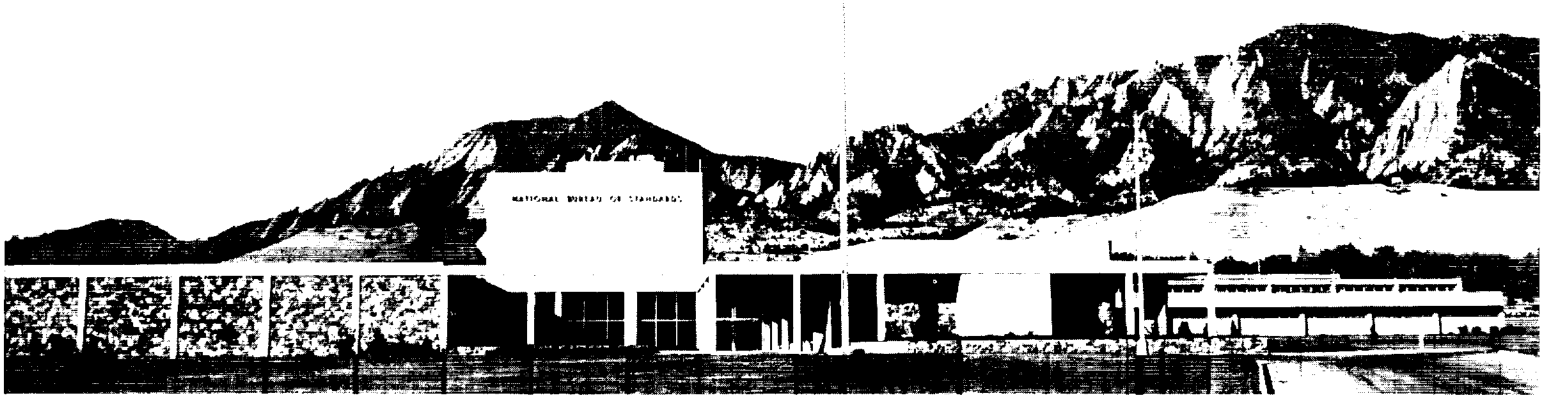

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NBS REPORT

9782

THERMODYNAMIC AND TRANSPORT PROPERTIES OF FLUIDS AND SELECTED SOLIDS FOR CRYOGENIC APPLICATIONS

by

Victor J. Johnson

Dwain E. Diller

NBS

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U. S. DEPARTMENT OF COMMERCE
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Boulder, Colorado

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27502-2750422 27504-2750445 27504-2750446	October 31, 1970	9782

THERMODYNAMIC AND TRANSPORT PROPERTIES OF FLUIDS AND SELECTED SOLIDS FOR CRYOGENIC APPLICATIONS

Summary Report of Work Performed on NASA Contracts R-06-006-046 and W-12, 745 from December 1, 1965 to November 1, 1970

by

Victor J. Johnson, Chief, Cryogenic Data Center
Dwain E. Diller, Chief, Cryogenic Properties of Fluids Section

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

Report to

National Aeronautics and Space Administration
Office of Advanced Research and Technology
NASA Headquarters, Washington, D.C.

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Summary Report of Work Performed on
NASA Contracts R-06-006-046 and W-12, 745
October 31, 1970

by

V. J. Johnson and D. E. Diller

ABSTRACT

The report is a summary of work done under the sponsorship of NASA - Office of Advanced Research and Technology (OART) by the Data Compilation Group of the Cryogenic Data Center from December 1, 1965 to November 1, 1970, and by the experimental measurements staff of the Cryogenic Properties of Fluids Section from November 1, 1966 to November 1, 1970. The activities and accomplishments for the data evaluation and compilation program are summarized in the description of the following tasks:

a) Properties of Hydrogen and Related Studies Including Curve Fitting Techniques and Survey of Temperature Scales.
b) Thermodynamic Properties of Oxygen.
c) Thermodynamic Properties of Argon.
d) Correlation of the Thermodynamic Properties of Deuterium.
e) Transport Phenomena in Cryogenic Fluids.
f) Correlation of the Thermodynamic Properties of Helium.
g) Annotated Bibliography on the Properties of Methane.
h) Electrical Resistivity of Metals.
i) Annotated Bibliography on the Properties of Air.
j) Thermal Conductivity of Metals, Alloys, and Non-metallic Solids.

More than 30 publications and reports of significant value were produced for the NASA Aerospace program. Included were tables and large size charts for the thermodynamic and transport properties of many of the cryogenic fluids such as hydrogen, deuterium, oxygen and argon. Page size reproductions of a number of the charts are shown. The time period and level of NASA support of the program is illustrated in conjunction with associate tasks for other sponsors.

A major experimental measurements program for the thermophysical properties of compressed gaseous and liquid oxygen was also undertaken and completed under the NASA-OART Sponsorship. Fourteen publications and reports were produced including NBS Report 9710 on "Thermodynamic and related properties of oxygen from the triple point to 300 K at pressures to 330 atmospheres," which is the single most significant and comprehensive publication produced for oxygen and which presented an estimated 80% of the world's experimental data for the region covered. An experimental measurements program for the thermodynamic properties of helium was initiated in the final year of the program as the result of a need for better data. Support is being sought to complete this task as described in the proposal appended to the report.

Key Words: Bibliographies, Critical Evaluation Program, Experimental Measurements, Helium Properties, Oxygen Properties, Properties of Fluids, Properties of Solids, Summary Report, Tabulations, Thermodynamic Properties, Transport Properties.

1.0 INTRODUCTION

This report summarizes the work done under the sponsorship of NASA - Office of Advanced Research and Technology (OART) by the Data Compilation Group of the Cryogenic Data Center from December 1, 1965 to November 1, 1970, and by the experimental measurements staff of the Cryogenic Properties of Fluids Section from November 1, 1966 to November 1, 1970. This represents a continuation of work sponsored by NASA's Space Nuclear Propulsion Office (Cleveland) and the George C. Marshall Space Flight Center (Huntsville) as described in the "background" information presented in the two sections of this report. The section 2.0 describes the work done by the Data Compilation Group, and section 3.0 covers the experimental measurements program of the Properties of Fluids Section.

1.1 Major Accomplishments

A number of very significant publications have been prepared during this period of NASA-OART support. The most important of these are for the properties of such fluids as Oxygen, Argon, and Helium.

The thermophysical properties of Oxygen have been most extensively covered. Starting with complete bibliographic coverage [10, 26]* of the world's literature, a thorough evaluation of the thermodynamic property data was done by R. B. Stewart and published as a Ph.D. dissertation [26]*. Parallel with and succeeding this effort was one of the most extensive thermodynamic properties measurements program ever undertaken for a common fluid. Precise, closely spaced, P-ρ-T and C_v measurements from the triple point to 350 atmospheres pressure and 300 K for both the liquid and gaseous phases were made. The data acquired represent nearly 80% of the world's experimental data for this region and were first made available in NBS Report 9710 June 20, 1968 [1]+. Important subsequent publications of these data are listed in section 3.5, references [4, 5, 7, 13, 14].

A compilation of the thermodynamic properties of Argon is considered another of the major tasks completed, although it did not involve an experimental measurements program. Again a comprehensive search of the world's literature was made and from this all significant data were compared and evaluated. A single continuous equation of state was developed to present the most probable values of pressure, density and temperature (P-ρ-T) well within the uncertainty of the experimental data from the triple point to 1000 atmospheres pressure and to 300 K. Tables of derived properties (enthalpy, entropy and internal

---

* Section 2.8

† Section 3.5

energy) are presented as well as charts for specific heats at constant pressure and at constant volume. These data are published in the NBS National Standard Reference Data Series as Monograph 27 [29]*.

Another major accomplishment was the evaluation and compilation of the thermodynamic properties of Helium. This was an important task from a number of points of view because of the importance of this fluid to the aerospace program as well as to the scientific community. The "best values" for the region from 2 to 1500 K for pressures from 0.1 to 1000 atmospheres for P-ρ-T, enthalpy, entropy, internal energy, C_p, C_v, and speed of sound are presented in NBS Report 9762 [51]. Final publication will be made in the NBS-NSRDS Series. This task has not only made available the best thermodynamic property data for helium-4 but has revealed the regions of greatest uncertainty of the data and the need for better experimental measurements (see section 2.6 item F and section 3.6 appendix C).

The progress made on the transport properties of fluids and many of the results that have been published [39, 40, 41, 42, 45, 46, 49, 50]* are considered a real advance in the state-of-the-art for analyzing, correlating and compiling data for viscosity, thermal conductivity and thermal diffusion of the simple gases (helium, hydrogen, neon, nitrogen, oxygen, argon, krypton, and xenon) in both dilute and dense gas states. This work is of real and timely value to the areas of heat transfer and fluid flow and also provides guidelines to experimentalists measuring transport properties. It establishes levels of precision necessary for data to be useful to evaluators as well as other criteria for optimum measurement procedures and requirements. (See section 2.6 item E).

1.2 Tasks to be Completed

In a continuing long term program of collecting, extracting, evaluating and compiling data on the thermophysical properties of fluids and solids essential to the aerospace and other important industrial and scientific areas many tasks are in progress at the same time and some will be incomplete at particular termination periods. This is true for both the Cryogenic Data Center's data compilation program and the experimental measurements program. In this Summary of Work accomplished under the current 5-year period of NASA-OART support it will be noted that the following tasks were only partially completed:

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*Section 2.8

a) Thermodynamic Properties of Methane. The original plan was to follow the bibliographic effort with an extensive data evaluation and compilation effort. This latter phase was not undertaken, however, because of preference for applying available support to other tasks. (See section 2.6 item G.) As a result segments of the task are being done under a variety of sponsorships for immediate needs. (For example see reference [63]).

b) Thermodynamic Properties of Air. Just as for a) above, this task,when undertaken, was intended to be a complete evaluation and compilation of the thermodynamic properties of air. However, it too was suspended upon completion of the bibliography for about the same reason. (See section 2.6 item I).

c) Transport Properties of Cryogenic Fluids. This is a continuing task for which sponsorship was transfered to the NBS Office of Standard Reference Data. (See section 2.6 item E.)

d) Experimental Program for the Measurement of the Thermodynamic Properties of Helium. This program was only initiated last year. The time and funds available have made it possible to complete much of the experimental apparatus needed and plan the measurement program. Continuing support will be needed, however, to complete the apparatus and make the measurements. (See sections 3.1 and 3.5 appendix C.)

