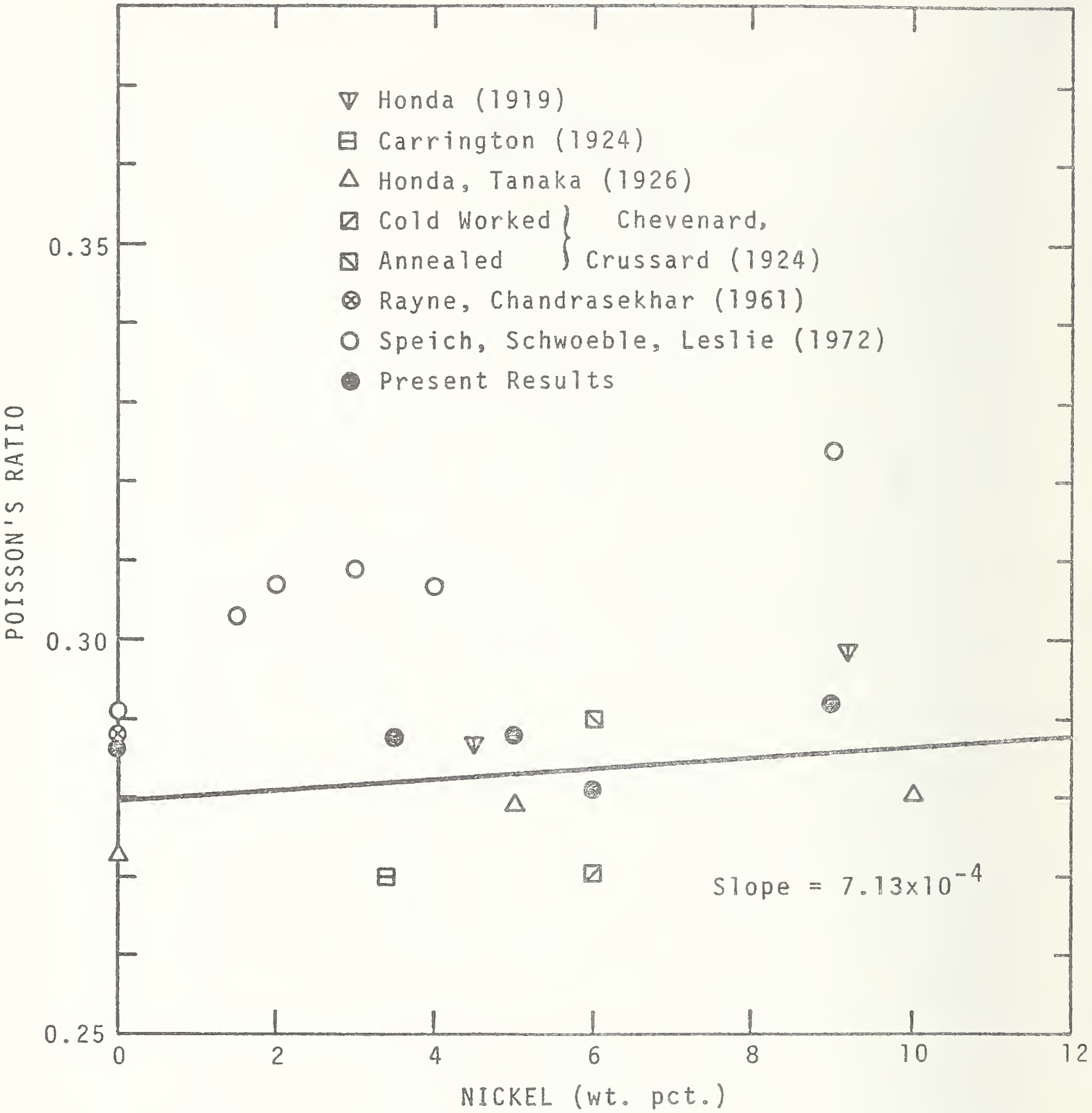

Fe-3.5Ni
Fe-9Ni
Fe-5Ni
Fe-6Ni
0.660
0.640
0.620
0.600
0.580
0.560
0.540
0.520
BULK MODULUS (10^{11}N/m^2)
0
50
100
150
200
250
300
TEMPERATURE (K)


Fe-9Ni
Fe-5Ni
Fe-3.5Ni
Fe-6Ni
POISSON'S RATIO
0.295
0.290
0.285
0.280
0.275
0.270
0
50
100
150
200
250
300
TEMPERATURE (K)


2.40
2.32
2.24
2.16
2.08
2.00
1.92
1.84
1.76
YOUNG'S MODULUS (10^{11} N/m^2)
0
2
4
6
8
10
12
NICKEL (wt. pct.)
Guillaume (1897)
Carpenter, Hadfield, Longmuir (1905)
Honda (1919)
Müller (1922)
Nishiyama (1929)
Honda, Tanaka (1926)
Nakamura (1935)
Köster (1943)
Scheil, Reinacher (1944)
Rayne, Chandrasekhar (1961)
Speich, Schwoeble, Leslie (1972)
Present Results
Slope = -2.22×10^9 N/m^2


0.86
0.84
0.82
0.80
0.78
0.76
0.74
0.72
0.70
SHEAR MODULUS (10^{11} N/m^2)
0
2
4
6
8
10
12
NICKEL (wt. pct.)
▽ Honda (1919)
△ Honda, Tanaka (1926)
⦶ Chevenard (1927)
◫ Markham (1957)
⊗ Rayne, Chandrasekhar (1961)
⬖ Smith, Stern, Stephens (1966)
◈ Roberts, Owen (1967)
○ Speich, Schwoeble, Leslie (1972)
● Present Results
Slope=-9.28x10^8 N/m^2


▽ Honda (1919)
◇ Ebert, Kussmann (1937)
⊗ Rayne, Chandrasekhar (1961)
☐ Takahashi, Bassett, Mao (1972)
○ Speich, Schwoeble, Leslie (1972)
● Present Results
Slope=-9.00x10^8 N/m^2
BULK MODULUS (10^{11} N/m^2)
1.90
1.80
1.70
1.60
1.50
NICKEL (wt. pct.)
0
2
4
6
8
10
12


▽ Honda (1919)
⊟ Carrington (1924)
△ Honda, Tanaka (1926)
⧄ Cold Worked } Chevenard, Crussard (1924)
⧅ Annealed
⊗ Rayne, Chandrasekhar (1961)
○ Speich, Schwoeble, Leslie (1972)
● Present Results
Slope = 7.13x10^{-4}
POISSON'S RATIO
0.25
0.30
0.35
NICKEL (wt. pct.)
0
2
4
6
8
10
12

APPENDIX O

A SURVEY OF LNG TECHNOLOGICAL NEEDS IN THE U.S.A. -- 1974 TO BEYOND 2000

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ABSTRACT

A comprehensive analysis of near and long term research needs has been conducted by the U. S. Gas Industry covering operational areas of Production and Exploration, Synthetic Supply, Transmission, Distribution, Utilization and LNG.

Identifiable research needs are reported for the area of LNG encompassing time frames of:

1974 - 1978	(In detail, year by year)
1979 - 1985	(In 5 year period)
1986 - 2000	(As specific as possible)
Beyond 2000	(As believed necessary).

A year by year examination of LNG research priorities for the first five years are considered vital to overcome the potential suppression of growth in the LNG industry that could result from lack of available technology. Assessments of technical LNG needs beyond 1978 cannot, of course, be too well defined and must be examined annually for purposes of updating.

The National Bureau of Standards Cryogenics Division has become the governmental focal point for LNG research. A survey of NBS LNG research and how these relate to the future technological growth of the LNG industry are discussed.

Paper presented at Fourth International Conference on Liquefied Natural Gas (Algiers, Algeria, June 24-27, 1974)

UN EXAMEN DES BESOINS TECHNOLOGIQUES DU GAZ NATUREL LIQUÉFIÉ AUX U.S.A. -- DE 1974 JUSQU' AU-DELÀ DE 2000

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

RÉSUMÉ

Une analyse complète des besoins d'études, à court et à long terme, est menée par l'Industrie du Gaz des U.S.A. (U. S. Gas Industry) concernant les secteurs opérationnels de la Production et de l'Exploitation, de la Production Synthétique, de l'Acheminement, de la Distribution, de l'Utilisation et du Gaz Naturel Liquéfié (G.N.L.).

Les besoins de recherche daus le domaine du G.N.L. sout passés en revue pour les périodes suivantes:

1974 - 1978	(En détail, année par année)
1979 - 1985	(Pour la période de 5 ans)
1986 - 2000	(Aussi précisément que possible)
Au-delà de 2000	(Ainsi que cela semble nécessaire).

Un examen, année par année, des priorités de la recherche en ce qui concerne le G.N.L., est considéré comme vital pour les cing premierès années, afin de surmonter la stagnation potentielle de l'industrie du G.N.L. qui pourrait résulter d'un manque de disponibilité technologique. La répartition des besoins techniques du G.N.L. au-delà de 1978 re peut évidemment pas étre parfaitement bien définie et doit ètre examineé annuellement en vue d'une mise à jour.

La Division Cryogénic du Bureau National des Etalons (National Bureau of Standards Cryogenic Division) est devenue le centre official d'études du G.N.L. Un examen des études du Bureau National des Etalons ainsi que leur relation avec la future croissance technologique de l'industrie du G.N.L. sont discutés.

A SURVEY OF LNG TECHNOLOGICAL NEEDS IN THE U.S.A. -- 1974 TO BEYOND 2000

The total energy needs of the United States are enormous and are continuously increasing. The nation's growing demand coupled with increasing concern for the environment, difficulties in meeting increased demand from traditional sources and current import uncertainties have led to shortages of all types of energy resources within the U.S. Between 1965 to 1970, the total U.S. domestic energy supply grew at a rate of 5% per year. Many energy economists now are foreseeing energy growth rates in the range of 4.1% to 4.8% per year during the 1970's [1].

The total energy consumed was 44.8×10^{15} btu in 1960, 54.0×10^{15} in 1965 and 68.8×10^{15} in 1970 (Figure 1). Assuming a total energy demand increase of $4\frac{1}{2}$% per year, 96×10^{15} btu will be required during 1980 and 122×10^{15} btu by 1985. Natural gas, coal and oil were the primary resources of the energy consumed in residential, commercial, industrial and transportation sectors of the economy during 1973-74 (Figure 2).

The goal of the gas industry in the United States is to continue to provide a major portion of these future energy needs through the use of untapped natural resources, Canadian imports, synthesized fuel gas production from coal, oil shale, solid wastes, biomass, other natural resources and through the importation of LNG. The options and alternatives in support of this goal have been well defined -- what remains to assure future gas supply is the technological capability to find, produce and deliver this gas to the consumer by new or improved techniques and procedures.

The U. S. gas industry has the incentive and resources to meet this goal. It currently provides about one-third of the nation's total energy requirements. At the end of 1973, it served 43,700,000 residential, commercial and industrial customers through a 981,000 mile underground network of transmission and and distribution lines. The gas industry has grown nearly twelvefold in terms of the book value of total assets since 1945, expanding from a 5 billion dollar industry to more than 59 billion dollars at the end of 1973. Preliminary figures for 1973 show a total consumption of $22\frac{1}{2}$ trillion cubic feet (637 billion cubic meters). The total annual gas requirements in the U. S. are expected to increase to 46.7 trillion cubic feet (1.32 trillion cubic meters) by 1990 as shown in Figure 3.

In the U. S., as in every industrialized nation of the world, the demand for natural gas is increasing. The growing intensity of the worldwide shortages over the past year has touched off a global scramble to obtain supply agreements with producing nations and arrange for construction of related facilities. In the U. S. alone some 10 LNG import terminals [2] are under construction or planned at a cost of almost 1 billion dollars per facility. Each liquefaction complex

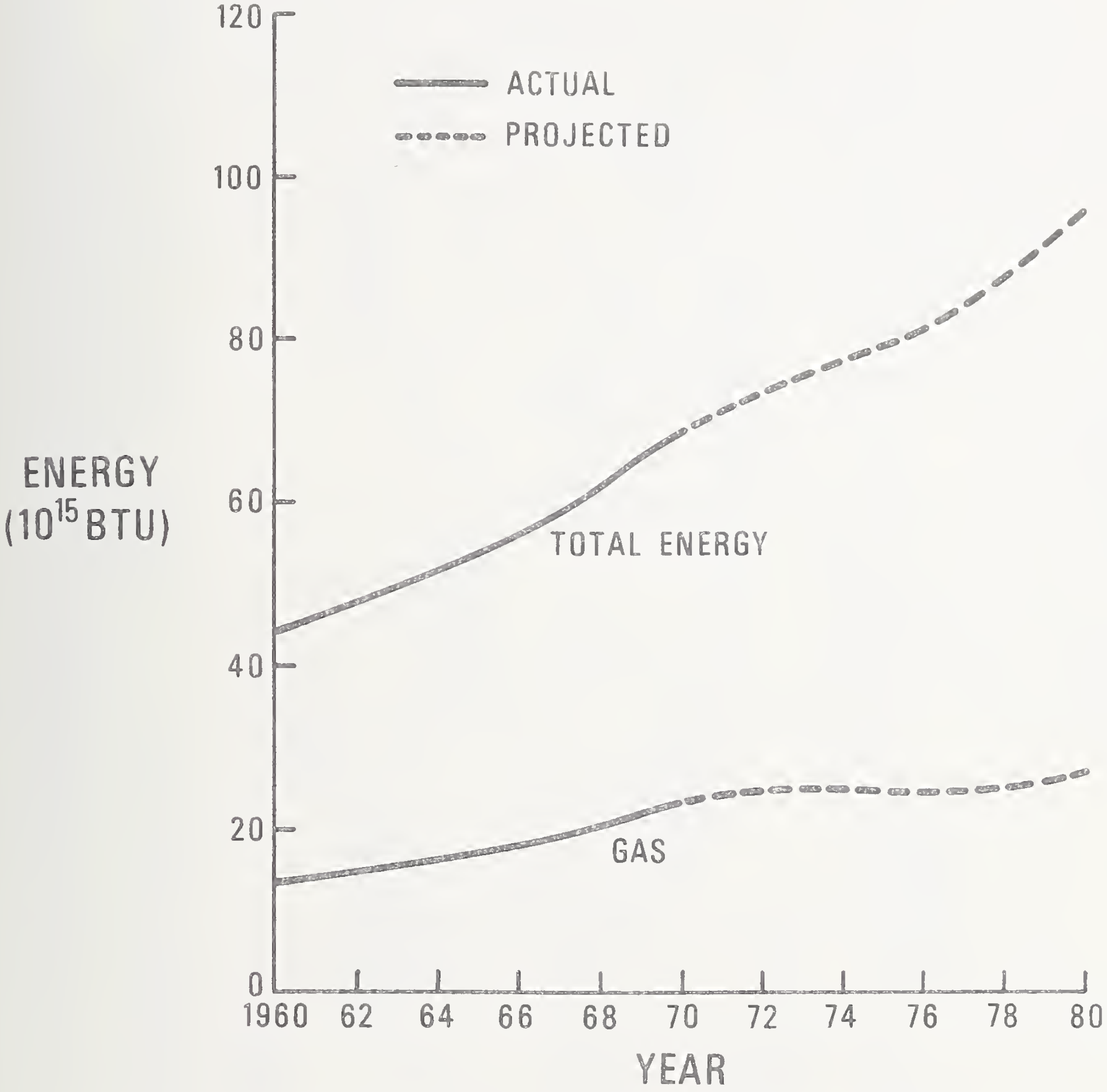
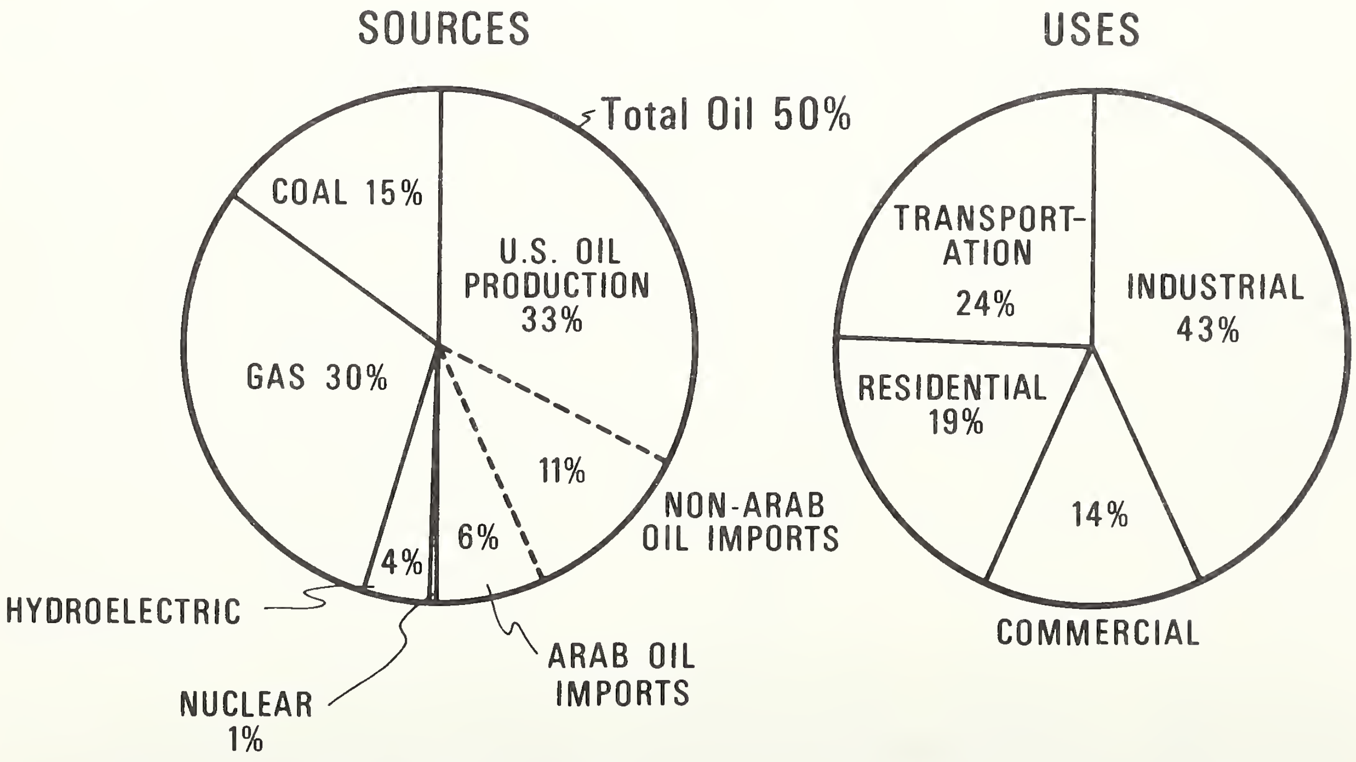


Figure 1. Energy consumption in the United States.

U.S. Energy Sources & Uses

Winter 1973-1974



UNCERTAIN SOURCES 8% OF TOTAL
(2-3 MILLION BARRELS PER DAY)*

**POSSIBLE SHORTAGE WHICH MUST BE OVERCOME THIS WINTER & FOR WHICH INCREASED DOMESTIC SOURCES MUST BE DEVELOPED FOR FUTURE USE.*

Figure 2.

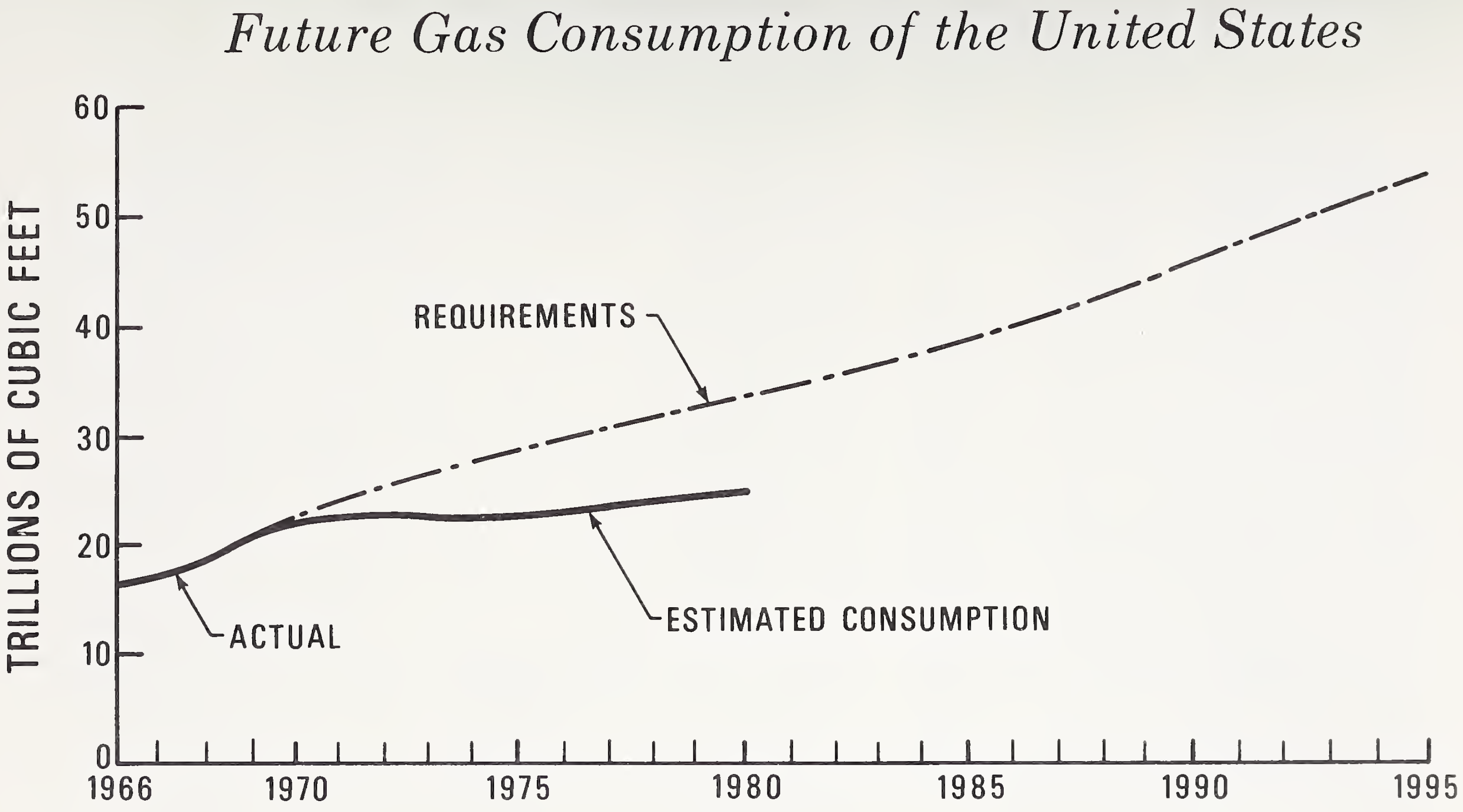


Figure 3. Future gas consumption of the United States.

accounts for approximately $300 million with the remainder of the $1 billion going for ships, pipelines, receiving terminals and storage facilities.

Supplemental gas supply projections for the period 1972-1990 prepared by A.G.A. forecast an LNG importation of 3.2 trillion cubic feet (91 billion cubic meters) by 1990. This projection (Table 1) represents 20% of the total estimated supplemental supply. This thousand-fold increase over the two billion cubic feet (57 million cubic meters) imported during 1972 demonstrates the massive dimension of the rapidly emerging LNG market in the U. S. alone. LNG technology has created a truly international gas industry.

It is axiomatic that this growing section of international gas operations be supported by a comprehensive, continuing research effort to assure energy conservation and safety of all elements, liquefaction, transportation, transfer, storage and plant operation.

Over the past year, the Natural Gas Industry has placed an accelerated emphasis on viewing its supply in relation to projected demand, the reasons for that demand and identification of future technological needs required to balance supply and demand.

Based on an awareness of the role played by Research and Development in furnishing the required advanced technology to assure continued supply and growth, the U. S. Natural Gas Industry undertook a comprehensive study to define the requirements for future research and development and formulated an R&D plan that would assist the gas industry to help satisfy the nation's future energy needs. This study [4] was structured to examine in detail the needs for research and development in each of six major areas, namely

- Exploration and Production
- Synthesized Natural Gas (SNG)
- Transmission
- Distribution
- LIQUEFIED NATURAL GAS
- Utilization

The basic technology required to import LNG exists today (no major technology "breakthrough" required). However, to respond to the rapidly changing demands for energy in all forms, a major research activity has been identified for the gas industry as necessary at this time to accelerate development of this market. The technology involved in ship transportation and large-scale liquefaction is being pursued aggressively and adequately by groups of companies with large financial commitments. We recognize, however, that many items of the research plan program we have recommended will impact on the development programs being conducted by companies outside the gas industry. Coordination between these various R&D programs is essential, therefore, particularly in such areas as LNG ship design and the configuration and construction of marine terminals.

TABLE 1.

Planning Division - A.G.A.

Supplemental Gas Supply Projections (10^{12}cubic feet)

November 1973

SOURCE	1972	1973	1974	1975	1976	1977	1980	1985	1990
Alaskan Imports	–	–	–	–	–	–	0.6	1.5	2.4
Canadian Imports*	1.0	1.1	1.2	1.3	1.4	1.5	1.8	2.4	3.0
LNG Imports	Nil	Nil	Nil	0.2	0.4	0.7	1.7	2.7	3.2
Oil Gasification	–	Nil	0.2	0.6	1.1	1.4	1.7	2.2	2.2
Coal Gasification	–	–	–	Nil	Nil	0.2	0.4	1.3	2.8
Advanced Fracturing	–	–	–	–	–	Nil	0.1	0.8	1.5
Total Supplemental Supply**	1.0	1.1	1.4	2.1	2.9	3.8	6.3	10.9	15.1

Bureau of Mines 1972 new receipts from Canada

***Supplemental supplies are defined as those which add to lower 48 states natural gas production*

Seven critical research needs were selected for immediate study. These items generally cover the metrology and the safety aspects of liquefied natural gas transport, transfer and storage.

This plan also recommends an additional allocation of research funding on an unassigned basis; the rapid changes occurring in the overall LNG picture will undoubtedly create new demands for research. Total cost of the R&D program to meet the essential needs is estimated to be almost $13 million (Figures 4 and 5).

The LNG research plan includes the results of an industry-wide poll of LNG research needs, both foreign and domestic. Based on the responses to this poll, an original group of some forty-two research needs were defined and identified. It was obvious that many of these research needs were being, or should be undertaken by manufacturers, perhaps with the cooperation of the gas industry. Many of these topics are listed in Table 2.

The LNG plan identified four research projects that could properly be categorized as long-range research (beyond 1980) needs; long distance LNG transfer lines, novel LNG transport methods, improved concepts of LNG storage, and utilization of LNG refrigeration.

These tasks were suggested to provide a more definitive answer to constantly recurring questions such as: are long-range LNG pipelines really feasible and economic? ; are there really any new concepts for LNG storage or transportation? ; can the refrigeration available from LNG be utilized practically and economically?

It is recognized that specific LNG research is being sponsored by many segments of the International LNG Industry. These efforts are applauded and are expected to continue as the LNG market continues to grow. It is our purpose, however, to recognize and identify those research areas that can impact upon and re-enforce the many individual LNG research efforts underway or planned by the various elements of the LNG industry. Communication internationally between the various programs as exemplified by LNG-4 is deemed essential to assure an orderly and effective worldwide growth in LNG trade.

The National Bureau of Standards, having played a vital role in past LNG research in support of the gas industry plan, has a number of programs underway that are of importance to the future of the LNG industry.

LNG RESEARCH AT NBS

As the LNG industry has matured from concept through demonstration projects to full scale peak shaving, satellite and base load operations, the requirements for information necessary for implementation of current and future LNG application have been significant. This required information exists in many forms, including data for equipment design, decision making

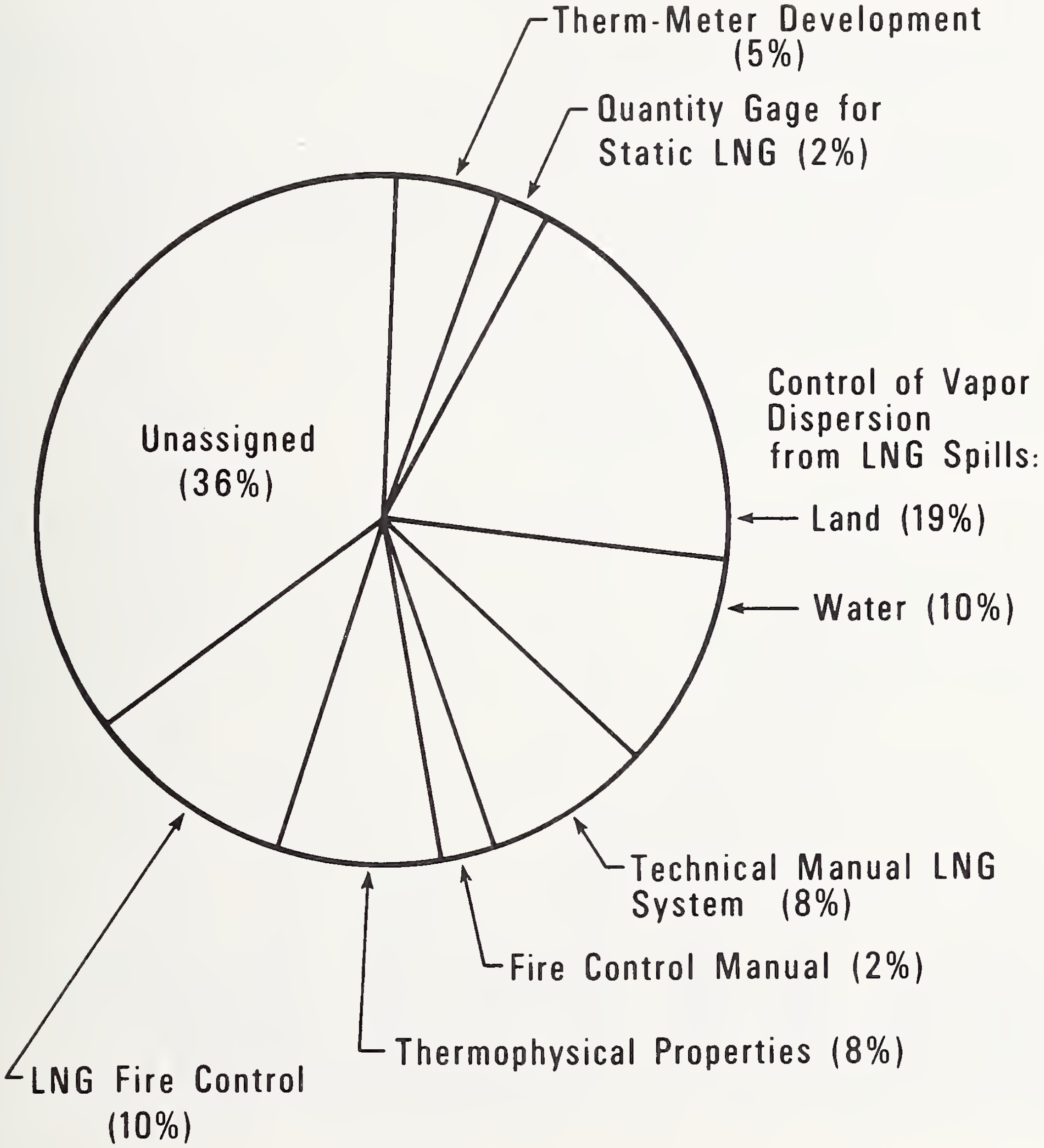


Figure 4. Allocation of LNG research and development costs - first five years [4].