2.0 DATA EVALUATION AND COMPILATION

2.1 Background

The work on this contract* was a continuation of work sponsored through the SNPO Contract R-45 and the NASA Marshall Space Flight Center at Huntsville (NASA Order H-76797). The SNPO support was provided from early 1961 through November 1965 plus a small amount of continuing support to July 1970. The MSFC support was from February 1965 to February 1966, slightly overlapping contract R-46. Figure 1 illustrates the development of the Cryogenic Data Center's Data Compilation Program prior to the transfer of support for the program to NASA Headquarters in Washington, D. C. under the Office of Advanced Research and Technology (OART). Figure 2 shows the support of the program by NASA-OART from December 1, 1965 to November 1, 1970.

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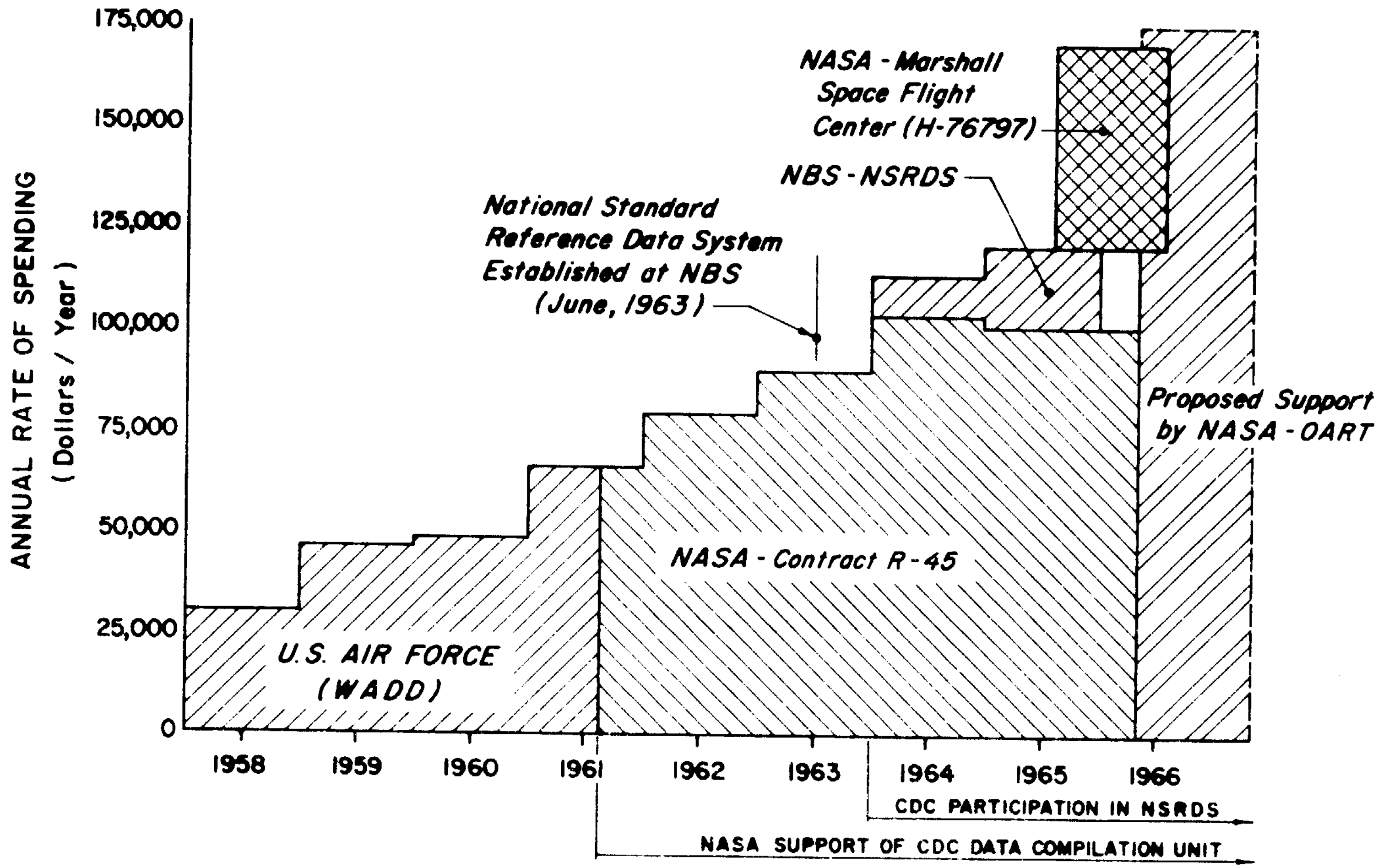
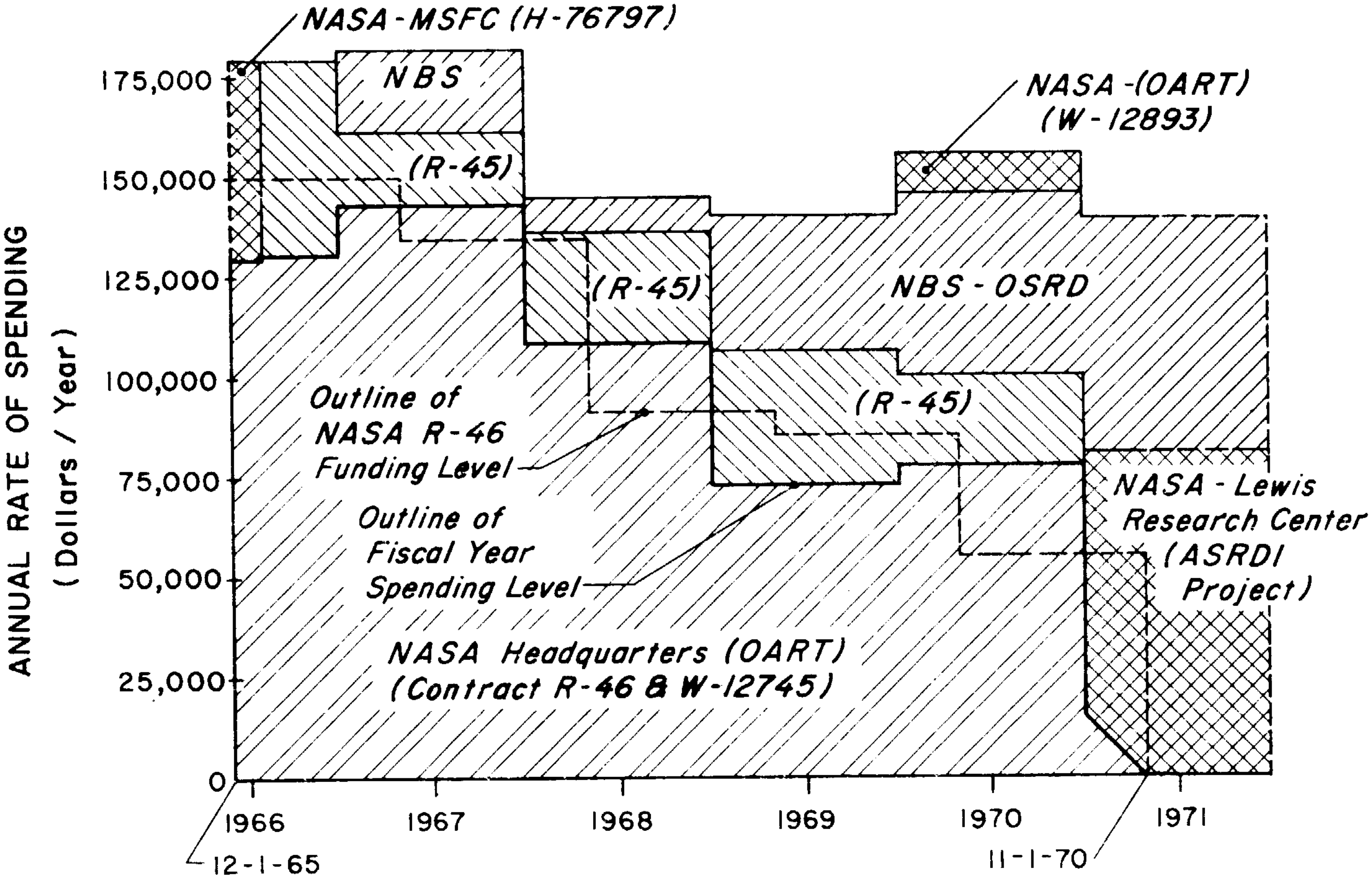
* NASA Orders R-06-006-046 and W-12,745, hereinafter referred to throughout this report as NASA Contract R-46.



Project Support for the THERMOPHYSICAL DATA COMPILATION PROGRAM for Materials at Cryogenic Temperatures, at the NBS Cryogenic Data Center.

FIGURE 1



Project Support for the THERMOPHYSICAL DATA COMPILATION PROGRAM for Materials at Cryogenic Temperatures, Since December 1, 1965, at the NBS Cryogenic Data Center.

FIGURE 2

The Data Compilation Unit is engaged in the critical evaluation of thermophysical property data from the scientific literature for materials at cryogenic temperatures. The objective is the compilation of extensive tables of property values over wide ranges of temperature and pressure. This Unit is a charter participant in the National Standard Reference Data System which was established in the NBS Institute for Basic Standards in 1963. The Data Compilation Unit has long been recognized as a national authority for data on the properties of materials at cryogenic temperatures and as a primary center for the entry of such data into the national system.

2.2 The Cryogenic Data Center

The Data Center is organized into two principal units: the Documentation Unit for operation of a computerized bibliographic service, and the Data Compilation Unit for the evaluation and compilation of data on the thermophysical properties of materials at low temperatures. The bibliographic function has been funded primarily by NBS except for reimbursement for services to the Cryogenics Division's projects, to other government agencies and to the public. The Documentation Unit's services to the data evaluation and compilation program have been extensive and essential, since each compilation task is started with a comprehensive literature search and bibliography.

2.3 Data Compilation Procedures

Upon the initiation of tasks for data compilation, a bibliography is prepared by the Cryogenic Data Center's Documentation Unit. A systematic and comprehensive search of the abstract journals on the subject is then made and appropriate items added to the bibliography. Copies of all documents in the bibliography are procured which are in turn searched for additional references related to the subject. Following the compilation of the bibliography, the numerical data and pertinent facts related to it are extracted from the literature and compiled on data sheets which are assembled in task notebooks. Related data are then compared and evaluated on appropriate statistical and theoretical basis. Using the experimental data from the literature and appropriate theoretical and empirical techniques, comprehensive data tables, thermodynamic charts, and mathematical functions over extended ranges of temperature and pressure are compiled.

The task is concluded by the publication of a document which describes the data evaluation procedures, and the methods used in generating data tables; also included are comprehensive data tables and appropriate graphical representations. In addition to the final publication, various interim reports and documents may be issued. These interim documents include the bibliographies resulting from the literature search, compilations of the data extracted from the literature which may be prepared from the task notebooks, and interim tables of property values which may be calculated prior to the final analysis and evaluation of the data. The purpose of these interim publications is to make this material available to the sponsoring agency, prior to the completion of the specific task.