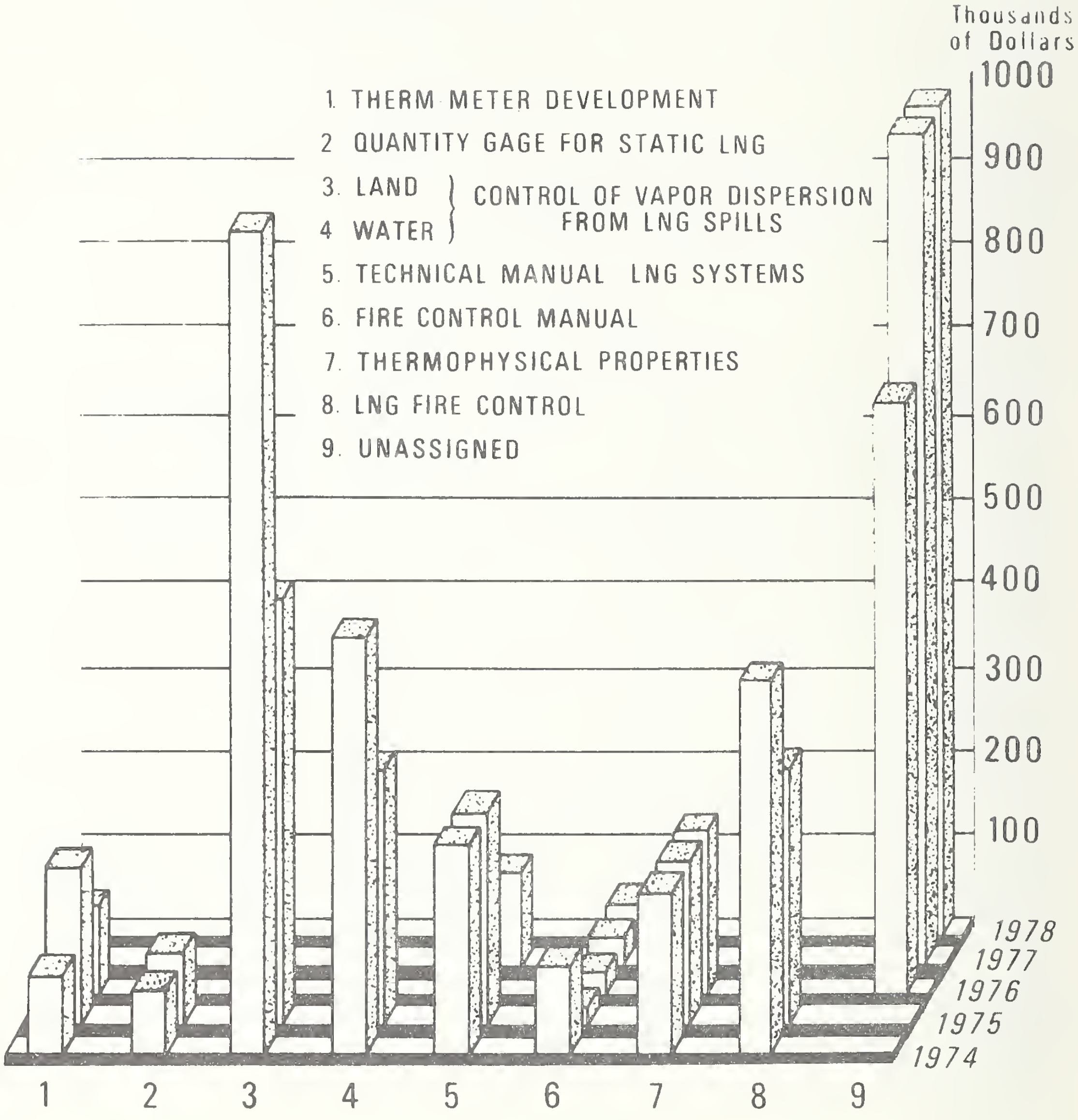


Figure 5. Annual LNG research and development funding [4].

TABLE 2.

SECONDARY LNG RESEARCH TASKS -- AGA GAS RESEARCH PLAN [4]

LNG Facility Siting Criteria
- Definition of standards and codes
- Risk analysis
- Analysis of hazards to LNG from adjacent facilities
- Environmental impact of LNG (cold, vapor and fire)
- Flame detection systems

Properties of Materials Used in LNG Service
- Insulation research
- Structural materials
- Other materials

LNG Transportation Systems Research
- Development of new ship unloading concepts
- Reliquefiers for ships
- Risk analysis re: storage, tanks, equipment
- Purge of LNG transfer systems
- Develop effective, quick shut-down systems (e.g., water hammer)
- New concepts in moorings
- Supertanker port
- Supmarine pipeline
- Economics of long distance transport
- Ship construction and strength during collision

Processing Improvements
- Improved liquefiers, vaporizers, etc.
- Limits of water, CO_2 and other trace contaminents as a function of onstream time without deriming
- Thermal and chlorine pollution of cooling water

Long Range Research Area

Short Distance LNG Pipelines
- Review existing files and literature to search for new technology

Other
- LNG conservation research
- Effect of SNG and imported LNG on peak shaving LNG operations
- Static electricity in plants and ships: sources, effects, methods of preventative design
- Earthquake design
- Effects of LNG spill on outer, non-cryogenic hull plate of tanker
- Tanker disturbance of shore and bottom life in shallow canals
- Contingency plans for LNG industry

(which process to choose), commodity transfer (providing equity in trade), data for safety applications as well as information for local, state, federal and international codes and standards, preparation of environmental impact statements and data for establishing insurance rates and financial considerations.

Certain well defined areas of required information fall within NBS traditional roles in this specialized field of cryoengineering and cryophysics. It was believed that NBS could combine both leadership and supportive roles to other government agencies and industry by (1) providing physical data of national importance not previously available in sufficient accuracy, (2) measurement methods, test methods and instrumentation, (3) standard assistance to voluntary and regulatory standardizing bodies, and (4) innovative technological leadership in methods and systems to reduce losses in transport and storage and to provide necessary expertise to facilitate and reduce the time required for program implementation.

Historically, NBS, through its Cryogenics Division in Boulder, Colorado, has supported government and industrial programs in cryoengineering and cryophysics since 1952. Concerted efforts in the general field of liquefied natural gas were begun in 1968. Currently, our program (having 14 elements or parts) provides the content of liquefied natural gas technology at NBS and is supported by a group of government agencies and industrial organizations (Table 3) which have a broad range of requirements. For purposes of explanation the 14 programs can be categorized into three more or less traditional NBS areas -- reference data, measurement science, and technology transfer.

Reference Data

By 1965 programs involving liquefied natural gas had demonstrated its viability as a peak shaving, satellite and supplemental fuel. Requirements for property data included PVT relationships, enthalpy, entropy, internal energy, dielectric properties, specific heats, heats of vaporization, speed of sound and the transport properties of viscosity, thermal conductivity and thermal diffusivity. Properties data were available from a number or sources and, where useful for certain purposes, were found to be insufficient for future planning, inadequate for many process designs and of either undefined or of inadequate precision and accuracy. What was needed therefore were accurate precise reference data over a broad range of pressures and temperatures generally extending from near the triple point of methane to well above ambient conditions. LNG presented an additional challenge since it is a non-ideal mixture of five or more hydrocarbon fluids and nitrogen, and the LNG mixture fraction will vary with source, time and storage treatment. The reference data must be of such quality as to classify it as basic reference values where foreseeable advances in measurement technology would not materially affect the listed values.

TABLE 3.

LIST OF AGENCIES AND COMPANIES CURRENTLY SUPPORTING LNG RESEARCH AT NBS

U. S. Department of Commerce

- National Bureau of Standards
- Maritime Administration

American Gas Association, Incorporated

Pipeline Research Committee (AGA)

U. S. General Services Administration

U. S. Federal Power Commission

LNG Density Committee consisting of:

- El Paso Natural Gas
- Tennessee Gas Pipeline
- Distrigas Corporation
- Columbia Gas Service Corp.
- Gaz de France
- Natural Gas pipeline Company
- Easco Gas LNG, Incorporated
- Transcontinental Gas Pipe Line Corporation
- Chicago Bridge & Iron Company
- Shell International Gas, Ltd.
- Sonatrach
- Southern California Gas Company
- Phillips Petroleum Company
- Texas Eastern Pipeline Company
- Marathon Oil Company
- Mobil R&D Company
- Tokyo Gas Company, Ltd.

A comprehensive program including both interim and long term objectives is currently in progress. The interim program involves the definition of densities of LNG as a function of pressure, temperature and mixture fraction. A 17 company committee is participating in the development of these accurate data of liquefied natural gas mixtures to provide a basis for custody transfer methods and equitable custody transfer agreements. The program will provide a data base for mass and density gauging. The objective of this LNG density measurement program is to provide accurate (0.1%) measurements of the densities of saturated liquid methane, ethane, propane, butanes, nitrogen and their mixtures, mainly in the temperature range 90-150 K. at pressures to 10 atmospheres. Measurements are in progress and will include six pure components, about 60 binary mixture compositions, and about 13 multicomponent mixture compositions. A high precision (0.05%) magnetic densitometer (based on Archimedes Principle) has been designed and constructed and is in the final stage of proving. The program is in its second year of operation with anticipated completion in 1975.

The long term fluids program involves a wide range of properties in addition to density. In general, the pure components of LNG are being studied and analyzed extensively over broad ranges of pressure and temperature, and then mixture laws applied or developed and confirmed with experimental verification. An example of this approach is the recently completed program on pure methane. Prior to 1970, interest in methane was general and was primarily directed to pure methane considered as a cryogenic fluid [5-17]. Several progress reports were published by Goodwin [18,19] and the final report is now available [20]. This latter report includes extensive physical properties data for methane such as fixed point constants, melting line, vapor pressure, orthobaric densities, virial equations, equation of state, specific heats, heats of vaporization and speed of sound. In addition, derived properties of entropy, enthalpy, and internal energy are included along with detailed explanations of computational methods including computer programs. Tabular data in both SI and British Units are also provided with estimates of uncertainties of all data. Figure 6 shows pressure and temperature boundaries of properties described by Goodwin.

It is acknowledged that this publication of the thermophysical properties data is not necessarily in the form most useful for engineering applications. Various charts and graphs will be required as well as other data forms of lessor or greater detail. This major three-year program has produced what we believe to be "best value" reference data on the major component of LNG.

The work on methane has also resulted in publication of accurate dielectric constants data for pure, compressed and liquefied methane [21]. This data should prove useful in providing a data base for mass and density gauging.

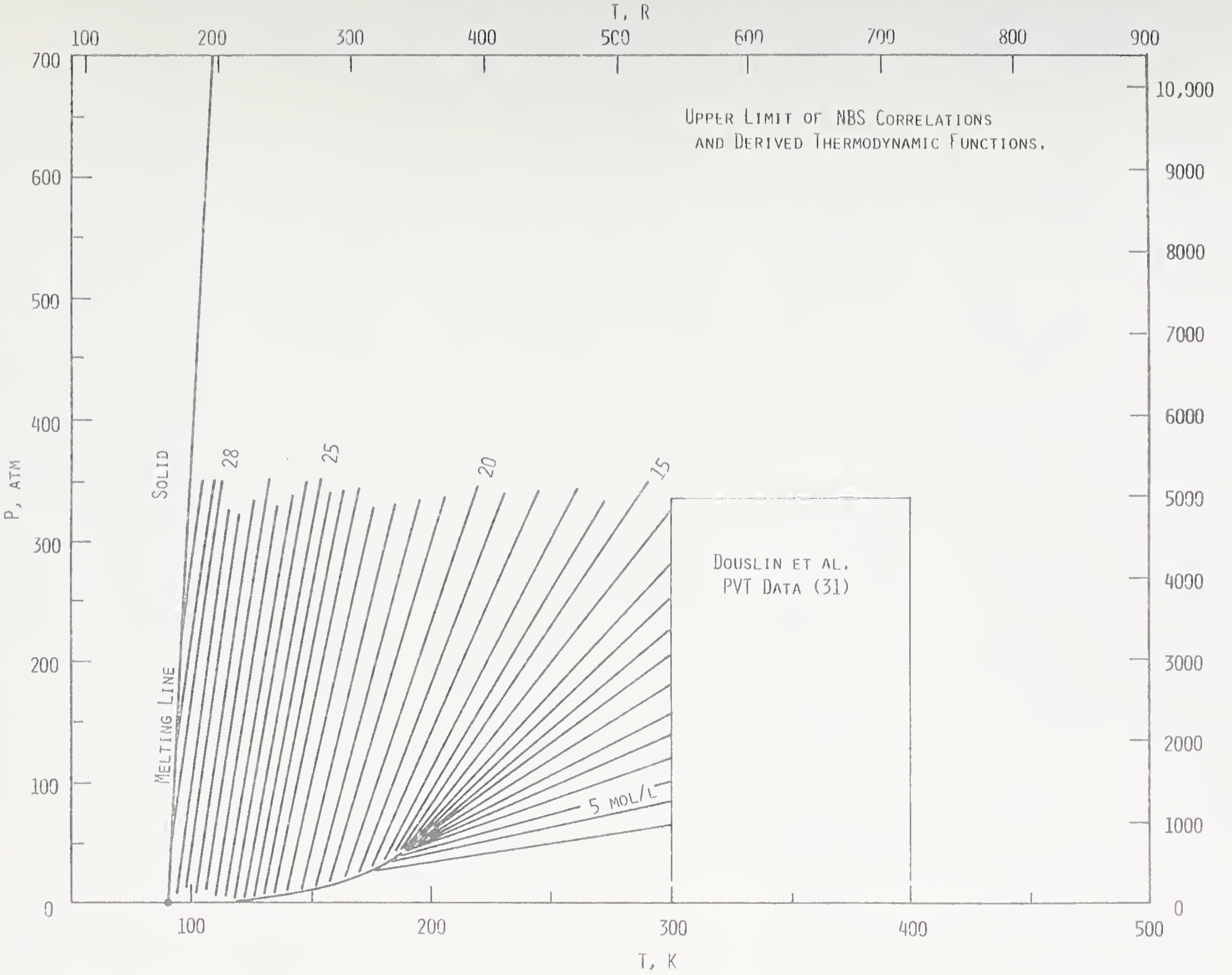


Figure 6. The locus of NBS P-V-T data on isochores is shown by solid lines. Extrapolation by Goodwin [20] to the limits of NBS correlations are confirmed with limited available data.

Current work in the long term LNG properties program is directed to the second most important constituent of LNG -- ethane. It is the intention of the program to methodically consider each of the pure constituents of LNG in a similar manner as previously described for methane. Current status of the ethane work involves establishing a firm foundation for computing tables of provisional values of thermodynamic functions. The activity has two purposes: to indicate those physical properties for which experimental data are lacking or inadequate and to provide useful results at an early date. These properties include vapor pressure, virial state equation, orthobaric densities, and formulations of the melting line of the ideal gas thermofunctions. Under the present level of effort the work on ethane should be completed in April 1975; propane, the butane and LNG mixtures will follow with a completion date for the entire program by 1980.

Measurements of the liquid vapor equilibria of cryogenic fluids [22], refractive index of liquid and vapor methane and direct measurement of sound velocity and thermal diffusivity are well underway. A program on transport properties -- viscosity, thermal conductivity -- is in the initial state of development.

Reference data on thermal and mechanical properties of structural and insulation materials are essential to facilitate material selection on the basis of cost and safety. Proper material choice is of major economic importance for cryogenic containers, particularly in sea transport of LNG. Studies to define fracture toughness and fatigue crack growth rate in the temperature range 76-300 K are currently being conducted on a series of iron-nickel alloys and aluminum alloys. This materials properties assessment has included the compilation of all the fatigue and fracture data on iron-nickel steels and their weldments; a collection of ship design data and analysis of materials and use; an assessment of the current materials requirements for LNG containers by the American Bureau of Shipping, the U. S. Coast Guard and ASME Pressure Vessel Code. In addition, a bibliography of literature containing data on aluminum alloys, non-metallics and insulation materials is in progress. Results and data for this program should be available after 1 July 1974.

Measurement Science and Methodology

Instrumentation and instrumentation methods are essential to process control, safety and custody transfer of liquefied natural gas. The NBS LNG program contains two examples of application of field type measurements. The objective is to define the ability of the instrument to determine and maintain a known accuracy and precision of the parameter of interest, such as density or flow rate.

A density reference system consists of a volume of LNG of adequate size and dimension to accept the measurement element of candidate densitometers. This volume will be filled with LNG of known density traceable to the reference data established under the mixtures program referred to in the previous section. Density, pressure, temperature and constituent fraction will be varied over a range of controlled conditions.and the performance of the densitometer will be evaluated. Long term stability of calibration will be of interest as a logical extension of this work would be the development of a transfer standard for field type densitometer certification. The LNG density reference system is currently in the second year of a three year planned program. The reference system is under construction and proving, with the completion date of the program scheduled for 1975.

The demonstration of an instrumentation method which would measure the heating value of liquefied natural gas flowing in a pipeline is the subject of the second example of measurement science in our LNG program. The project approach combines existing and evolving measurement technology with industry standard practices. The experience gained on a previous cryogenic flowmetering program [23-26] will provide necessary scaling information for the flowmetering portion of this three element measurement system. The second element of the heating value measurement system is a densitometer evaluated and calibrated as described previously. The third element of the heating value measurement involves an industry compatible flow calorimeter which will provide heating value per unit mass. A combination of these three measurement elements should provide a time-based rate for heating value of liquefied natural gas flowing in a pipeline. The objective of this three-year program will be to demonstrate the precision and accuracy of such a measurement system and to provide necessary supportive data for scaling to large pipe sizes. The program is scheduled for completion in 1976.

Technology Transfer

It is the objective of this portion of the LNG program to provide a broad dissemination of information on general cryogenic subjects. An LNG Quarterly [27] is published and distributed each April, July, October and January listing all significant papers, reports, and patents relating to LNG, LNG properties and technology. LNG related information has been entered into the NBS Cryogenic Data Center's information system for quick retrieval and comprehensive bibliographies on the properties and technology of LNG are available. There are presently three bibliographies involved; methane properties, methane mixture properties and processes and equipment involving methane and LNG. These three are updated each October [28-30].

A second example of technology transfer is a program concerned with safety of large LNG storage tanks. This program is primarily a consultation and advisory type service to a regulatory agency charged with the responsibility of approval for the location and safe operation of such storage containers.

These examples are of a short term transitory type but indicate the approach in providing this type of information where it is needed and where NBS can provide a proven capability.

FUTURE PLANS

The ongoing program of providing reference data, measurement science methodology and technology transfer can be projected into the early 1980's. An outline of such research topics is suggested by Table 2. The definition of priorities for these secondary tasks will certainly provide the framework for LNG research in the period 1980-1990 and beyond.