2.4 Work in Progress at the Beginning of the Contract Period

The following major tasks were in progress when the sponsorship of the Data Compilation program was consolidated under the direction of OART:

Item A): Thermodynamic Properties of Hydrogen

An extensive amount of work had been done under the previous NASA contract (R-45) which produced a number of publications and thermodynamic charts [1-9]. Only a limited amount of additional work on hydrogen was proposed for the R-46 contract since the SNPO planned to continue their support of work on hydrogen properties as a particular requirement for the NERVA program under contract R-45. This additional work (for R-46) involved the development of curve fitting techniques for evaluation of thermodynamic data, completion of a study of temperature scales to allow conversions to the thermodynamic scale for data from various laboratories, and preparation of some special Temperature-Entropy charts for liquid parahydrogen (as described in section 2.6, item A of this report).

Item B): Thermodynamic Properties of Oxygen

The compilation and critical evaluation of existing properties data was well along at the start of this contract. There remained the final selection of constants for the equation of state, the preparation of the tables of thermodynamic properties and the construction of the thermodynamic charts based on existing data in the literature, since the new experimental measurements program (described in section 3.0 of this report) had not yet been initiated. Later, however, some of the new measurements were used for this task. (See 2.6 item B for detailed description.)

Item C): Thermodynamic Properties of Argon

This major task was also well advanced. The principal author, A. L. Gosman, had completed sufficient work for a doctoral dissertation that had just been accepted at the University of Iowa [14]. Considerable work was yet required (as described in section 2.6, item C) to complete the evaluation and compilation of the thermodynamic property data for an NBS-NSRDS Monograph.

Item D): Thermodynamic Properties of Deuterium

This task was being carried on by a guest worker, Rolf Prydz, who was correlating and compiling all the available data on the properties of deuterium for a masters thesis in the Chemical Engineering Department of the University of Colorado. He was in the final stages of evaluating the data, preparing a suitable equation of state, compiling the numerical tables of property values and having the thermodynamic charts prepared when the task came under the cognizance of contract R-46. It resulted in a Master of Science theses [32] and NBS report [33] that are accepted as the best thermodynamic properties data for deuterium.

Item E): Transport Phenomena in Cryogenic Fluids

The task for compiling the transport properties of the cryogenic fluids was in the initial phases at the beginning of contract R-46. Dr. H. J. M. Hanley was hired in June 1965 to undertake this major program area and had made encouraging progress on the properties for the dilute gases by December 1st when this contract assumed cognizance.

2.5 List of Additional Tasks Completed Under Contract R-46

The following five tasks were initiated during the period of this contract and received all or most of their support from NASA (R-46).

Item F): Correlation of the Thermodynamic Properties of Helium (in the Liquid and Vapor Phases from 2 to 1500 K for Pressures to 1000 Atmospheres).

Item G): Annotated Bibliography on the Properties of Methane.

Item H): Electrical Resistivity of Metals.

Item I): Annotated Bibliography on the Properties of Air.

Item J): Thermal Conductivity of Metals, Alloys, and Non-metallic Solids.

A detailed description of each task is given under its corresponding item number in section 2.6. A chronology bar graph, figure 3, shows the activity periods for all the tasks:

2.6 Description of the Tasks

Item A: PROPERTIES OF HYDROGEN AND RELATED STUDIES INCLUDING CURVE FITTING TECHNIQUES AND SURVEY OF TEMPERATURE SCALES

Principal Evaluators: J. G. Hust and R. D. McCarty.

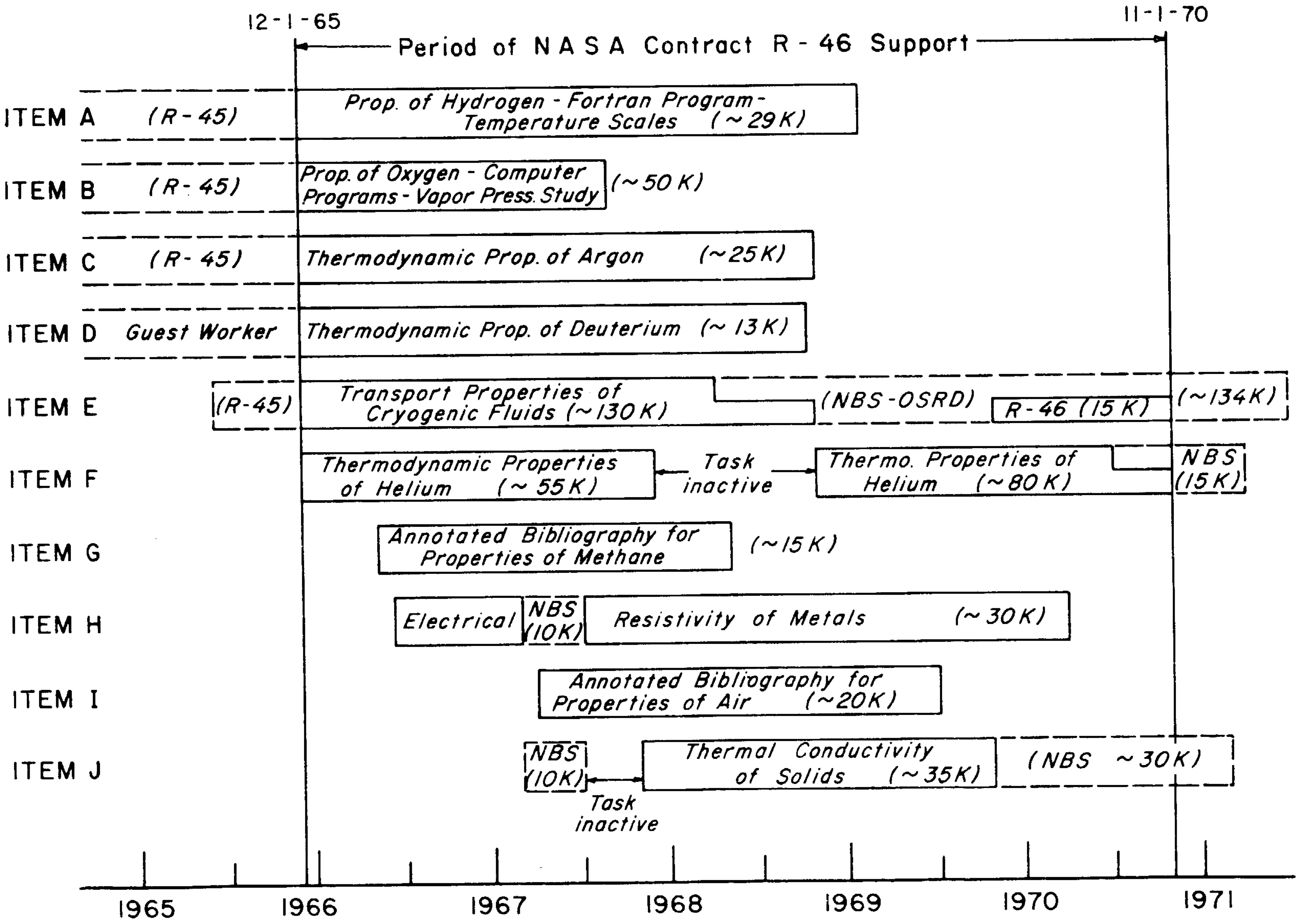


FIGURE 3. Chronology of DATA COMPILATION TASKS.

Associates: R. B. Stewart and H. M. Roder.

Time period: December 1965* - November 1966, plus low level of effort through July 1969 on temperature scales study.

Publications:

Thermodynamic Property Charts of Saturated Liquid Parahydrogen; NBS Report 9263 (Nov. 15, 1966) [22].

Fortran Package for Least Squares Curve Fitting and the Solution of Simultaneous Equations; NBS Report 9258 (Oct. 10, 1966) [23]. Also paper entitled, "Curve-fitting Techniques and Applications to Thermodynamics" Cryogenics, Vol. 7, No. 4 (August 1967) [24].

A Compilation and Historical Review of Temperature Scale Differences; Cryogenics, Vol. 9, No. 6 (December 1969) [25].

Summary:

The task had been active for several years under NASA Contract R-45 and was continued at a reduced level of effort under that Contract during much of the period of Contract R-46. As a result, only three studies were pursued: the development of curve fitting techniques for the evaluation of thermodynamic data; the completion of a study of temperature scales to allow conversions to the thermodynamic scale for data from various laboratories throughout the world; and the preparation of six special multicolor temperature-entropy diagrams for the saturated liquid region in parahydrogen.

Curve Fitting Techniques

Fundamental to the evaluation and intercomparison of thermodynamic and transport property data, not only for hydrogen but for all of the cryogenic fluids, is the development of a suitable equation of state from which a smooth and mathematically consistent P-V-T surface can be generated. Many mathematical techniques have been presented in the literature for representing data. The most popular, but not necessarily the best method, has been the least-squares fitting of data to a particular function. The solution of the least squares problem, although mathematically unique, can be programmed in many ways. The initial phase of the curve fitting study was to develop a Fortran package for least squares curve fitting and the solution of simultaneous equations. This was summarized and made available in NBS Report 9258 [23].

---

* Continuation of task previously supported on NASA Contract R-45.

Following this initial effort, more sophisticated applications of the least squares fitting approach were developed, particularly in the method of constraining the functions to fixed points simultaneously fitting different, but theoretically related data and in statistically weighting certain data to control their effect on the shape of the surfaces generated. Several of these techniques are described in Hust and McCarty's paper [24] published in Cryogenics (August 1967). Covered are subjects such as:

a) Simultaneous Least Squares Determination of a Single Set of Parameters from Several Types of Property Data.

b) Simultaneous Least Squares Determination of Several Sets of Parameters from a Single Set of Property Data.

c) Least Squares with Non-linear Equations.

d) Entropy Discontinuity at the Critical Point Removed by Constraint.

e) Application to an Equation for the Vapour Pressure of Oxygen and to the Joule-Thomson Inversion Curve of Neon.

The study and development of curve fitting techniques is a continuing requirement in the correlation and compilation of data; however it has become an integral part of each data compilation task rather than as a separate subtask as was the case for hydrogen.

Review of Temperature Scales

In the intercomparison and analysis of data that are particularly sensitive to temperature, it is essential that a known temperature base be established for each data set. Often times this is difficult if not impossible to do unless information is available on the temperature scales various experimenters used in reporting their values.

Early in 1966 J. G. Hust undertook a fairly extensive survey of temperature scales used in many of the world's leading laboratories, both currently and historically. The results of this study were published in Cryogenics (December 1969) [25] although most of the work was completed by early 1968. Because of the imminent revision and extension of the International Practical Temperature Scale as agreed to by the International Committee of Weights and Measures at its meeting in 1968, the publication of Hust's survey was delayed until it could be properly referenced to the 1968 Practical Temperature Scale (IPTS-68). This study was helpful to many of the data compilation tasks, particularly the task for evaluation and compilation of thermodynamic properties of helium (Item F).

Special T-S Charts for Liquid Parahydrogen

The need by NASA and a number of NASA Contractors (as well as others) for precise graphical presentation of thermodynamic data for parahydrogen in the compressed liquid region near saturation prompted the preparation of six large size (19" x 30") charts. Because of the dense spacing of constant property lines for both the P-ρ-T and derived properties in the region near the saturated liquid line on a conventional T-S diagram, it was necessary to divide the region into six parts. Even this left the spacing of the constant property lines so close that it was necessary to have them printed in four colors to improve their readability. Figure 4 (reproduced from NBS Report 9263 [22]) shows the approximate area covered by each of the six charts. Figure 5 is a reduced black and white copy of a typical chart. The data used for plotting the charts were calculated with the aid of computer programs used in compiling NBS Monograph 94 [2]. The British system of units was used by request and the temperature range covered was from 29.16°R to 42.48°R: the density range: 3.0 to 4.69 $\mathrm{lbs/ft^3}$; pressure range: from < 5 to 100 psi; enthalpy -93.0 to -124.5 Btu/lb; and entropy from 1.47 to 2.30 Btu/lb-°R. Although the charts have a very specialized use they have been used extensively.

Item B: THERMODYNAMIC PROPERTIES OF OXYGEN

Principal Evaluator: R. B. Stewart

Associates: J. G. Hust and R. D. McCarty

Time Period: December 1965* to September 1967

Publications:

Doctoral Dissertation, submitted to Mechanical Engineering Department, University of Iowa, June 1966 [26].

Temperature-Entropy Chart for Oxygen (65 to 300 K; .002 to 340 atm); NBS-CDC D-56 (1966)[27]. (See figure 6).

Compressibility Factor Chart for Oxygen (70 to 300 K; 1 to 340 atm); NBS-CDC D-57 (1966)[28]. (See figure 7).

Prior Publications*:

A Bibliography of the Thermophysical Properties of Oxygen at Low Temperatures, NBS Technical Note 137 (February 1962)[10].

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* Continuation of task previously supported on NASA Contract R-45.

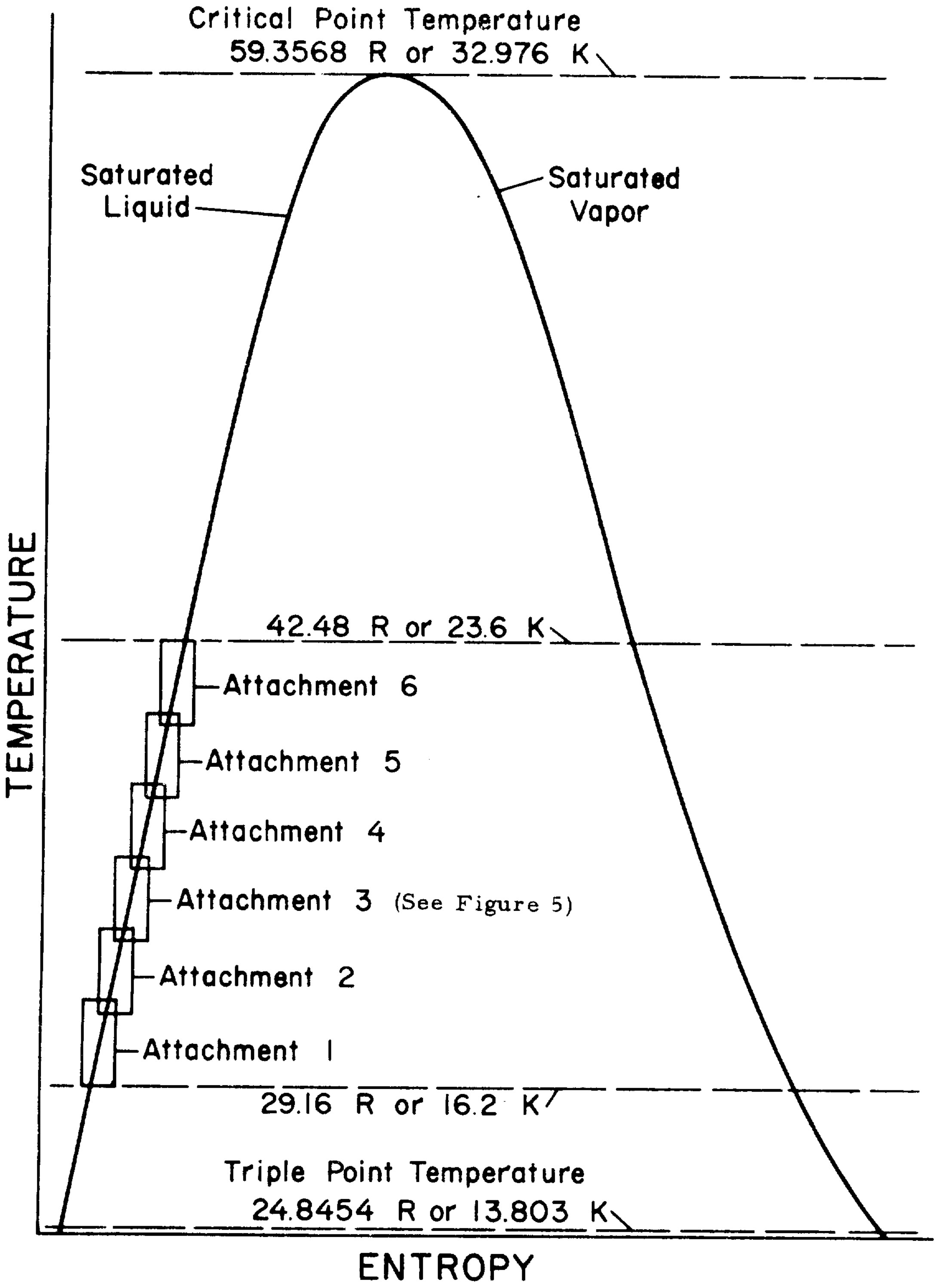

FIGURE 4 Location of T-S Charts for Liquid Parahydrogen

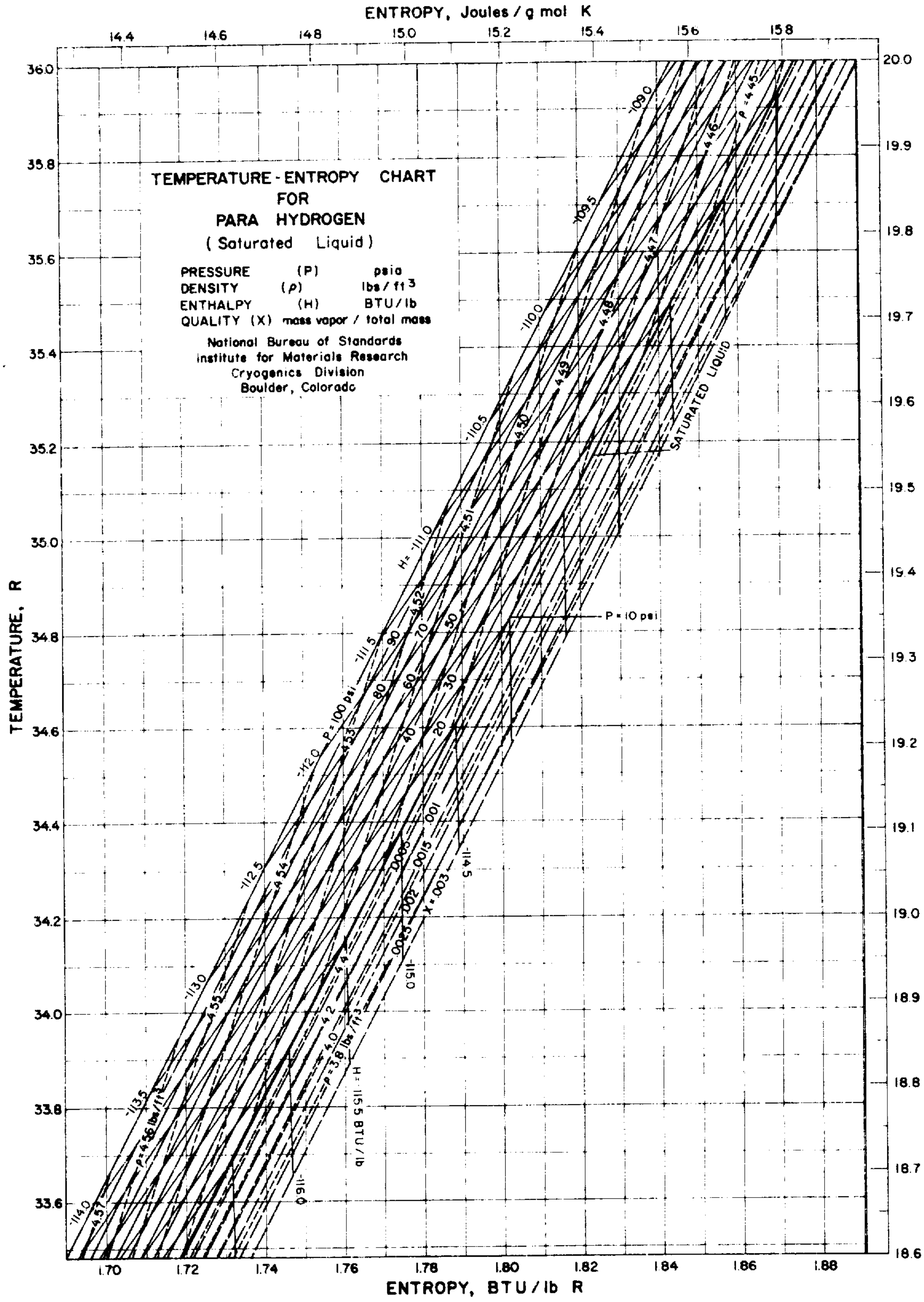

FIGURE 5. Typical T-S Chart for Liquid Parahydrogen

Interim Thermodynamic Properties for Gaseous and Liquid Oxygen at Temperatures from 55 to 300 K and Pressures to 300 atm, NBS Report 7922 (October 1, 1963)[11].

A Vapor Pressure Equation for Oxygen, NBS Report 8753 (February 16, 1965)[12].