In the long-range future, there may be a number of possibilities for pipeline distribution of energy or development of new sources of energy that will impinge upon gas utility operations, and require continuing definition of research objectives and goals. Several of these possibilities are listed below.

Methanol, distributed as vapor or liquid

Low-btu gas

Coal slurries

Solar energy supplementation

Clathrates, hydrates, and hydrides

Hydrogen

Ammonia-hydrazine

Geothermal energy

Many of these opportunities will require new facilities and new concepts of business strategy by the gas utilities, but offer important opportunities either on a general basis or in specific localities. A research planning system to monitor and review these alternatives will be the most effective way for the gas utilities to understand and posture themselves to capitalize upon these shifts in a timely fashion.

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APPENDIX P

LOW TEMPERATURE FRACTURE BEHAVIOR OF FERRITIC Fe-Ni ALLOY STEELS*

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Fracture toughness tests over the interval 298-4K and fatigue crack growth rate tests at 298, 111, and 76K are reported on selected Fe-Ni alloys which are commerically available for potential use in storage or transportation of LNG. These alloys include Fe-6Ni and Fe-5Ni in the QLT or austenitized, temperized, and reversion annealed condition, and Fe-9Ni in the quenched and tempered condition. Linear elastic fracture mechanics parameters (K_Q, K_{IC}) and J-integral (J_{IC}) test data are presented for 1.25 inch thick compact tensile specimens. Discussion includes comparisons of fatigue crack growth rate and fracture data between alloys.

Key words: Crack propagation, cryogenics, fracture toughness, iron alloys, mechanical properties, nickel alloys, steels.

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*This work was conducted at the National Bureau of Standards under the sponsorship of the Maritime Administration, U. S. Department of Commerce.

INTRODUCTION

The increasing role of natural gas as a source of energy has prompted recent research into the mechanical and physical properties of materials related to LNG technology. Considerable effort has been devoted to characterizing the mechanical behavior of materials for use in LNG storage and transportation. The basic design considerations for tankage materials are low temperature strength, fracture toughness, and fatigue properties. Recent research has concentrated on providing such design data for 5083 aluminum alloy and the ferritic 5, 6, and 9Ni steels.

The most important characteristic of the low temperature mechanical behavior of ferritic steels is the ductile-to-brittle transition. The transition occurs over a narrow temperature interval and is marked by an abrupt change in the fracture behavior of sharply notched or cracked specimens. At higher temperatures these materials are ductile and fail by fibrous or dimpled rupture. At temperatures below the transition regime, failure occurs predominantly by cleavage, a brittle fracture mode.

To reduce the probability of brittle fracture in service, the structural applications of ferritic materials are limited to environments where the service temperatures remain above the ductile to brittle transition temperature. A mild steel may be brittle at temperatures near the ice point but, for similarly heat treated steels, the transition can be lowered progressively by increasing nickel concentration[1,2]

Nine percent nickel steel is a weldable ferritic material which was developed in the 1940's for cryogenic applications[1,3]. Because it has relatively high strength and retains toughness down to liquid nitrogen temperatures (77 K, -320 °F), it has been used extensively for LNG containment (111 K, 260 °F). Nickel is an expensive alloying element, however, and for economic reasons it has become desirable to optimize the nickel content of ferritic steels intended for LNG tankage.

Five and 6 percent nickel steels were recently developed having reduced nickel concentration while retaining high toughness at 111 K. In these steels the effect of decreased nickel is compensated by the application of a special three step heat treatment. The heat treatment of 5 percent Ni steel has been termed the austenitized, temperized, and reversion annealed condition[4]. The heat treatment of 6 percent Ni steel has been referred to as the QLT condition[2]. Such treatments are departures from the double normalized and tempered or quenched and tempered heat treatments which are applied to 9 percent nickel steel. The details and benefits of the three step heat treatment are described elsewhere[4,5]

The high toughness levels achieved with nickel steels have created difficulties in measuring valid fracture toughness design data. The transition temperatures are easy to determine by a number of mechanical tests[6], including Charpy impact; but these tests do not provide data on allowable stress levels for materials in service. Linear eleastic fracture mechanics tests are capable of providing a useful design parameter, K_{IC}; but K_{IC} testing of nickel steels has not proven very successful because large and impractical specimen sizes are required for valid test results.

The recently developed J-integral technique is an important tool for evaluating tough materials such as the nickel steels. The theory of the J-integral was originated by Rice.[7] Subsequent experiments by Begley and Landes[8-10] verified that J can be used as a fracture criterion in cases where the specimen exhibits elastic, elastic-plastic, or fully plastic load-deflection behavior.

A practical consideration is that the specimen size required for J-integral testing is not as large as that for linear elastic K_{IC} testing. A tentative size criterion for the J-integral test is that[10]:

$$B,\ b,\ a \geq 25\ (J/\sigma_{flow})$$

where B is specimen thickness, b is ligament length, a is crack length, and σ_{flow} is the average value of the 0.2 percent offset yield stress and the ultimate flow stress. B is typically an order of magnitude smaller than the value required for linear elastic behavior as calculated from the size criterion of the ASTM Test for Plan Strain Fracture Toughness of Metallic Materials (E-399-72):

$$B,\ a \geq 2.5\ \left(\frac{K_{IC}}{\sigma_{ys}}\right)^2$$

This paper describes fatigue crack growth rate and fracture toughness tests on 5, 6, and 9 percent Ni steels. J-integral tests are applied to these materials and the fracture parameter J_{IC} is reported over a wide range of temperatures. J_{IC} measurements are converted to K_{IC} values, thus providing useful design data at LNG temperatures and other temperatures of interest.

EXPERIMENTAL PROCEDURES AND APPARATUS

Materials

Five, 6 and 9 percent nickel steels were obtained in the form of 1.25 inch thick plates. All materials were commerically heat treated. The 5 percent Ni steel was austenitized, temperized and reversion annealed according to the ASTM Specification for Pressure Vessels Plates, Five Percent Nickel Alloy Steel, Specially Heat Treated (A - 645 - 72a). The 9 percent nickel steel was quenched and tempered according to the ASTM Specification for Pressure Vessel Plates, Alloy Steel, Quenched and Tempered 8 and 9 Percent Nickel (A 553-72a). The 6%Ni steel was in the QLT condition[2]; at present, there is no specification on the heat treatment of this material.

Chemical compositions and mechanical property data are presented in Tables 1 and 2. All tensile properties referred to in this investigation were the average values of two tests performed in accordance with the ASTM Methods of Tension Testing of Metallic Materials (E 8-69).

All fatigue and fracture experiments were performed on 1.25 inch (3.17 cm) thick compact tensile specimens having the geometry illustrated in Figure 1. The width of thickness ratio (W/B) was 2.4, and the planar dimensions were equal to those of a 1.50 inch (3.81 cm) thick specimen proportioned according to ASTM E-399-72. The notch was machined parallel to the rolling direction, producing a TL orientation. Loadline displacement was measured by means of a modified notch configuration as shown in Figure 1. Roberts' K calibration was used[11].

Test Procedures

The majority of tests were conducted at 298 K (70°F), 195 K (-108°F), 111 K (-260°F) and 76 K (-320°F). Two fracture tests were performed in liquid helium at 4 K (-459°F). The temperature of 76 K was obtained by immersion in liquid nitrogen; 195 K was obtained by immersion in a mixture of alcohol and dry ice; and 111 K was obtained by testing in nitrogen vapor. Before testing specimens were allowed between thirty and sixty minutes to reach thermal equilibrium.

A temperature control system with a chromel-constantan thermocouple sensor was used to maintain a temperature of 111 K ± 3K. The control thermocouple was located on the specimen at the level of the fatigue crack. Vapor from a pressurized liquid nitrogen dewar was introduced to the cryostat through a solenoid valve. The solenoid valve permitted the flow of cold vapor as required by opening and closing automatically in response to the electrical signal from a commercial temperature recorder.

Fatigue testing was conducted on a 20,000 lbs. (100 kN) capacity MTS servo-hydraulic mechanical test system*. This was a "cryogenic" model

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*Tradenames of equipment and materials are used for clarity and to conform with standard usage in the literature. Their use does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment or materials are necessarily the best available for the purpose.

with the accuator positioned above the level of the specimen to accommodate the cryostat and to allow access from below for assembling dewars. The testing machine and associated equipment are illustrated in Figure 2.

A 20,000 lb. (100 kN) cryostat was used for fatigue tests. The load carrying frame consists of two tubular stand-off compression members linked at the lower ends with a maraging steel bridge. Fiberglass reinforced plastic was used in construction of the stand-off columns to minimize heat conduction. The lower specimen grip was pinned in place in the center of the bridge, and the upper grip was threaded to the end of the pull rod. A cylindrical fiberglass reinforced plastic dewar was used to enclose the load frame, specimen, and clip gage for cryogenic tests. A similar cryostat was employed in fracture testing, except that the stand-off columns were stainless stell and load carrying capacity was 60,000 lbs. (267 MN).

ASTM type clip gages were used at all testing temperatures. Commercially available foil resistance strain gage films were bonded to the clip gage beams using an adhesive suitable for low temperature applications. The clip gages were calibrated at temperatures from 298 K to 76 K, but there was not a large change in sensitivity. Clip gage linearity met the requirements of ASTM E-399-72 over the maximum operating range of up to 0.090 inches (0.229 cm) displacement.

Crack Growth Rate Tests

Fatigue tests were performed using load control at a frequency of 24 Hz. The load cycle was sinusoidal at a constant stress ratio (minimum/maximum load) of 0.1. Dynamic fatigue loads were measured and controlled to within 1-2 percent by means of a digital peak recording device.

The change in crack length during crack growth rate tests was monitored by compliance measurements. Direct measurement of crack lengths at the specimen surface was not possible during cryogenic tests. The compliance technique is based on the fact that for a given load, the specimen compliance (reciprocal of stiffness) increases with increasing crack length. Compliance methods are discussed in detail elsewhere[12,13].

Experimental crack length-compliance correlations were obtained for each material and temperature. An X-Y recorder was used to measure the compliance for a number of specimens of varying crack lengths. Fatigue striations were generated by load changes during precracking and crack growth rate tests so that several crack length-compliance measurements were obtained from each specimen. The data were plotted as a function of crack length which was measured as an average of three readings at the center and quarter points of specimen thickness.

Theoretical crack length-compliance curves were calculated from the generalized solution given by Roberts[11] but these were not in complete agreement with the experimental correlations. Comparison showed that the calculated curves consistently under estimated the true crack lengths by 2-4%. The difference between the calculated and the experimental curves may result from crack front curvature effects, but it can not be attributed to uncertainty in calculations since Young's moduli were known to within 1% at all temperatures from tests on the same stock materials[14].

The procedure for determining crack growth rates involved plotting the static compliance at intervals during the tests. Using the experimental crack length - exompliance correlation, crack length could then be obtained, to within ± 1.5 percent. Crack length (a) was plotted versus the total number (N) of fatigue cycles and the crack growth rate (da/dN) was determined by graphical differentiation of the a vs. N curve.

It is well known that the rate of crack growth may be retarded by changing from a higher to a lower stress intensity range. Crack growth rates may also be influenced by abrupt temperature changes. Whenever these kinds of changes were made the crack growth rate was allowed to stabilize before data were accepted as valid. Crack growth data under the new conditions were ignored until the crack had advanced an increment equal to or greater than the plastic zone size as calculated from Irwin's formula[15].

Fracture Toughness Tests

Fracture tests were conducted using a 60,000 lb. (267 kN) capacity hydraulic testing machine. The loading rate was constant, corresponding to a crosshead displacement of 0.02 in min^{-1} (8.5×10^{-4} cm · sec^{-1}).

Most specimens were precracked at the temperature of subsequent fracture testing; the few exceptions are noted in the text. The final crack length was deep, corresponding to a ratio a/W of between 0.60 and 0.62. Precracking was performed at fatigue loads always less than half of the specimen limit load and at stress intensities never exceeding a value of 0.002 $\text{in}^{1/2}$ × Young's modulus. K_Q was measured according to the method described in E-399, using the same J-integral test specimens.

For the deeply cracked compact tensile specimens described in this report, J was calculated from the equation[16,10]:

$$J = \frac{2A}{Bb}$$

where A is the area under the load deflection curve to a particular value of displacement. The critical value J_{IC} is the value of J just prior to crack extension. For specimens which exhibited unstable crack extension (pop-in), J_{IC} was calculated using the load at the first pop-in. When crack extension took place by stable ductile tearing the J_{IC} value was obtained by extrapolation of the J versus crack extension curve.

The extrapolation technique was based on a method outlined by Landes and Begley[10]. According to the procedure, 3-5 nearly identical specimens with average crack lengths agreeing to approximately 3 percent were tested at each temperature. A series of load-deflection curves were obtained by loading each specimen to a level sufficient to cause decreasing amounts of crack extension. The specimens were then unloaded and heat tinted 20 minutes at 538 K (1000 °F) to oxidize the surfaces where crack extension had taken place. The samples were subsequently pulled apart at 298 K. The average value of Δa was measured and plotted versus the corresponding value of J.

It was observed in these tests that deformation at the crack tip preceded material separation. Apparent crack extension therefore included a contribution due to deformation in addition to actual material separation. The deformation was visible on the fractured samples as a zone between the fatigue cracked region and the torn ligament. The material in the stretch zone had been deformed out of the plane of the fatigue crack surface.

The length of the stretch zone was measured with a traveling microscope. An average value of several measurements from each specimen was plotted as a vertical line on the J vs. Δa graphs. The intersection of the J vs. Δa curve with the stretch zone line was taken to represent the initial point of material separation, and J_{IC} was obtained as the value of J at the point of intersection.

Landes and Begley[10] recommend construction of the $J/2\sigma_{flow}$ line to establish the J resistance curve over the stretch zone interval.

For 9% Ni steel, construction of the $J/2\sigma_{flow}$ line resulted in a triple intersection with the vertical stretch zone line and the J vs. Δa curve. For the other materials, the $J/2\sigma_{flow}$ line intersection point was less compatible with the data. In some cases, material separation was observed at values of Δa less than those predicted by the $J/2\sigma_{flow}$ intersection point and it appeared that a $J/3\sigma_{flow}$ line would have resulted in better agreement. The intersection point defined by the vertical stretch zone line was chosen for consistency. The attempt to measure the extension of the stretch zone directly is a technique which may not be generally applicable; it depends on the ease of identifying the stretch zone visually.

When the J versus Δa graphs appeared to be linear, J_{IC} was determined by a "best" straight line extrapolation. In other cases a linear trend was not clearly defined. Scatter in the data was accounted for by examining a number of reasonable extrapolations and a range of possible J_{IC} values were determined.

K_{IC} values were calculated from the J_{IC} measurements according to the relation[8,9]:

$$K_{JC} = (J_{IC} \cdot \frac{E}{1-\nu^2})^{1/2}$$

where E is Young's modulus and ν is Poisson's ratio. Data on the elastic constants at all temperatures were available from the work of Weston et al.[14]

RESULTS

Fatigue Crack Growth Rate

Figures 3 - 5 summarize the fatigue crack growth rate results for all three materials. The data conform to the relation[17]

$$da/dN = C(\Delta K)^n$$

where da/dN is the change in crack length per cycle, ΔK is the range of stress intensity and C and n are empirical constants.

Figure 3 illustrates that the crack growth rate behavior of 5 percent Ni steel appears to be temperature independent for stress intensity ranges from 20-25 ksi $\cdot$ $in^{1/2}$ (22 - 27 MNm^{-22}. $m^{1/2}$). Above ΔK = ksi $\cdot$ $in^{1/2}$ (33 $MNm^{-2} \cdot m^{1/2}$) growth rates at 76 K are definitely higher than at room temperature or 111 K.

Superimposed on the data of Figure 3 are straight line approximations of the data reported by Bucci, et al.[18]. The straight line approximations are used for clarity in illustrating data trends, but do not indicate the degree of scatter in their results. The present results are in good agreement with the data from this source.

Fatigue crack growth rate data for 6 percent and 9 percent Ni steel followed the same trend observed for 5 percent Ni steel. As shown in Figures 4 and 5, the crack growth rates were somewhat higher at 76 K than at 298 K for stress intensity ranges above 25 ksi $\cdot$ $in^{1/2}$ (27.5 $MNm^{-2} \cdot m^{1/2}$).

Figure 4 shows that the crack growth rate results for 6 percent Ni steel at 111 K agreed well with room temperature data over the entire range of ΔK. The increase in growth rates occurred between 111 and 76 K. This effect may be related to the fact that 6 percent Ni alloy begins its ductile-to-brittle transition near liquid nitrogen temperatures. There is no published data in the literature with which to compare the present results for 6 percent Ni steel.

The results of Bucci, et al.[18] for 9 percent Ni steel are represented in Figure 5. The present results reveal a somewhat higher growth rate at 76 K, but the general agreement is good.