Summary:

Interest in determining the best values for the thermodynamic properties of oxygen from the published literature dates back to the initial NASA sponsorship of the data compilation program in the Cryogenic Data Center. An exhaustive search of the world's literature was made and the results published in NBS Technical Note 137 in 1962 [10]. Because of the urgent need for the thermodynamic properties of oxygen an interim report was prepared in 1963 [11] and widely distributed. This work revealed the need for a better evaluation of existing data using the best theoretical and mathematical techniques as well as the need for better experimental data. Both programs were soon undertaken with the expectation that a more thorough evaluation of the existing data would be completed before it would be possible to obtain new experimental data. Before the evaluation of the existing data was completed, however, a considerable amount of the new experimental data became available*. As a result, Stewart, in his dissertation on the "Thermodynamic Properties of Oxygen", was able to use much of the new experimental data in the development of an equation of state and in the evaluation of other data. Stewart's dissertation thus made a significant improvement in the quality of oxygen data available for use by NASA, its contractors and others at an early date.

Another output of the thermodynamic properties of oxygen study was a Fortran IV program for calculating the thermodynamic property data as presented in Stewart's dissertation. This was prompted by requests from several NASA contractors. Several decks of the program have been distributed by the Cryogenic Data Center and are still widely used in design and process calculations needing oxygen data in a continuous functional form.

The vapor pressure of oxygen was also given further study after publication of Stewart's dissertation. New experimental data from the Leiden Laboratory

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* Much of the data that was later presented in NBS Report 9710, (June 1968) by L. A. Weber. (Reference [1] in section 3.5).

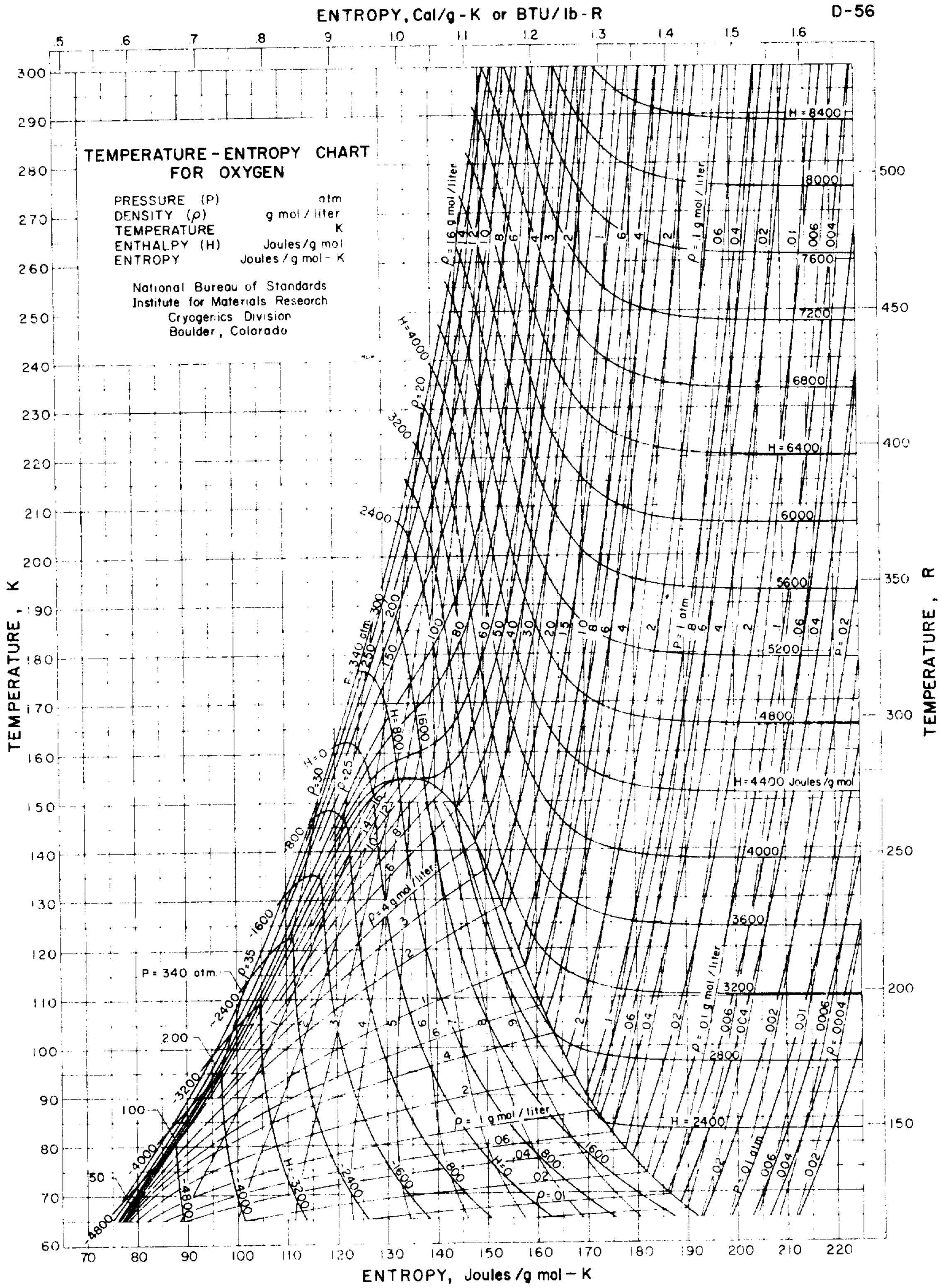

FIGURE 6. T-S Chart for Oxygen

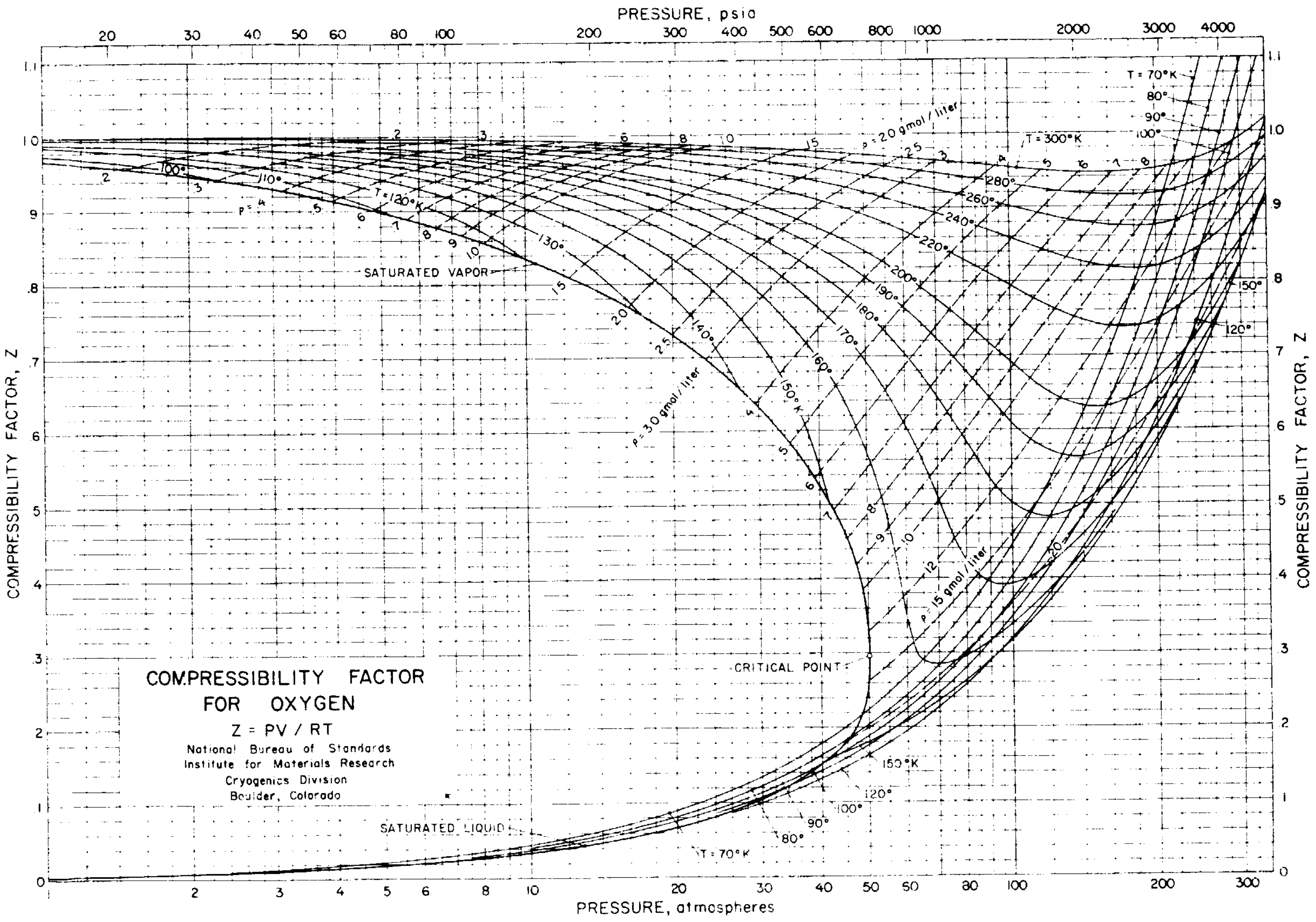

FIGURE 7. Compressibility Factor Chart for Oxygen

(Netherlands) published in 1966 by Muijlwijk, Moussa and van Dijk* for the region from the triple point to the normal boiling point had a random scatter of an order of magnitude less than previously available data. As a result Stewart was able to significantly improve the correlation of the vapor pressure data with the heat capacity data. Computer programs for making these comparisons and for the development of an improved vapor pressure equation were prepared. These were subsequently used by Weber and Goodwin in the evaluation of their new experimental data. (See section 3.0).

No further work has been done in the Cryogenic Data Center on the evaluation and correlation of the thermodynamic properties of oxygen since September 1967, although,in future plans, is the task of preparing an NSRDS Monograph based on the new experimental data measured by Weber and Goodwin correlated with the rest of the world's data.

Item C: THERMODYNAMIC PROPERTIES OF ARGON

Principal Evaluator: A. L. Gosman (Prof. of Mech. Engr.)

Associates: R. D. McCarty (Physicist)
J. G. Hust (Physicist)
R. B. Stewart (Project Mgr. to Sept. 1966)
H. M. Roder (Project Mgr. since Sept. 1966)

Time Period: December 1965† to November 1968

Publications:

Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres; NSRDS-NBS Monograph 27 (March 1969)[29].

Temperature-Entropy Chart for Argon (85 - 300 K; .02 to 1000 atm.); NBS-CDC D-61 (1969)[30]. (See figure 8).

Compressibility Factor Chart for Argon (90 to 300 K; 0.5 to 500 atm); NBS-CDC D-62 (1969)[31]. (See figure 9).

Prior Publications:

A Bibliography of Thermodynamic Properties of Argon from 0 to 300 K; NBS Technical Note 217 (June 1964)[13].

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* Muijlwijk, R. Moussa, M. R., and van Dijk, H., The Vapour Pressure of Liquid Oxygen, Physica 32, 805-22 (1966).

† Continuation of task initiated under NASA Contract R-45.

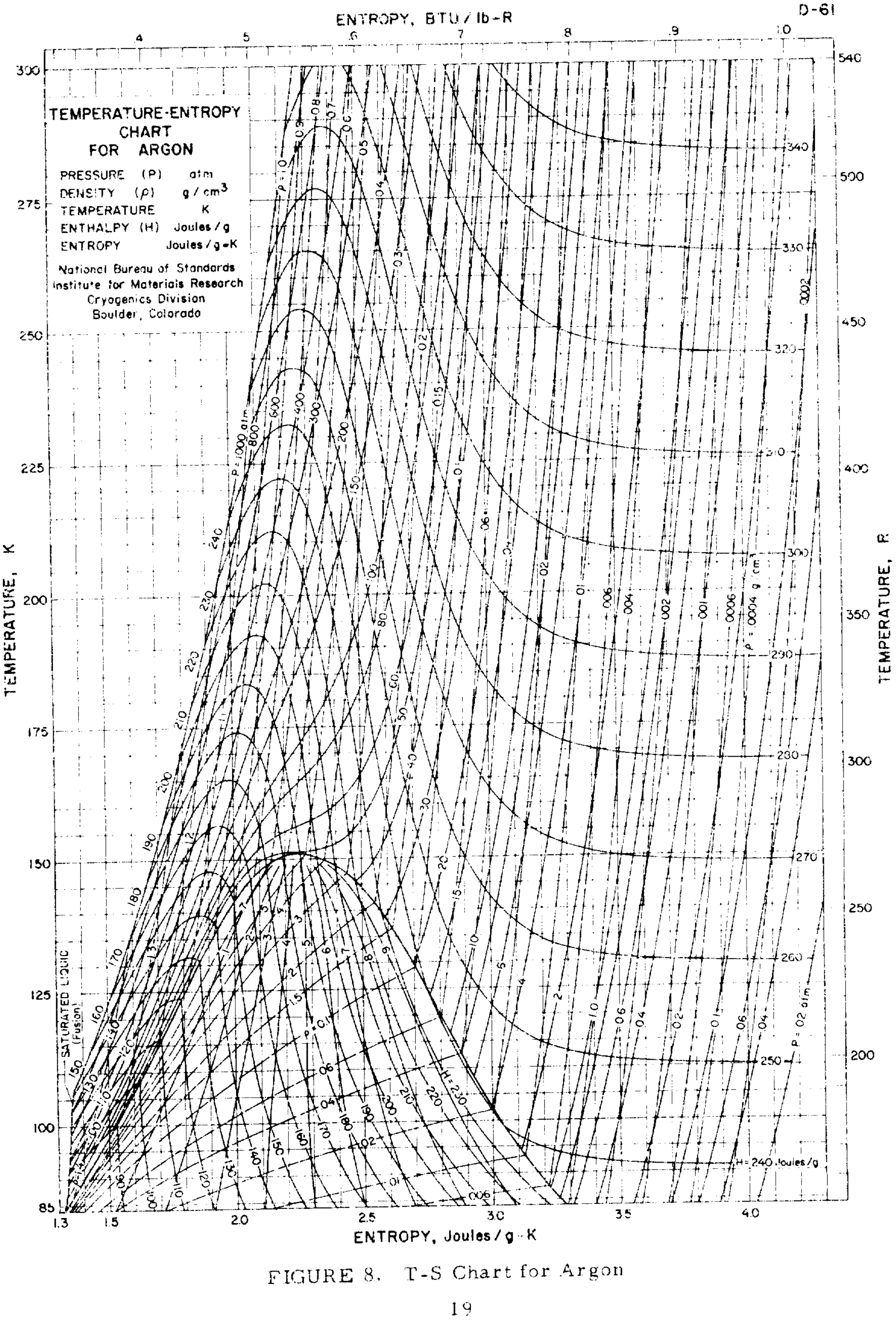

FIGURE 8. T-S Chart for Argon

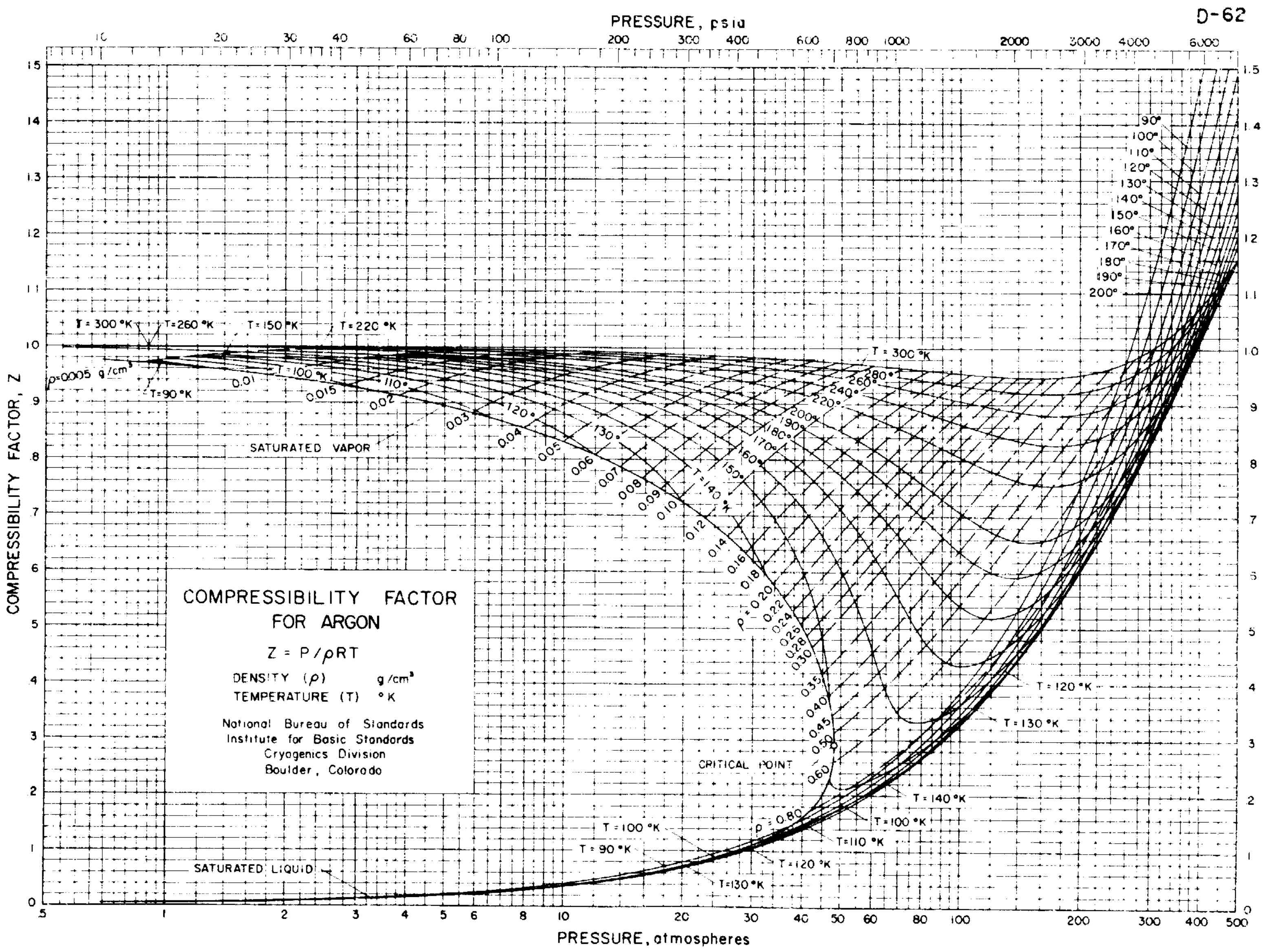

FIGURE 9. Compressibility Factor Chart for Argon

Ph. D. Dissertation by A. L. Gosman entitled "Thermodynamic Properties of Argon in the Liquid and Gaseous State for Temperatures from the Triple Point to 300 K with Pressures to 1000 Atmospheres", submitted to the University of Iowa, Mechanical Engineering Dept., Iowa City (Aug. 1965)[14].

Summary:

Following the preparation of an extensive bibliography on the thermodynamic properties of argon [13], A. L. Gosman, who was employed on a full time basis each summer for a number of years, undertook the task of critically evaluating all of the published data with the objective of producing a comprehensive monograph on the thermodynamic properties of argon as an item of Standard Reference Data. The initial phase of the task served as his dissertation submitted to the University of Iowa, Mechanical Engineering Department in partial fulfillment for the Doctor of Philosophy degree that was awarded to him in the fall of 1965 [14].

In recent years technical interest in pure argon had greatly accelerated. This accelerated interest had been evidenced by a demand which had more than sextupled in 12 years. United States production had continued to increase from less than 200,000,000 cubic feet per year in 1953 to almost 1,300,000,000 cubic feet in 1965, with about 80 percent being shipped in liquid form.

In addition, scientific interest in argon had arisen because of its characteristically "ideal" structural makeup. That is, argon is monatomic, with the relatively uncomplicated interatomic forces being approximated by spherically symmetric, nonpolar models. Further, the quantum effects on argon are relatively small. Although helium and neon might be considered to be more "ideal" fluids from the standpoint of simple models, the quantum effects are relatively large for these two fluids as compared to argon. For these reasons argon was expected to permit a more direct classical investigation and experimental verification of the theoretical model predictions.

In view of the increased activity in cryogenic engineering and physics, it was apparent that a set of consistent thermodynamic properties, over a relatively large region of the thermodynamic surface, was needed. Although many investigators had published data for the thermodynamic properties of argon, each tabulation was, in general, limited to the property range of interest of the specific investigator, and large gaps in the data existed. In addition, where the ranges of data did overlap, there was a substantial degree of inconsistency in some instances. For these reasons, this task was undertaken to make a critical analysis of the thermodynamic properties of argon in the cryogenic temperature range, including the low temperature-high density region.

In recent years, much of the technical design and synthesis had been done with the aid of high speed digital computers. Thus,the need for an analytical equation of state had become quite significant when compared with the use of tables and charts of thermodynamic properties. Many equations of state had been proposed in the literature, each with its own peculiar strengths and weaknesses. Some of these equations represented the data in certain regions of the thermodynamic surface, but were quite inadequate in other regions of the surface. Therefore, the need was established for a single equation of state which could accurately and consistently represent the data for both the liquid and vapor phases with a consistent transition from the low temperature-high density region to the low density region.

In the case of argon, it was difficult to assess the general overall adequacy of an equation of state in terms of deviations from the experimental P-V-T surface. Due to the inconsistency of some of the overlapping experimental data sources, there was no single experimental P-V-T surface which could be used as a reference. Also, the significance of the deviations was wholly dependent upon the variable chosen for the comparison and the specific region of the thermodynamic surface which was being studied. In certain regions of the surface, large pressure deviations were caused by insignificant density errors, while in other regions the reverse was true. In general, the equation of state that was developed represents the different sources of experimental data to within the accuracy of the data, except at the higher temperatures on the coexistence boundary and the critical region where the deviations are, in a few cases, greater than the accuracy of the data.