The fatigue crack growth rate behavior of 5, 6, and 9 percent Ni steels appears to be similar. If all data from this report are superimposed on a single graph, it appears that the fatigue crack growth rates of the three materials are nearly equivalent for ΔK values ranging from 20 - 60 ksi $\cdot$ $in^{1/2}$ (22 - 66 $Nm^{-2} \cdot m^{1/2}$).

Fracture Toughness

Representative load-deflection curves for 5 percent Ni steel are illustrated in Figure 6. The arrows terminating the curves at 298 K and 195 K indicate that ductile tearing continued to larger deflections without the occurrence of pop-in. At 111 K an appreciable amount of plastic deformation occurred, followed by a single pop-in. Multiple pop-ins occurred at temperatures below 111 K where linear elastic behavior was approached. At 76 K, the load continued to increase significantly after the first pop-in. The deviation from linearity at the upper end of the 4 K load-defection curve was due to a series of faint but audible pop-ins.

The load-deflection cuves for 6 percent and 9 percent Ni steels are illustrated in Figures 7 and 8. In comparison, it is significant to note that pop-in did not occur in tests of 6 percent Ni at 111 K.

The fracture surfaces of 6 percent and 9 percent Ni steel specimens exhibited 40 - 50 percent slant fracture at 298 K. Shear lips took the form of hugh cusps rising 0.4 inch (1 cm) above the plane of the fatigue crack. There was also a large lateral contraction in the thickness direction, amounting to 12 percent. As temperature decreased to 76 K, the proportion of slant fracture descreased to about 15 percent, and the percentage of lateral contraction decreased to approximately 5 percent.

For 5 percent Ni steel, a lateral contraction of 18 percent was measured at room temperature, but the fracture surface was relatively flat compared to the other materials. The proportion of slant fracture decreased from about 25 percent at room temperature to zero at 5 K. At 4 K the fracture surface exhibited reflective cleavage facets.

For 6 percent and 9 percent Ni steels the degree of crack front curvature bordered on, but did not exceed, the limits established for fatigue crack uniformity (ASTM E-399-72). In the case of 5 percent Ni steel crack front straightness requirements were occasionally violated when the crack length at the specimen edge was found to be less than 90 percent of the average crack length. The difference in edge crack and average crack lengths ranged from 87-88 percent for the four specimens which did not meet this requirement. The degree of crack front curvature appears to depend on loading history. Crack growth rate specimens tested at higher stress intensities had less curvature; the specimens with excessive curvature were those used in low temperature fracture tests where the maximum stress intensities (K_f) were lowered to comply with the $K_f \leq .6K_Q$ criterion of ASTM E-399-72.

Graphs of J versus Δa are shown in Figures 9-11. Tabulations of the data used in determining the parameters J_{IC}, K_{IC} and K_Q are presented in Tables 3-8, and Table 9 presents an evaluation of the size criteria for valid testing.

The results are summarized in Figure 12, which illustrates the temperature dependence of the parameters K_Q and K_{IC}. For all three materials, K_Q increased with decreasing temperature over the interval 298 K - 76 K. At these temperatures K_Q does not represent a valid fracture parameter for 1.25 inch thick specimens - the ASTM E-399-72 thickness requirement is not satisfied. The K_Q values measured under non-linear elastic conditions have no practical significance and are included merely for comparison. Over the interval 298-76 K, it was observed that:

1. The disagreement between K_Q and K_{IC} values was largest at ambient temperatures;

2. The effect of temperature on K_Q was opposite to the general trend displayed by K_{IC} values; and

3. The K_Q values did not provide an indication of the relative toughness of the materials. For example, 9 percent Ni steel exhibited the highest K_Q values but not the highest K_{IC} values.

Only in tests of 5 percent Ni steel at 76 K and 4 K did the K_Q values agree with the K_{IC} values converted from J-integral measurements. Nevertheless, these K_Q values did not qualify as valid K_{IC} according to ASTM E-299-72. This point is amplified in the discussion.

For 5 percent Ni steel, K_{IC} values decreased from 200 ksi · $in^{1/2}$ (220 MNm^{-2} · $m^{1/2}$) at room temperature to 50 ksi· $in^{1/2}$ (55 MNm^{-2} · $m^{1/2}$) at 4 K. The datum point at 195 K was determined by extrapolation of only two fracture tests and should not be heavily weighted. The fracture toughness remained nearly equivalent to that of 9 percent Ni steel at temperatures as low as 111 K. Below 111 K the K_{IC} values decreased abruptly.

The 9 percent Ni steel was tested at 298 K and 76 K. K_{IC} decreased from 210 ksi · $in^{1/2}$ (230 MNm^{-2} · $m^{1/2}$) at 298 K to 167 ksi · $in^{1/2}$ (184 MNm^{-2} · $m^{1/2}$) at 76 K, a reduction of 15 percent. A more drastic reduction in toughness over this temperature interval was not expected. Charpy impact data from the mill analysis of this material indicate that the ductile-to-brittle transition is just beginning at 76 K. Additional testing at temperatures lower than 76 K would be necessary to define the ductile-to-brittle transition temperature regime in terms of K_{IC} values.

The fracture toughness of the 6 percent Ni alloy exceeded that of the other materials tested. K_{IC} values indicated that the upper shelf toughness tended to increase from about 240 ksi · $in^{1/2}$ (263 MNm^{-2} · $m^{1/2}$) to 268 ksi · $in^{1/2}$ (294 MNm^{-2} · $m^{1/2}$) over the interval 298 - 111 K. However, a rather sharp drop in the data occurs between 111 and 76 K, indicating the beginning of the ductile-to-brittle transition. The value of K_{IC} declined to 195 ksi · $in^{1/2}$ (214 $MNm^{-2} \cdot m^{1/2}$), slightly higher than the value obtained for 9 percent Ni steel.

It was observed in a few tests on 6 percent Ni steel that a small amount of stable crack extension preceded pop-in at 76 K. For testing convenience, this effect was neglected and J_{IC} values were calculated at the point of pop-in. A rigorously determined J_{IC} measurement would be slightly lower than the value calculated at pop-in; but the error introduced in K_{IC} determinations was estimated to be less than 5 percent which is less than the degree of scatter observed in replicate tests. It is probable that some amount of stable crack extension preceded pop-in tests of 5 percent Ni steel at 111 K, but observations were inconclusive.

DISCUSSION

Previous authors[19-23] have not reported valid K_{IC} data for 5, 6, or 9 percent nickel base metal steels. The J-integral test procedures used in this investigation appeared to provide valid K_{IC} data. Several factors must be considered in assessing the validity of the present results.

The J-integral test results indicated ambient temperature K_{IC} values as high as 200-240 ksi · $in^{1/2}$ (220-263 $MNm^{-2} \cdot m^{1/2}$). These values are quite reasonable. The size criterion was satisfied at all temperatures. Confidence in the data stems from the fact that this size criterion was established from tests on steels [8-10] equivalent in fracture toughness (J_{IC} = 1000-2000 in· lb · in^{-2} or 0.175 - 0.350 MJ · m^{-2}) to the nickel steels tested in this report.

Serious problems regarding test validity arose only in tests of 5 percent Ni steel at 76 K and 4 K. At 4 K the linear elastic size criterion was satisfied but precracking stress intensities could not be lowered successfully to comply with the criterion that $K_f \leq .6 K_Q$. At 4 K the K_Q was relatively low and crack front curvature increased significantly at the lower fatigue stress intensities. To keep the crack front curvature within reasonable limits, one specimen was precracked at 298 K ($K_f \leq 0.6 K_Q$) and a second specimen was precracked at 76 K ($K_f \leq .75 K_Q$). The first specimen satisfied crack front curvature requirements but K_Q was 10 ksi · $in^{1/2}$ higher than the specimen precracked at 76 K. It is probable that precracking at 298 K introduced disparities in plastic zone size and crack sharpness. The specimen precracked at 76 K fell 2 percent short of the requirement that the edge crack length be 90% or more of the average crack length. For this specimen, the measured value of 50 ksi · $in^{1/2}$ is probably closer to the true value of fracture toughness; however, neither of the tests at 4 K can be considered valid.

For 5 percent Ni steel at 76 K, the ASTM Method E-399-72 requires a specimen thickness of 1.5 - 1.6 inches (≃ 4 cm). In two tests at 76 K, K_f was maintained $< 0.6 K_Q$ but the edge crack lengths were 87-88 percent of the average crack lengths; 90 percent or more is required. Therefore the K_Q data are invalid according to a strict interpretation of ASTM E-399-82. On the other hand, the size criterion for J-integral testing is amply satisfied. The magnitude of the effect of a minor transgression in crack front curvature is not known, but it appears that there could be only a small error in the data for 5 percent Ni steel at 76 K.

Agreement of K_Q values with K_{IC} values converted from J_{IC} measurements implies that the linear elastic fracture mechanics test is valid from the standpoint of size considerations. J-integral results can then be used to evaluate the linear elastic thickness requirement. For 5 percent Ni steel at 76 K, the mean value of K_{IC} was 87 ksi $\cdot$ $in^{1/2}$ (95 $MNm^{-2} \cdot m^{1/2}$) and the 0.2 percent offset yield strength was ~ 110 ksi (76 Nm^{-2}). These data suggest that the ASTM size criterion factor of 2.5 is slightly conservative in the case of 5 percent Ni steel. The factor could be reduced to 2.0, since a calculation shows that:

$$B = 1.25 \text{ inch} \cong 2.0 \left(\frac{K_{IC}}{\sigma_{ys}}\right)^2_{76\text{ K}} .$$

The 6 percent Ni steel contained low levels of sulfur and phosphorous, a relatively high percentage of manganese, and some chrome (Table 1). Sulfur and phosphorous are tramp elements, usually deleterious in their effects on mechanical properties, whereas manganese is beneficial with respect to microstructural refinement[2]. Thus, compositional variations may account for the somewhat higher fracture toughness observed for 6 percent Ni steel.

The present results confirm that 5 percent and 6 percent Ni steels are promising materials for potential use in LNG tankage applications. At 111 K, the fracture properties of these newly developed steels are comparable to those of 9 percent Ni steel. Further evaluation is needed to determine the properties of weldments and their heat affected zones (HAZ). It is probable that the fracture toughness of these materials will be lowered somewhat by the deleterious effects of heat inputs from welding. Therefore, the ultimate suitability of 5 percent and 6 percent Ni steels must be determined by fracture toughness comparisons of both the base metals, the weld, and the HAZ.

SUMMARY

1. The fatigue crack growth rates of 5, 6, and 9 percent Ni steels were nearly equivalent at ΔK from 20-60 ksi · in$^{1/2}$ (22-66 MNm^{-2} · m$^{1/2}$).

2. At $\Delta K > 25$ ksi · in$^{1/2}$ (27.6 MNm^{-2}) the fatigue crack growth rates of 5 and 6 Ni steels were higher at 76 K than at 111 K or 298 K.

3. The J-integral test procedures used in this investigation appeared to yield valid K_{IC} data for the 5, 6, and 9 Ni steels.

4. For 9 Ni steel there was only a small decrease in fracture toughness over the interval 298 - 76 K; the fracture toughness of 5 and 6 Ni steels decreased abruptly over the interval 111 - 76 K.

5. At 111 K, the fracture toughness of these materials ranged from 160 ksi · in$^{1/2}$ to 270 ksi · in$^{1/2}$ (180 - 300 MNm^{-2} · m$^{1/2}$).

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Table 1. Chemical Composition

Alloy	Mill Analyses (wt. pct.)										
	Fe	C	Mn	P	S	Si	Ni	Cr	Mo	Al	N
Fe-5Ni	Bal	0.13	0.45	0.025	0.025	0.275	5.00	-	0.275	0.085	0.020
Fe-6Ni	Bal	0.06	1.12	0.005	0.004	0.24	5.66	0.63	0.18	-	-
Fe-9Ni	Bal	0.06	0.56	0.007	0.003	0.27	9.25	-	-	-	-

Table 2. Mechanical Properties

	0.2% Offset Yield Strength (ksi)	Tensile Strength (ksi)	Elongation (%)	Reduction of Area (%)	Hardness (Rc)	C_v (longitudinal) 76 K (ft·lbs)
Fe-5% Ni	77.5	97.9	34	79	20	38
Fe-6% Ni	82.0	106.6	30	81	23	166
Fe-9% Ni	99.9	109.1	27	78	25	130

NOTE: 1 ksi = 0.689 Nm^{-2}.

Temp (K)	Spec[*]	$\frac{a}{W}$	P_Q (lb)	K_Q (ksi $\sqrt{in}$)
298	16	0.597	10,200	62
298	3	0.60	9,150	56.4
298	11	0.60	9,900	60.8
298	A	0.597	14,100	86.8
			Avg =	66.5
195	21[†]	0.607	13,100	83.7
195	22[†]	0.611	11,450	74.4
195	23[†]	0.617	13,400	89.5
			Avg =	82.5
111	24	0.621	13,400	90.7
111	29	0.654	11,700	92.7
111	32	0.623	17,200	117
			Avg =	100
76	25	0.599	12,950	82.0
76	27	0.612	13,200	86.1
			Avg =	84.0
4	28[†]	0.624	8,550	60.1
4	26[††]	0.606	7,950	50.2
			Avg =	55.2

Notes: 1 lb = 4.448 N

1 ksi $\sqrt{in}$ = $1.098 \times 10^{6}\ \mathrm{Nm}^{-2}\sqrt{\mathrm{m}}$

[*] B = 1.228 in (3.119 cm) ± 0.5%,

W = 3.034 in (7.706 cm) ± 0.9%

[†] precracked at 298 K

[††] precracked at 76 K

Table 4. J-Integral and Converted K_{IC} of Fe-5% Ni

Temp (K)	Spec	b (in)	J $\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$	Δa_{ave} (in)	Stretch Zone	J_{IC} $\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$	K_{IC} (ksi $\sqrt{\text{in}}$)
298	16	1.240	3.42	0.041	0.004		
298	3	1.214	2.47	0.022	0.006		
298	11	1.216	1.76	0.011	0.003		
298	A	1.204	1.34	0.010	0.004		
				Avg =	0.004	1.27 ± 0.19	200 ± 15
195	21 †	1.191	4.16	0.046	0.005		
195	22 †	1.179	2.58	0.020	0.004		
				Avg =	0.0045	1.41	210
111	24	1.146	N/A	N/A	N/A	1.05	185
111	29	1.053	"	"	"	1.09	189
111	32	1.145	"	"	"	0.774	159
					Avg =	0.972	178
76	25	1.217	"	"	"	0.178	76.5
76	27	1.180	"	"	"	0.287	97.1
					Avg =	0.232	86.8
4	28 †	1.138	"	"	"	0.102	58
4	26 ††	1.193	"	"	"	0.074	49.4
					Avg =	0.088	53.7

Notes: 1 in = 2.54 cm

$1\ \frac{\text{in-lb}}{\text{in}^2} = 1.75 \times 10^2\ \text{Jm}^{-2}$

1 ksi $\sqrt{\text{in}}$ = $1.098 \times 10^6\ \text{Nm}^{-2}\sqrt{\text{m}}$

† precracked at 298 K

†† precracked at 76 K

Temp (K)	Spec*	$\frac{a}{W}$	P_Q (lb)	K_Q (ksi $\sqrt{in}$)
298	7	0.614	12,500	83
298	1	0.617	12,950	87
298	5	0.619	13,700	92
298	3	0.620	16,300	111
298	2	0.615	14,950	100
298	15	0.615	12,950	84
			Avg =	93
195	18	0.607	14,250	89
195	17	0.605	13,500	83
195	16	0.591	14,500	86
195	19	0.592	14,500	86
			Avg =	86
111	20	0.614	17,250	114
111	21	0.616	18,300	117
111	22	0.614	18,300	120
111	23	0.613	16,750	113
			Avg =	116
76	12	0.607	20,300	128
76	11	0.607	18,300	115
76	8	0.617	19,650	130
76	10	0.612	21,050	136
			Avg =	127

Notes:

1 lb = 4.448 N

1 ksi $\sqrt{in}$ = 1.098 X 10^6 Nm^{-2} $\sqrt{m}$

* B = 1.250 in (3.178 cm) ± 0.4%,

W = 3.046 in (7.737 cm) ± 0.6%.