As a part of the critical analysis, it was deemed necessary to develop a vapor pressure equation which would accurately represent the experimental vapor pressure data from the triple point to the critical point. This vapor pressure equation could then be used, in conjunction with the equation of state, to calculate some of the derived thermodynamic properties such as enthalpy, entropy, etc.

Thus, it was concluded that a critical analysis of thermodynamic properties of argon was to be made for temperatures to about 300 K and for pressures to about 1000 atm wherever the experimental data permitted this pressure range.

The comprehensive search of the literature resulted in a bibliography of about 425 references. The temperatures which were included in this search covered the range from 0 to 300 K. In addition to manual-reviewing techniques, the data retrieval personnel and the computerized search techniques of the Cryogenic Data Center were utilized. As the task progressed the literature search was continually updated so that current data were rapidly assimilated.

From this literature search, the most appropriate P-V-T data, vapor pressure data, coexistence density data, and fixed point data were selected for consideration and evaluation. In addition, virial coefficient data, Joule-Thomson data, specific heat data, and information on equations of state were acquired and considered.

This task was pursued, primarily during the summer months, for a period of over four years. The total expenditure of effort however was only equivalent to about two professional man years (about 1-1/4 being on the NASA R-46 contract). It resulted in the publication of the Cryogenic Division's first Monograph in the National Standard Reference Data Series.

Listed in the monograph are tabular values of density, internal energy, enthalpy, and entropy of liquid and gaseous argon for temperatures from 83.8 to 300 K at pressures of 0.01 to 1000 atmospheres. Diagrams of specific heats, compressibility factor, and entropy are included. The properties presented are calculated from an equation of state which was fitted to experimental P-ρ-T data from the world literature. Extensive comparisons were made between the equation of state and the experimental data, and deviation plots are presented. The second virial coefficient and Joule-Thomson inversion curve were also calculated and comparisons made with values from other sources. A vapor pressure equation which covers the range from the triple point to the critical point is also given.

Two thermodynamic property diagrams [30, 31] were prepared for the monograph and are also available as seperate items. Figures 8 and 9 are reduced copies of these disgrams.

This effort has been widely acclaimed by engineers and physicists alike: the engineers for the large body of consistent data including the thermofunctions for wide ranges of temperature and pressure useful in the design of processes and equipment; and the physicists for establishing a state-of-the-art review for such a vast amount of data that heretofore had not been too well correlated. As mentioned earlier, argon can serve as a good model for the study of the thermophysical properties of gases if consistent, critically evaluated data are available.

It might be interesting to note that soon after the publication of the argon monograph, the Atmospheric Gases Panel of the IUPAC* Thermodynamic Tables Project met in the USSR and selected this NBS argon monograph as the primary basis for an international table on the thermodynamic properties of argon.

Item D: CORRELATION OF THE THERMODYNAMIC PROPERTIES OF DEUTERIUM

Principal Evaluator: Rolf Prydz

Associates: R. B. Stewart and K. D. Timmerhaus (Thesis Advisors)
R. D. McCarty and J. G. Hust (Thermodynamic Consultants)
H. M. Roder (Project Manager)
W. J. Hall (Mathematical Consultant)

Time period: September 1965 to November 1968

Publications:

Master of Science Thesis, submitted to the Chemical Engineering Department, University of Colorado, March 16, 1967 [32]; also issued as NBS Report 9276, April 18, 1967 [33].

Paper F-5 "Thermodynamic Properties of Deuterium", published in Advances in Cryogenic Engineering (1968)[37].

Temperature-Entropy Chart for Deuterium (20 to 100 K; 0.1 to 100 atm) NBS-CDC D-58 (1967) (See figure 10).

Temperature-Entropy Chart for Deuterium (80 to 300 K; 1 to 400 atm) NBS-CDC D-59 (1967) (See figure 11).

Compressibility Factor Chart for Deuterium (20 to 300 K; 0.2 to 400 atm) NBS-CDC D-60 (1967) (see figure 12).

Summary:

Technical and scientific interest in deuterium arose from the recent use of deuterium in bubble chambers and its continuing importance in certain experimental physics studies. Also, as the principal isotope of hydrogen, the evaluation of deuterium data with the functions and methods used for hydrogen would provide additional confidence in the work that had been done for NASA on hydrogen. Thus, it was evident that there was a need for the development of thermodynamic property tables of deuterium in both the vapor and liquid ranges.

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* International Union of Pure and Applied Chemistry.

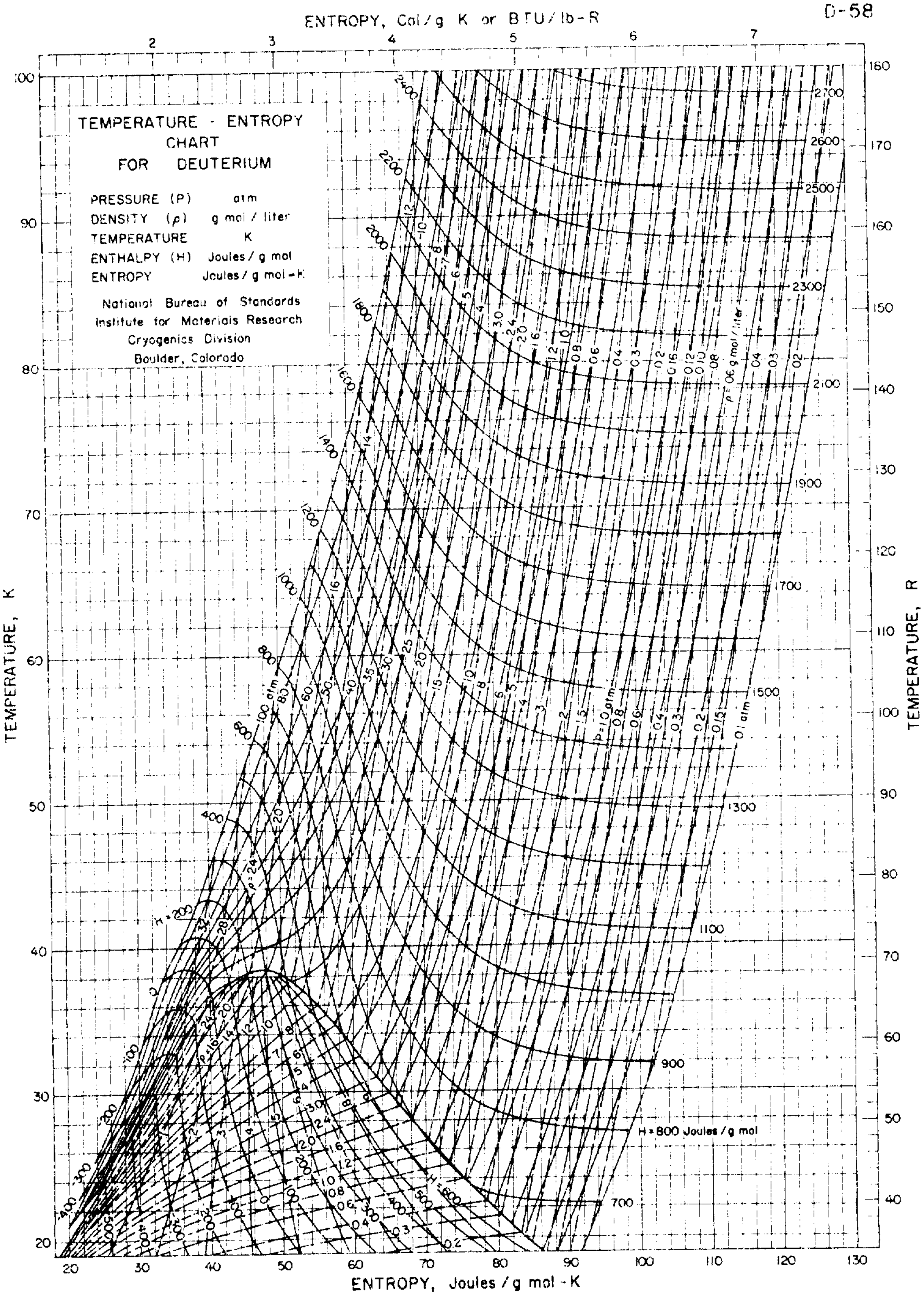

FIGURE 10. T-S Chart for Deuterium (20 - 100 K)