Table 6. J-Integral and Converted K_{IC} of Fe-6% Ni

Temp (K)	Spec	b (in)	J $\left(10^3 \frac{in\text{-}lb}{in^2}\right)$	Δa_{ave} (in)	Stretch Zone (in)	J_{IC} $\left(10^3 \frac{in\text{-}lb}{in^2}\right)$	K_{IC} (ksi $\sqrt{in}$)
298	7	1.159	6.14	0.052	0.006		
298	1	1.167	4.57	0.033	0.008		
298	5	1.159	2.07	0.008	0.005		
298	15	1.174	2.58	0.013	0.005		
				Avg =	0.006	1.75 ± 0.14	236 ± 9
195	18	1.208	2.90	0.015	0.006		
195	17	1.205	6.99	0.061	0.007		
195	16	1.247	5.18	0.034	0.007		
195	19	1.243	4.12	0.028	0.006		
				Avg =	0.006	2.25 ± 0.15	272 ± 9
111	20	1.172	5.86	0.040	0.004		
111	21	1.168	4.54	0.030	0.005		
111	22	1.176	2.74	0.011	0.005		
111	23	1.177	3.65	0.018	0.006		
				Avg =	0.005	2.15 ± 0.13	268 ± 9
76	12	1.194	N/A	N/A		1.30	208
76	11	1.195	"	"		1.30	208
76	8	1.165	"	"		0.944	177
76	10	1.180	"	"		1.14	195
					Avg =	1.17	197

Notes: 1 in = 2.54 cm

$1 \frac{in\text{-}lb}{in^2} = 1.75 \times 10^2 \ Jm^{-2}$

$1 \ ksi \sqrt{in} = 1.098 \times 10^6 \ Nm^{-2} \sqrt{m}$

Table 7. K_Q of Fe-9% Ni

Temp K	Spec*	$\frac{a}{W}$	P_Q (lb)	K_Q (ksi $\sqrt{in}$)
298	6	0.594	19,200	116
	9	0.606	19,200	121
	12	0.601	18,900	117
	4	0.599	19,050	116
	18	0.617	17,400	114
			Avg =	117
76	19	0.615	21,150	137
	20	0.609	22,700	142
	21	0.614	22,250	144
			Avg =	141

Notes: 1 lb = 4.448 N

1 ksi $\sqrt{in}$ = 1.098 X 10^6 Nm^{-2} $\sqrt{m}$

* B = 1.253 in (3.182 cm) ± .2%,

W = 3.036 in (7.711 cm) ± .5%.

Table 8. J - Integral and Converted K_{IC} of Fe-9% Ni

Temp (K)	Spec	b (in)	J $\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$	Δa_{ave} (in)	Stretch Zone (in)	J_{IC} $\left(10^3 \frac{\text{in-lb}}{\text{in}^2}\right)$	K_{IC} (ksi $\sqrt{\text{in}}$)
298	6	1.236	2.70	0.021	0.007		
298	9	1.20	4.02	0.028	0.007		
298	12	1.213	4.92	0.044	0.006		
298	4	1.219	6.80	0.054	0.007		
298	18	1.168	1.22		0.007		
				Avg =	0.007	1.14 ± 23	210 ± 3
76	19	1.159	N/A	N/A	N/A	0.810	162
76	20	1.185	"	"	"	0.935	174
76	21	1.172	"	"	"	0.846	165
					Avg =	0.864	167

Notes: 1 in = 2.54 cm

$1 \frac{\text{in-lb}}{\text{in}^2} = 1.75 \times 10^2 \frac{\text{m - N}}{\text{m}^2}$ Jm^{-2}

$1 \text{ ksi} \sqrt{\text{in}} = 1.098 \times 10^6 \frac{\text{N}}{\text{m}^2} \sqrt{\text{m}}$ $\text{Nm}^{-2}\sqrt{\text{m}}$

Table 9. Dimensional Criteria for Valid K_{IC} and J_{IC}

Alloy	Temp (K)	a (in)	B (in)	b (in)	$2.5\left(\frac{K_Q}{\sigma_{ys}}\right)^2$ (in)	$2.5\left(\frac{K_{IC}^*}{\sigma_{ys}}\right)^2$ (in)	$25\left(\frac{J_Q}{\sigma_{flow}}\right)$ (in)	$50\left(\frac{J_Q}{\sigma_{flow}}\right)$ (in)
Fe-5% Ni	298	1.80	1.23	1.22	1.84	16.1	0.36	0.72
	195	1.85	1.23	1.18	3.3	20.9	0.36	0.72
	111	1.92	1.23	1.12	2.4	9.1	0.20	0.40
	76	1.81	1.23	1.20	1.47	1.60	0.04	0.08
	4	1.84	1.22	1.19	0.25	0.25	0.01	0.02
Fe-6% Ni	298	1.88	1.25	1.16	3.2	20.7	0.46	0.93
	195	1.82	1.25	1.23	2.5	24.9	0.53	1.07
	111	1.86	1.25	1.17	2.6	14.1	0.40	0.81
	76	1.86	1.25	1.18	2.6	6.2	0.20	0.40
Fe-9% Ni	298	1.83	1.22	1.21	3.3	10.8	0.27	0.54
	76	1.85	1.25	1.17	2.5	3.5	0.14	0.29

* K_{IC} value obtained from J-integral results

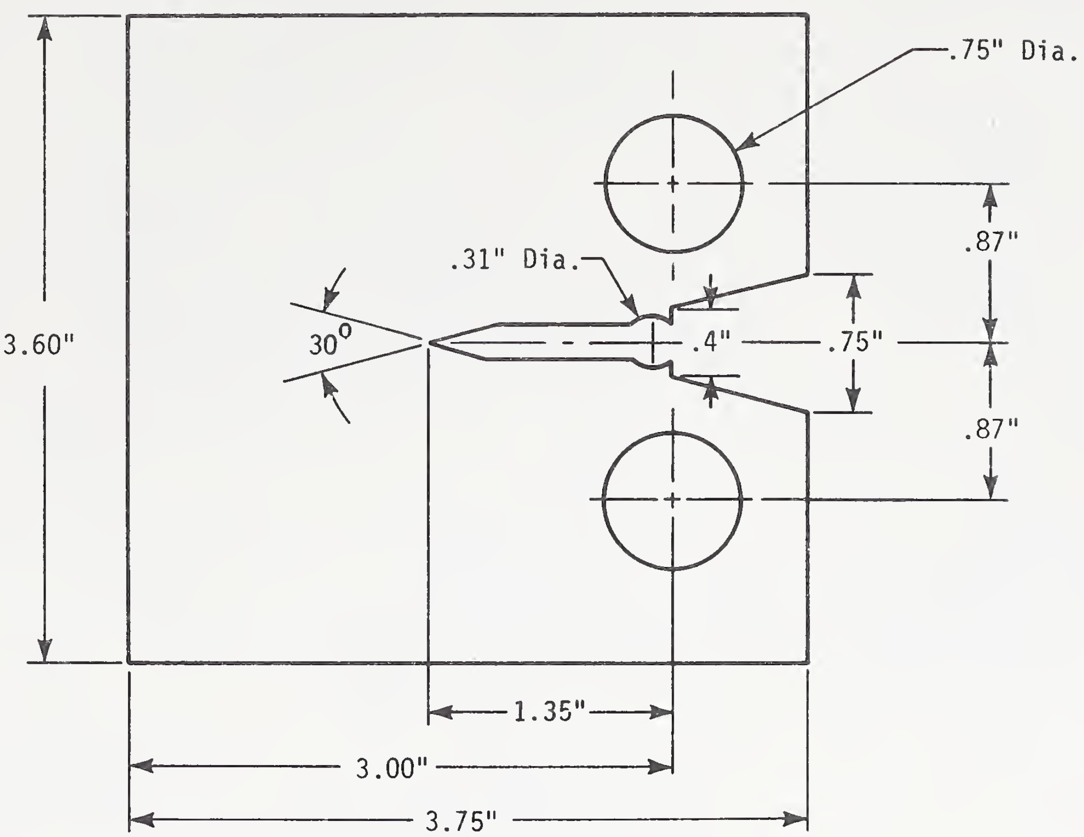

Figure 1. Fracture Toughness Specimen

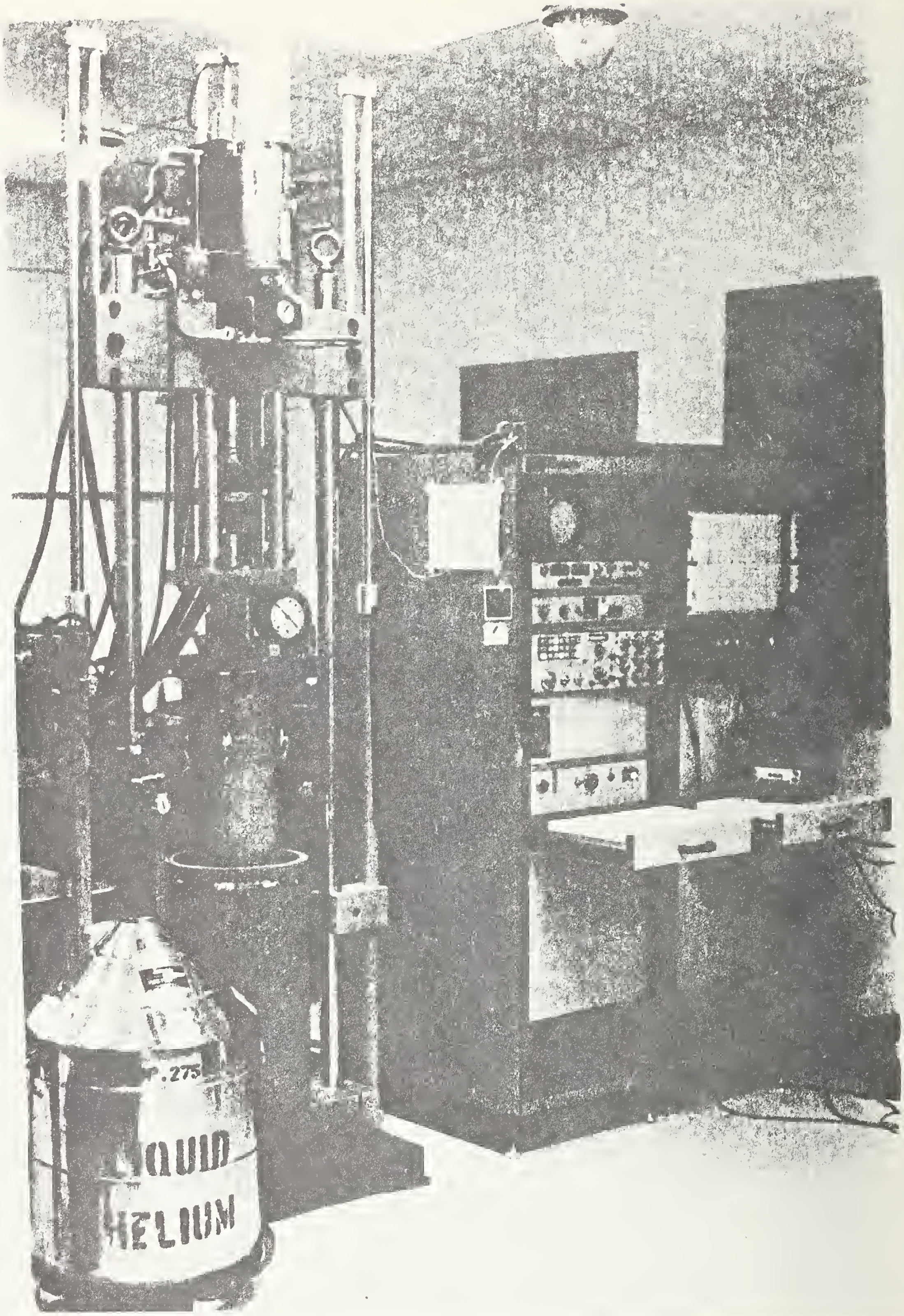

Figure 2 Cryogenic Fatigue Testing Apparatus

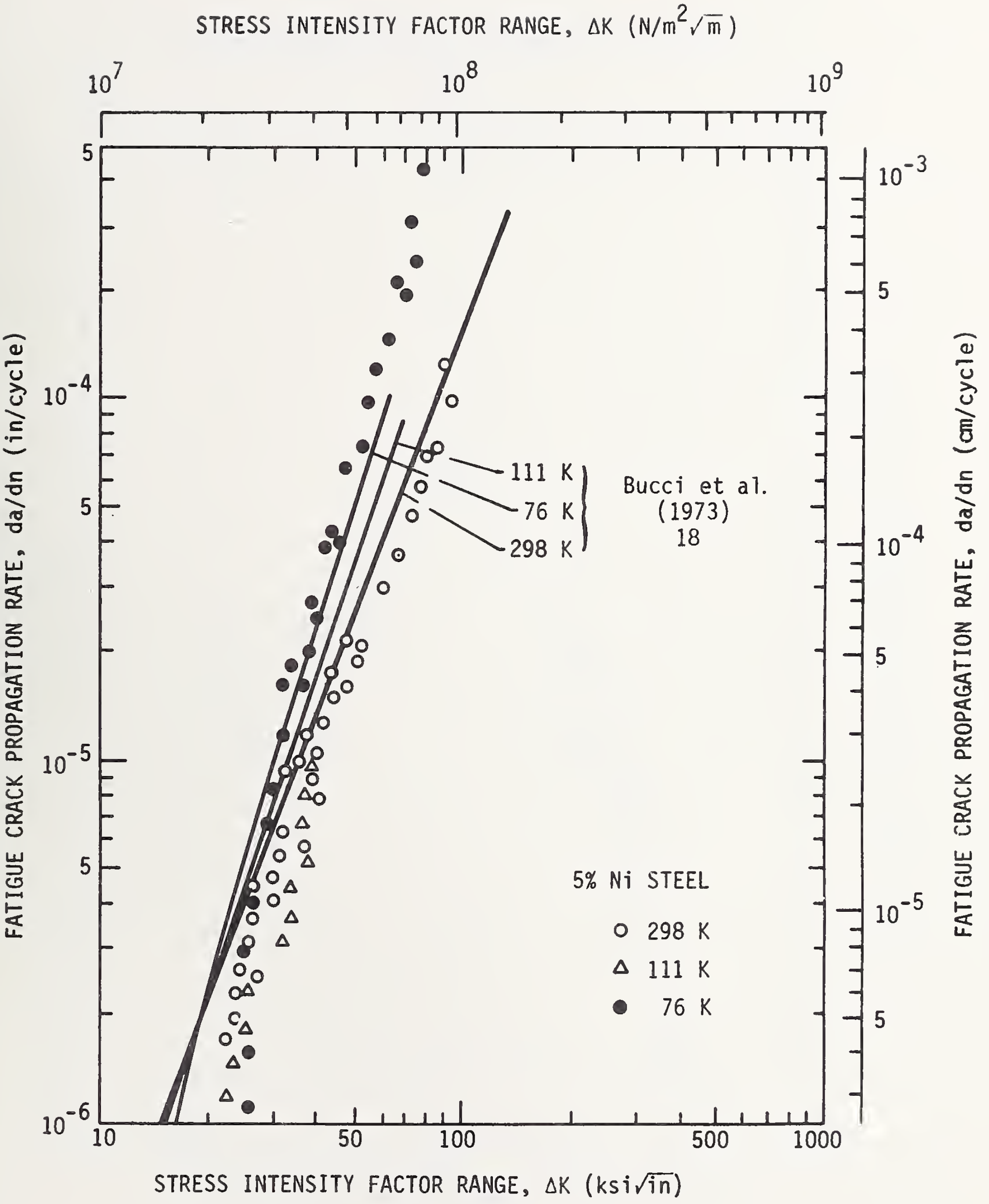

Figure 3. Fatigue Crack Growth Rate of Fe-5 Ni

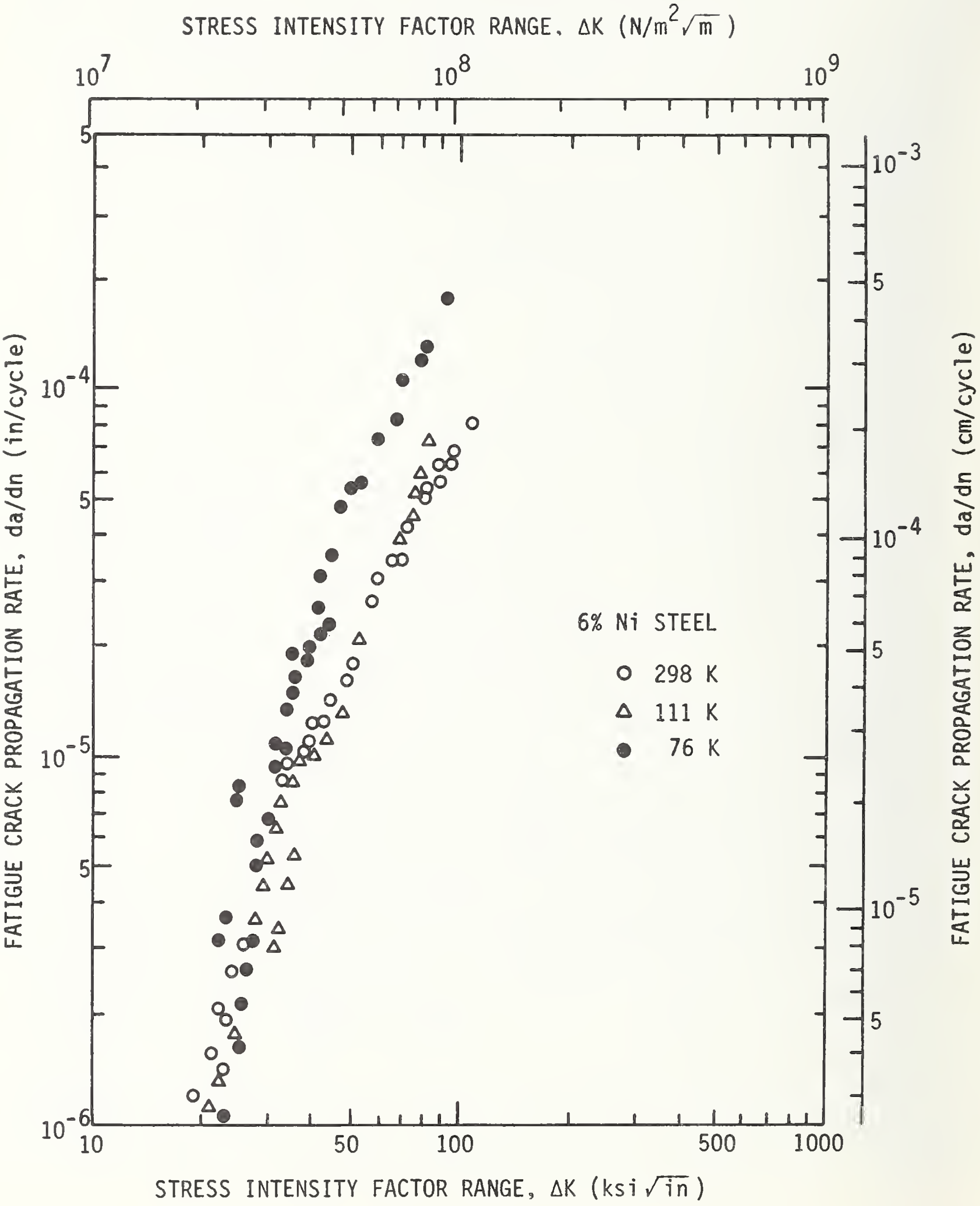

Figure 4. Fatigue Crack Growth Rate of Fe-6 Ni

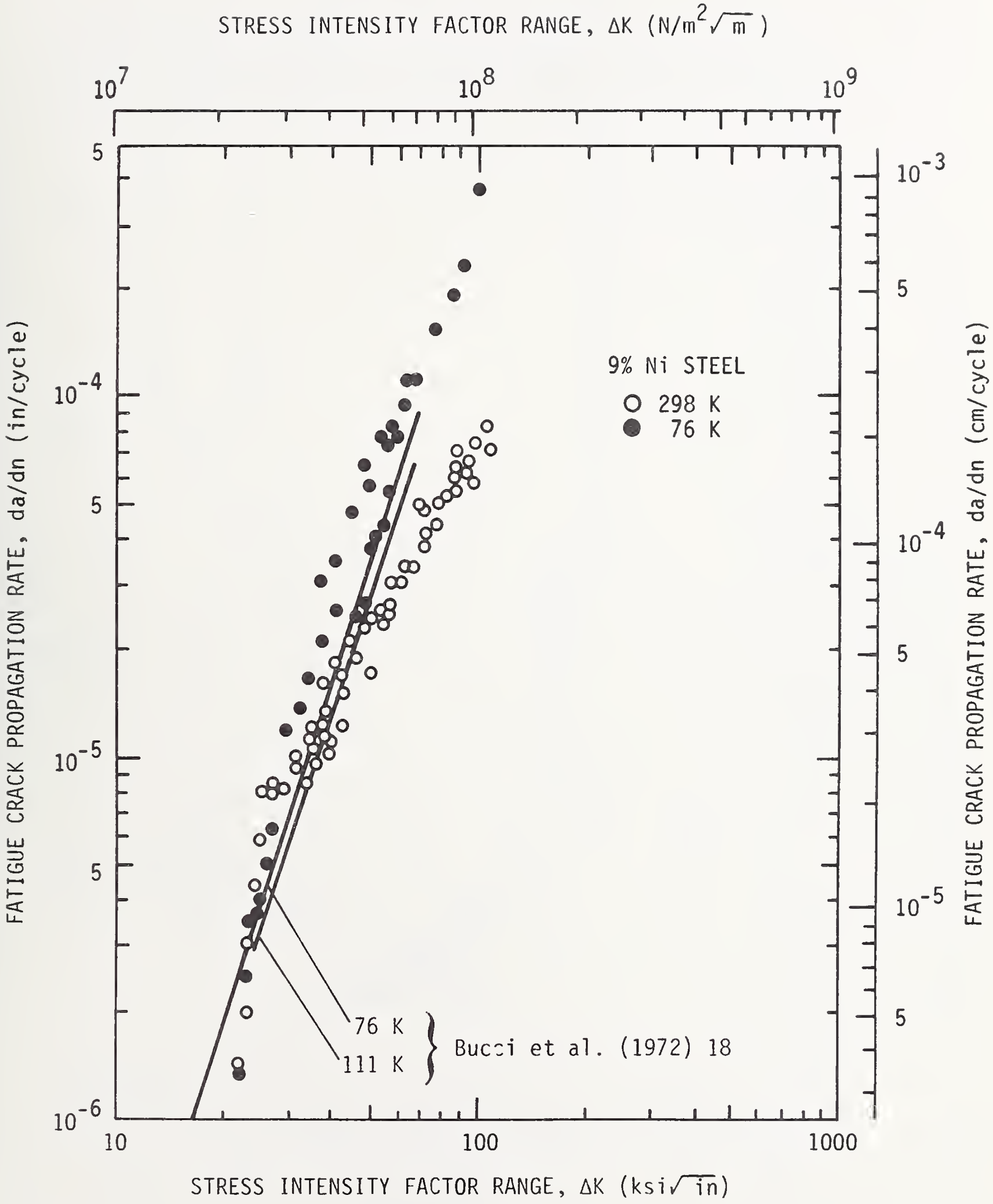

Figure 5. Fatigue Crack Growth Rate of Fe-9 Ni

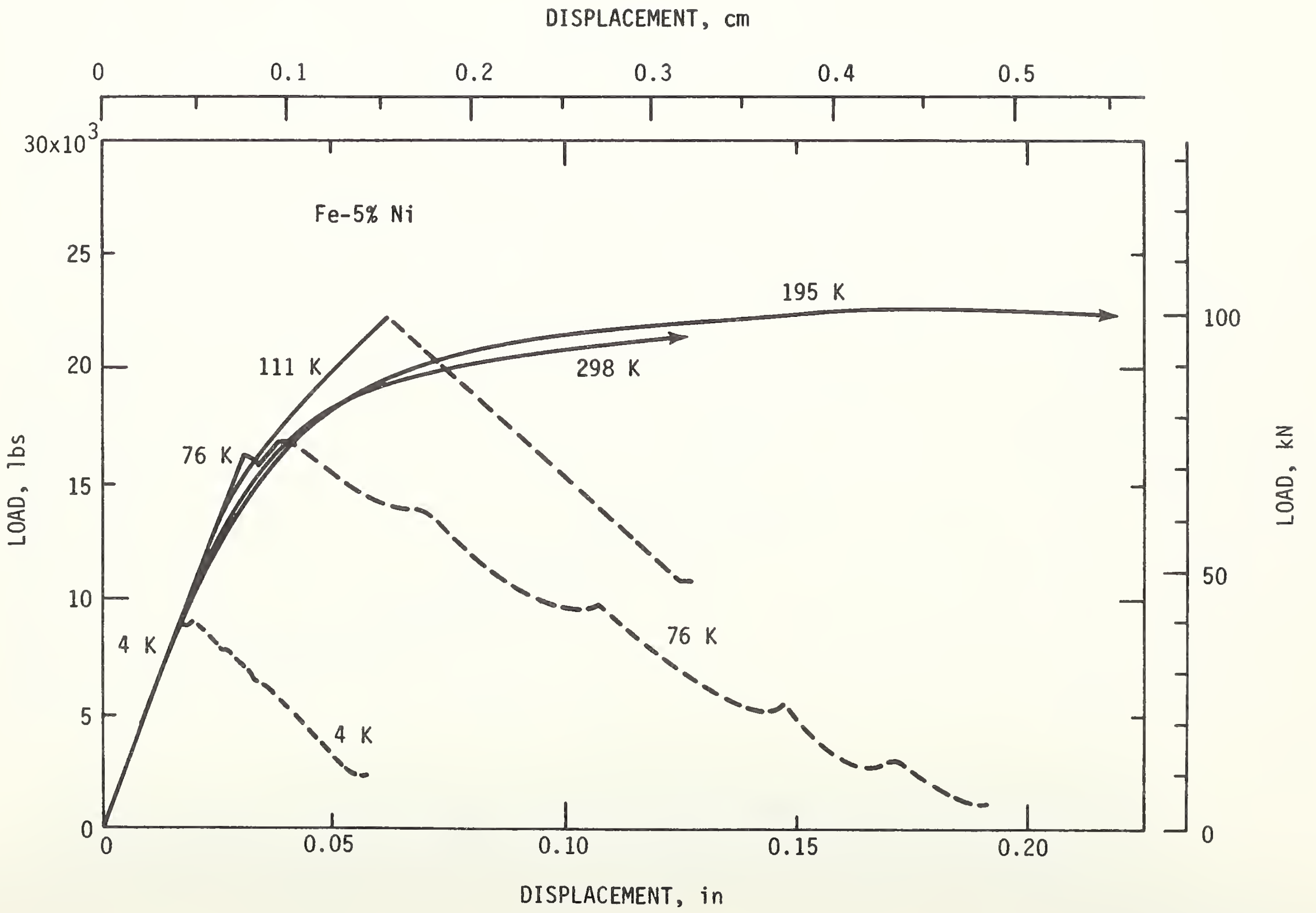

Figure 6. Load-Loadline Displacement Curves for Fe-5 Ni

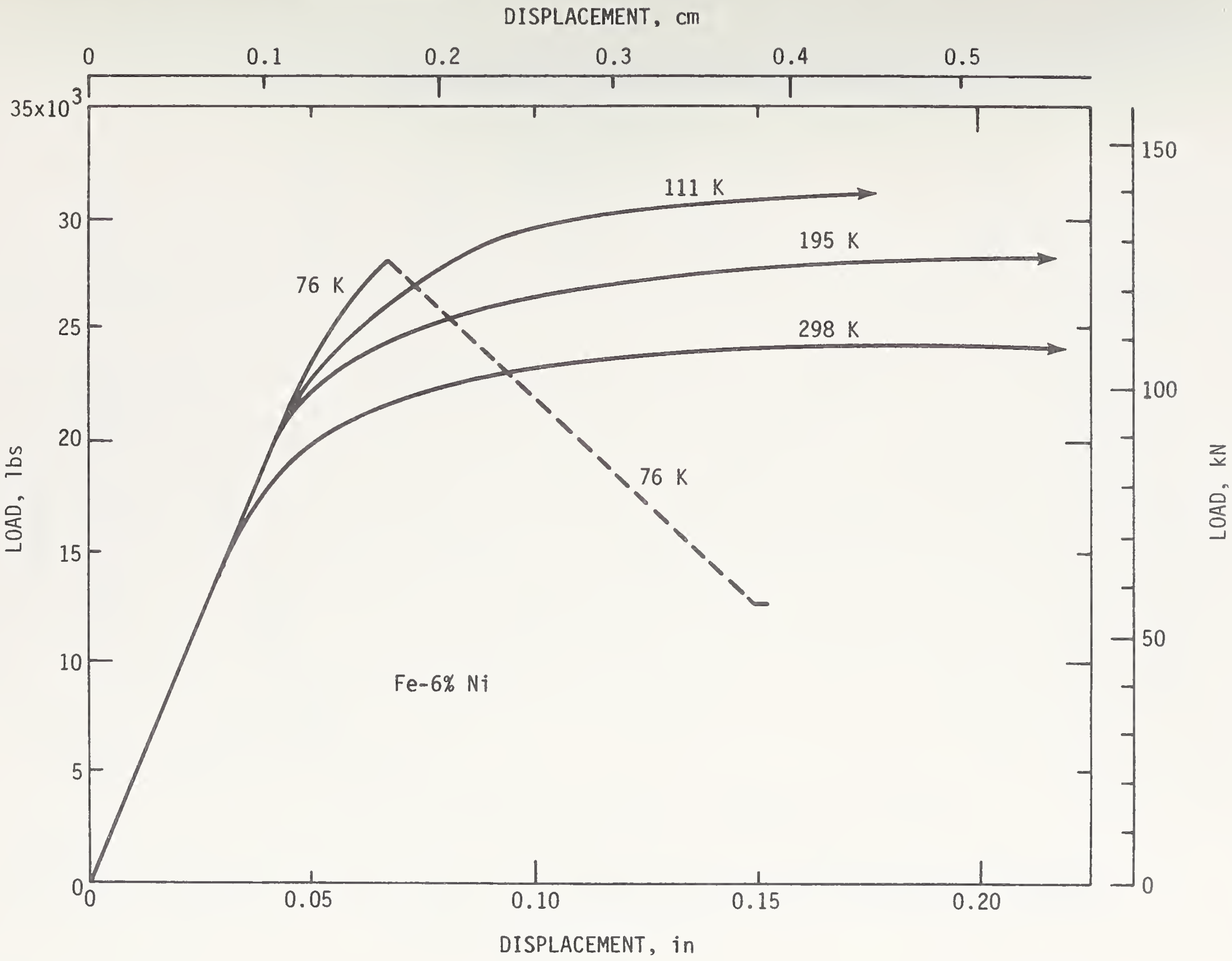

Figure 7. Load-Loadline Displacement Curves for Fe-6 Ni

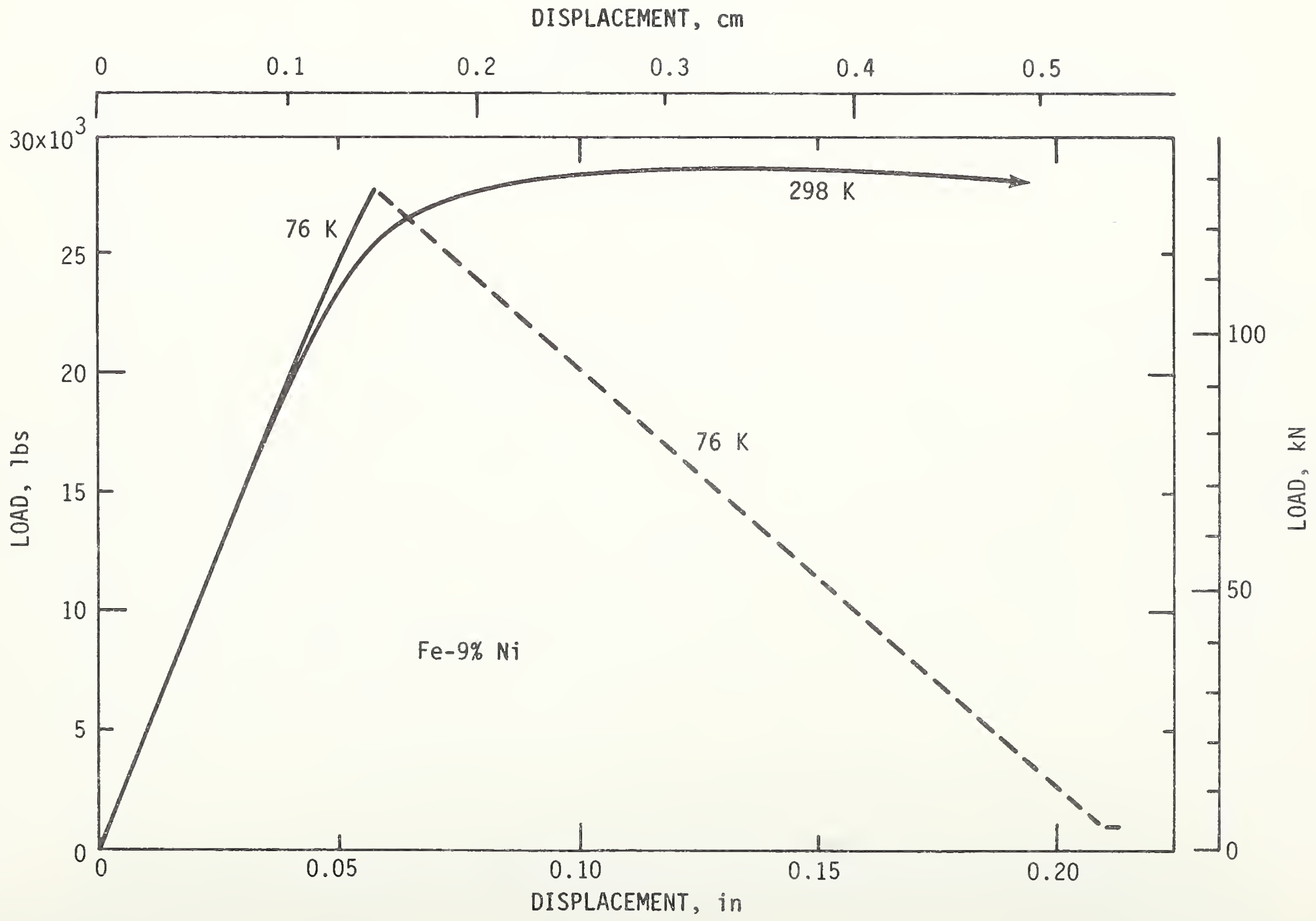

Figure 8. Load-Loadline Displacement Curves for Fe-9 Ni

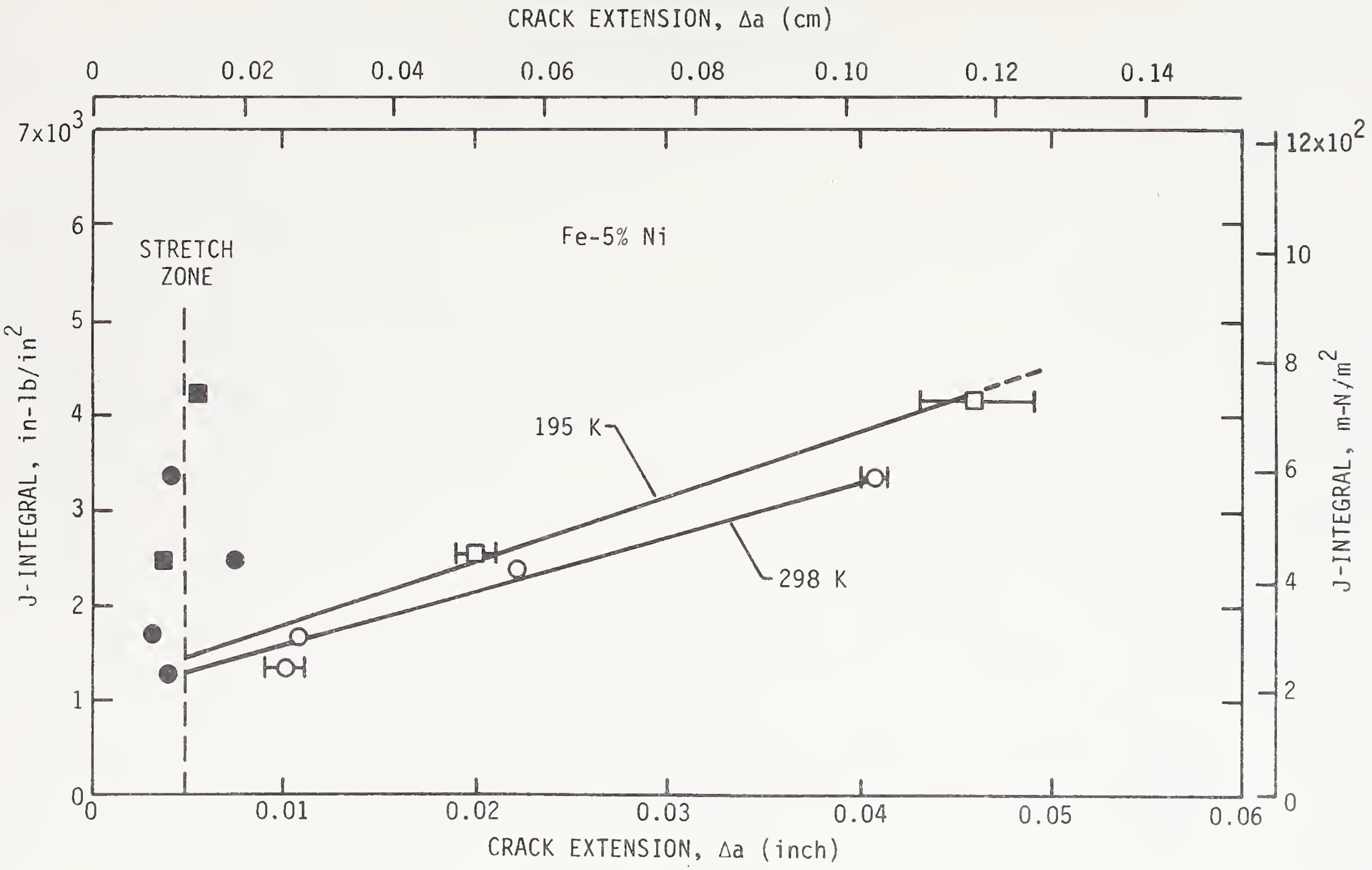

Figure 9. J Resistance Curves for Fe-5 Ni

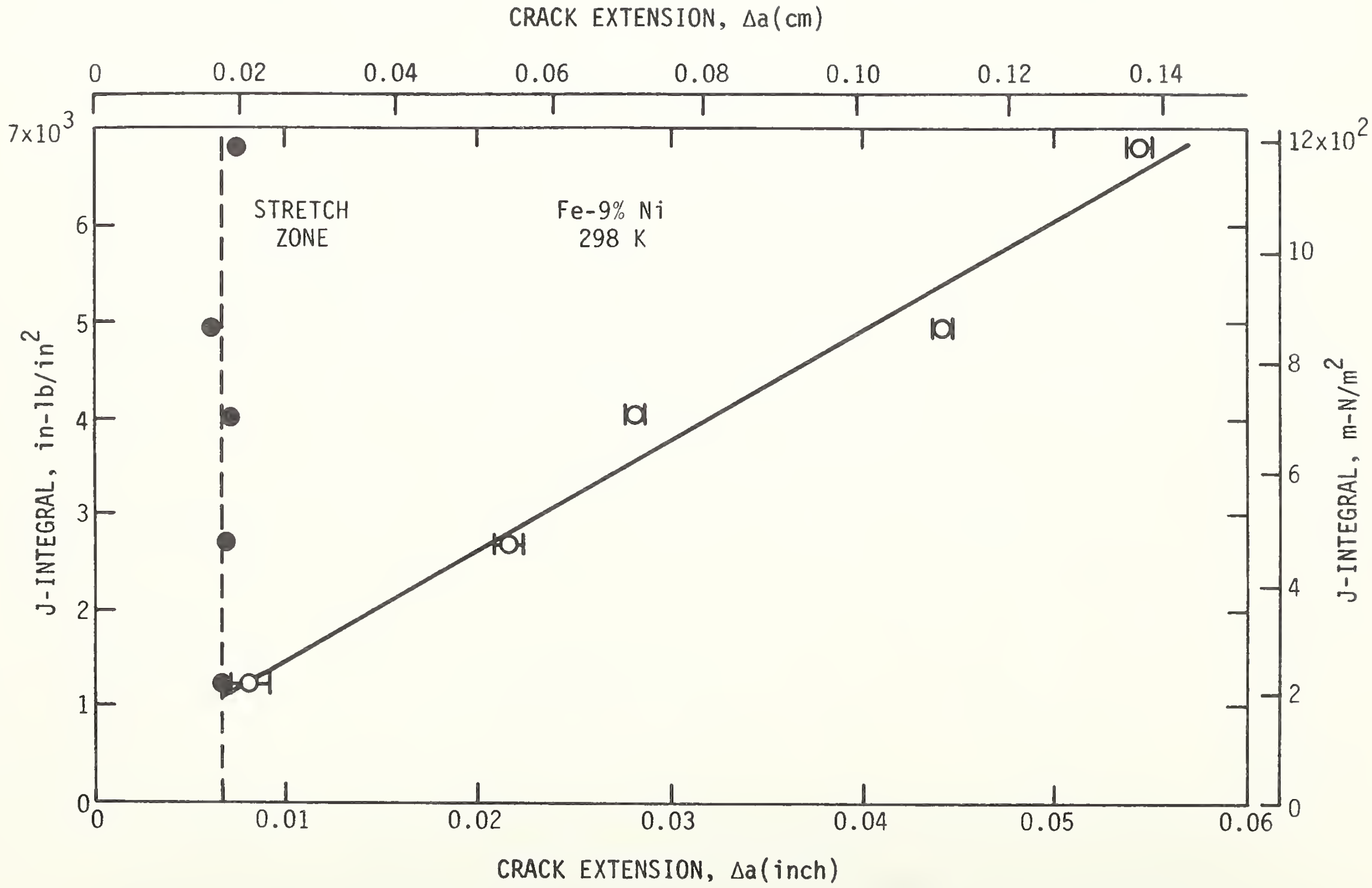

Figure 10. J Resistance Curves for Fe-9 Ni

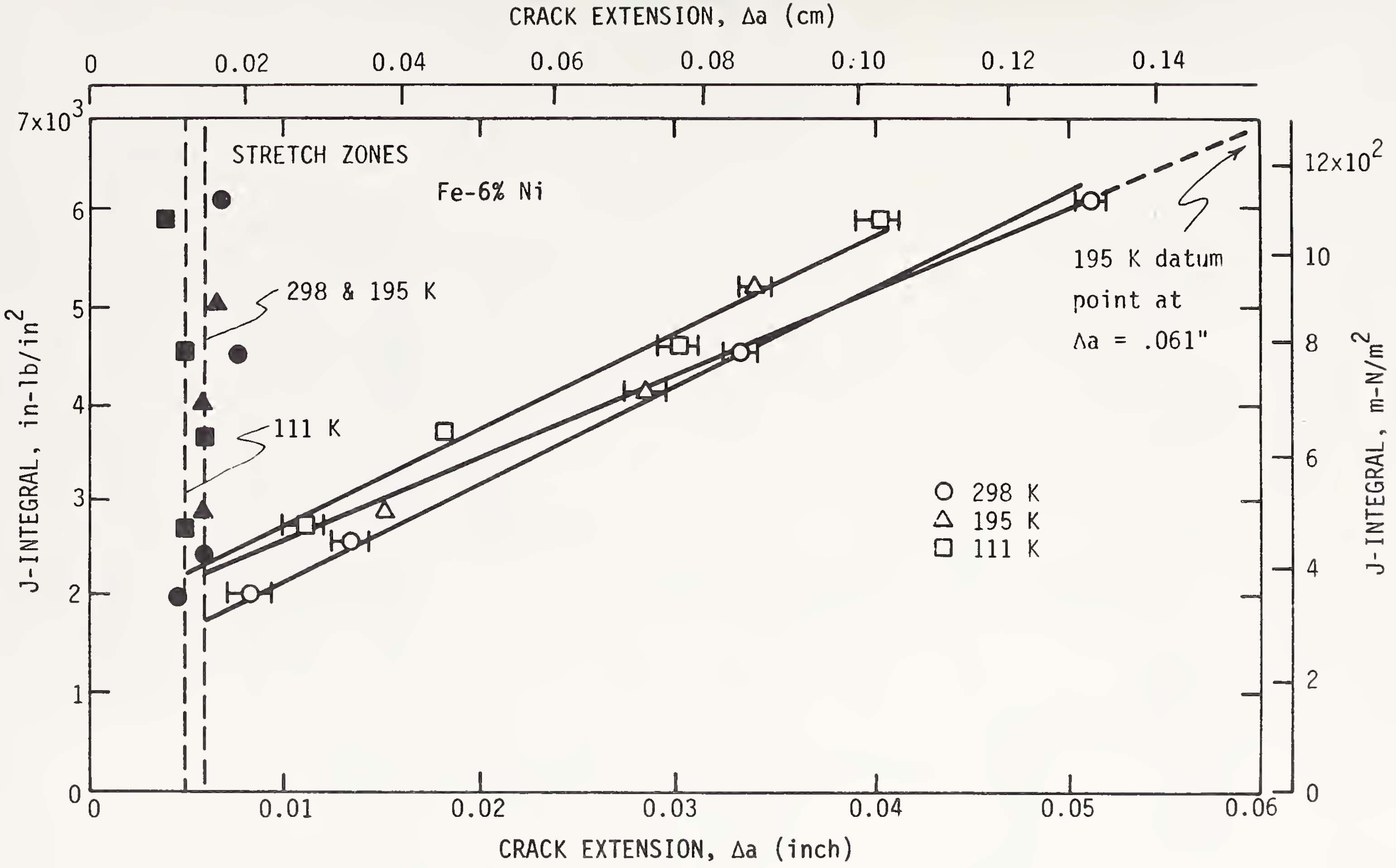

Figure 11. J Resistance Curves for Fe-6 Ni

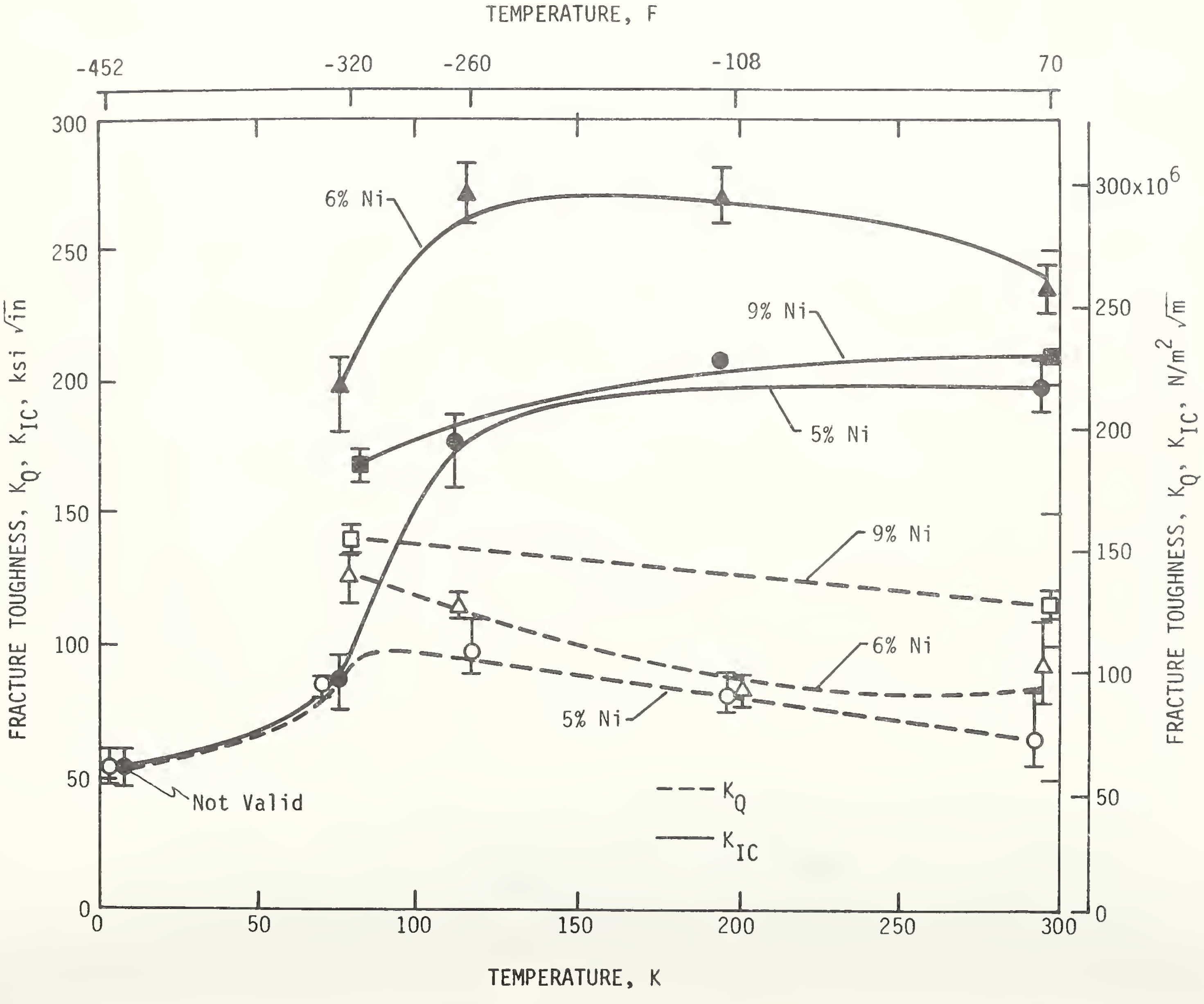

Figure 12. Temperature Dependence of the Fracture Toughness of 5, 6, and 9% Nickel Steels

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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.)*

Seventeen cost centers supported by seven other agency sponsors in addition to NBS provide the basis for liquefied natural gas (LNG) research at NBS. During this six month reporting period the level of effort was at a 20 man-year level with funding expenditures of over $500,000. This integrated progress report to be issued in January and July is designed to:

1) Provide all sponsoring agencies with a semi-annual and annual report on the activities of their individual programs.
2) Inform all sponsoring agencies on related research being conducted at the Cryogenics Division of NBS-IBS.
3) Provide a uniform reporting procedure which should maintain and improve communication while minimizing the time, effort and paper work at the cost center level.

The contents of this report will augment the quarterly progress meetings of some sponsors, but will not necessarily replace such meetings. Distribution of this document is limited and intended primarily for the supporting agencies. Data or other information must be considered preliminary, subject to change and unpublished; and therefore not for citation in the open literature.

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