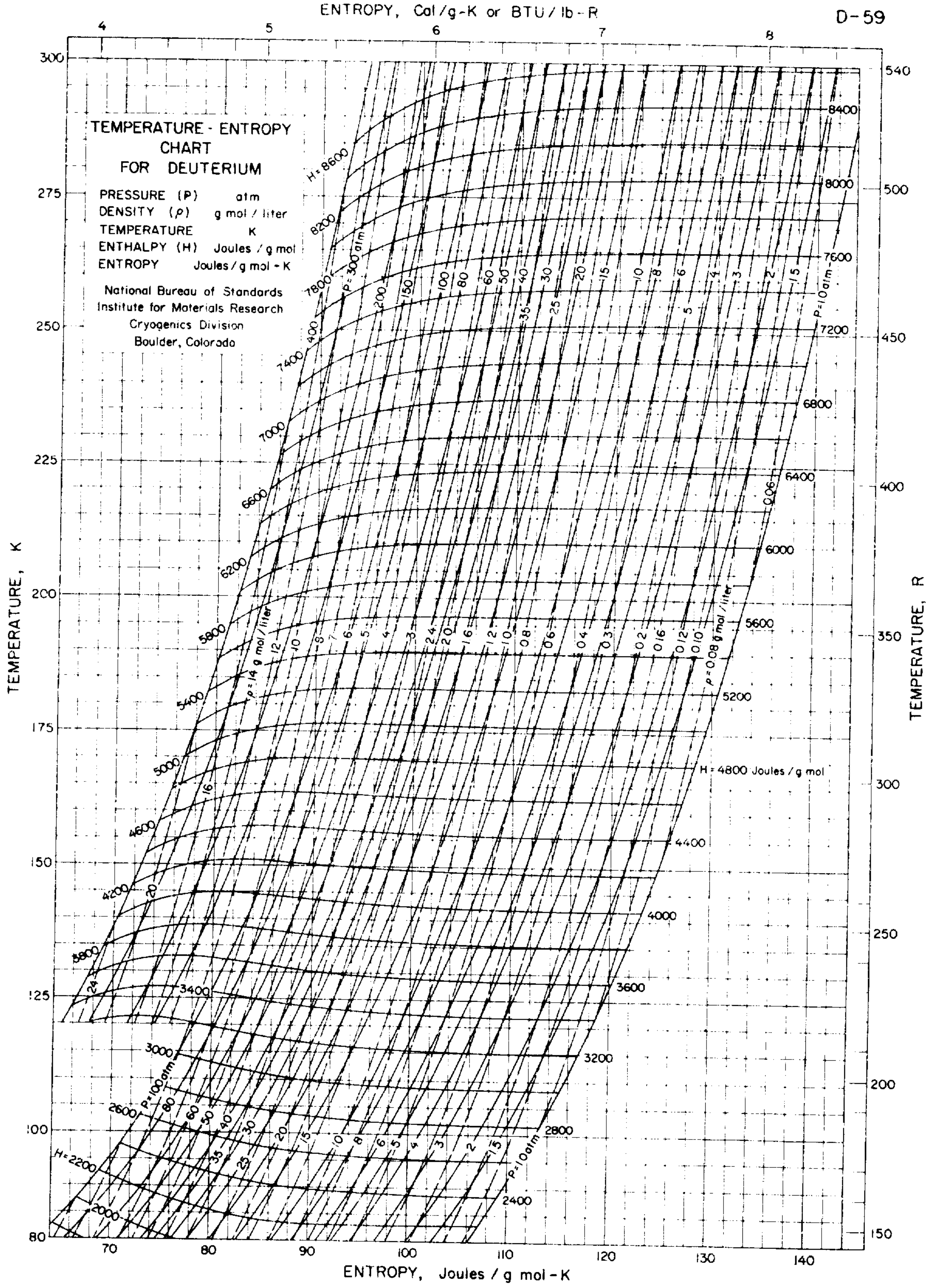

FIGURE 11. T-S Chart for Deuterium (80 - 300 K)

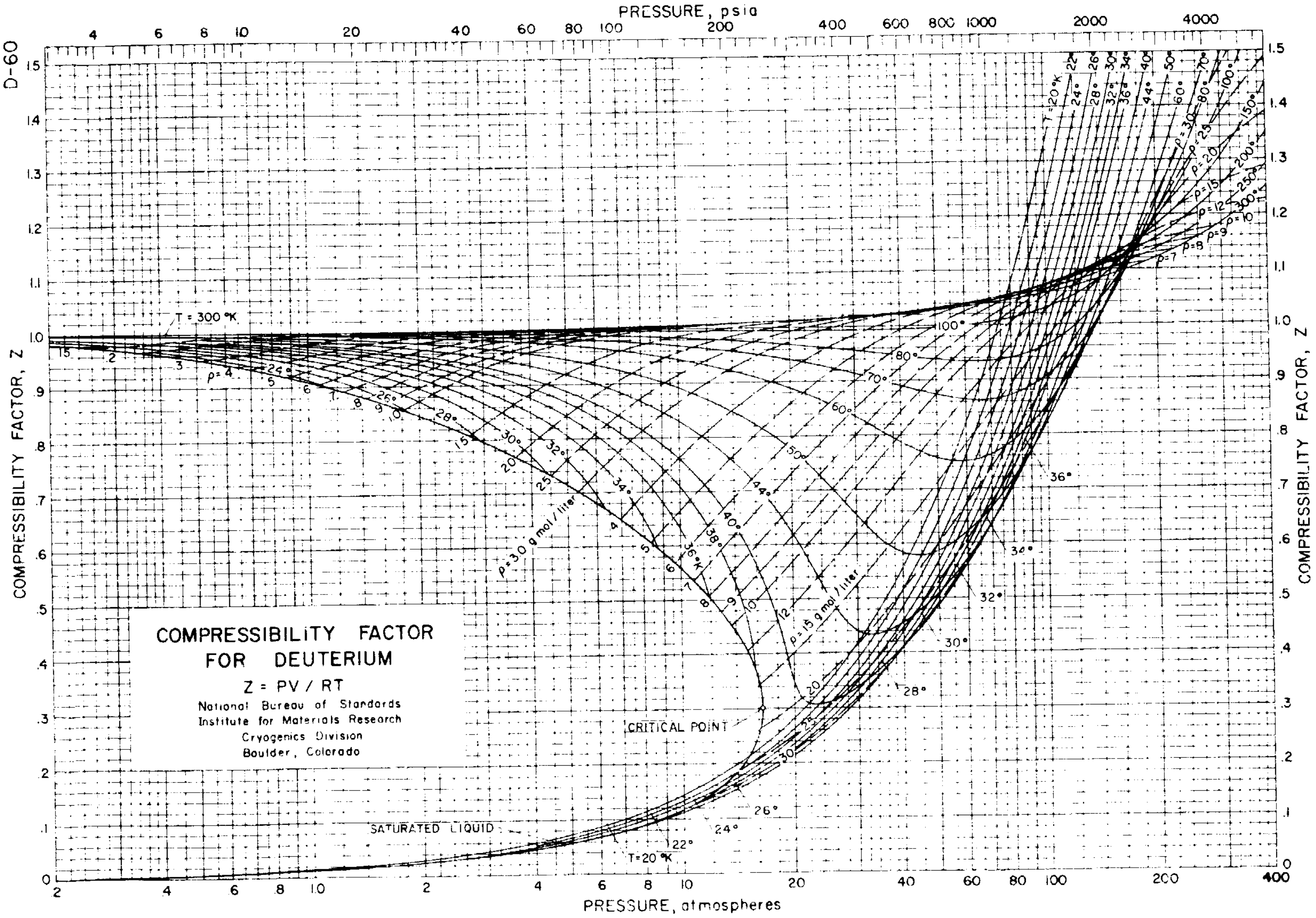

FIGURE 12. Compressibility Factor Chart for Deuterium

The task was undertaken by Rolf Prydz as a masters thesis project while he was studying at the University of Colorado. This task was a cooperative venture of the NBS Cryogenic Data Center and the University of Colorado Chemical Engineering Department with R. B. Stewart serving as thesis advisor for Mr. Prydz who was employed as a guest worker. Initially, NASA Project R-45 supported the incidental expenses such as for preliminary literature searches and computer usage. This support was assumed by project R-46 in December 1965.

The primary objective of the task was, therefore, to determine an equation of state that would represent the available deuterium data in both phases to within the precision of the experimental data. A vapor-pressure equation that would represent the data from the triple point to the critical point was also required. Further, comparisons with data for second and third virial coefficients, the Joule-Thomson inversion curve, and latent heat of vaporization with values calculated from the equation of state with the vapor-pressure equation were also desired. Finally, extensive tables of thermodynamic properties with tabular values of pressure, temperature, density, enthalpy, internal energy, and entropy were to be produced.

In order to obtain thermodynamic consistency in pressure, density, and temperature as well as the other derived properties, the equation of state and the vapor-pressure equation had to be constrained to the same critical point. For this reason, the slope of the critical isometric of the equation of state at the critical point needed to be equal to the slope of the vapor-pressure equation at this point. These criteria then were the basis upon which the task was pursued.

The resulting compilation of the thermodynamic properties of deuterium [32, 33] provided tabular values of pressure, temperature, density, enthalpy, internal energy, and entropy, presented for both liquid and gaseous phases for pressures to 400 atm and temperatures between the triple point and 300 K. These tables are based on the equation of state and a vapor-pressure equation developed for this fluid. The equation of state is valid from the triple point to 425 K at pressures up to 400 atm. Extrapolation to 3000 atm introduces only small deviations from actual P-ρ-T data. All the P-ρ-T data in the literature were critically evaluated. Then the equation of state was fitted to the data by weighted-least-squares. Measured and calculated density values were compared and deviations were calculated to illustrate the accuracy with which the equation of state represents the P-ρ-T surface of deuterium. Comparisons were also made of virial coefficients, Joule-Thomson inversion curve, and latent heat of vaporization with values calculated from the equation of state. Further, deviations between the vapor-pressure data and the values obtained from the vapor-pressure equation were determined. Two temperature-entropy charts[34, 35] and a compressibility factor chart [36] for deuterium are included.

This study of all known experimental data for deuterium revealed a number of defects or inconsistencies in the P-ρ-T relationships which made it difficult to fit the data to a smooth surface generated by the equation of state. This is particularly apparent in the region of the critical temperature for the higher pressures. After Prydz completed his thesis, Roder and Hall made a concerted effort to remove the "hump" in the P-ρ-T surface by modifying the equation of state but every attempt worsened the fit in other areas. It was finally concluded that the paucity (especially between the critical temperature and 98 K) and uncertainty of experimental data in critical areas were too great to resolve the problem of determining the "best values". Obviously, without a precise and smoothly continuous equation-of-state, derived properties such as the specific heats, enthalpy, internal energy and entropy could not be calculated to a sufficiently small level of uncertainty to adequately correlate with the small amount of calorimetric data available. The conclusion was that no significant improvement could be made in the work that Rolf Prydz had done until more and better experimental data became available. As a result, the task has been held in abeyance since 1968. Whenever it becomes apparent that significant improvement can be made in the correlation of the thermodynamic properties of deuterium, particularly in the critical region, we would like to reactivate the task for preparation of an NBS-NSRDS* monograph.

Item E: TRANSPORT PHENOMENA IN CRYOGENIC FLUIDS

Principal Evaluator: H. J. M. Hanley (Physical Chemist)

Associates: G. E. Childs (Physicist)
R. D. McCarty (Consultant)
H. M. Roder (Project Manager)

Associates from other Institutes:
Max Klein (Equation of State Section, NBS-Gaithersburg)
J. V. Sengers (NBS-Gaithersburg and Univ. of Maryland)
E. G. D. Cohen (Rockefeller University)
B. B. McInteer (Los Alamos Sci. Lab.)

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* National Standard Reference Data System.

Time period: December 1965 to November 1968[†]

Publications:

Comparison of the Lennard-Jones, Exp: 6 and Kihara Potential Functions using Viscosity Data of Dilute Argon., J. Chem. Phys. 44, 4219 (1966)[38].

The Viscosity and Thermal Conductivity Coefficients of Dilute Argon between 90 and 2000 K., Natl. Bur. Standards Tech. Note No. 333 (Mar 1966) [39].

The Viscosity and Thermal Conductivity of Dilute Nitrogen and Oxygen., Natl. Bur. Standards Tech. Note 350 (Oct 1966)[40].

The Viscosity and Thermal Conductivity of Dilute Neon, Krypton, and Xenon., Natl. Bur. Standards Tech. Note 352 (Mar 1967)[41].

On the Selection of the Intermolecular Potential Function: Application of Statistical Mechanical Theory to Experiment., Natl. Bur. Standards Tech. Note 360 (Nov 1967)[42].

The Thermodynamics of Transport Phenomena in Membrane Systems., J. Chem. Educ. 44, 717 (1967)[43].

Application of Dilute Gas Transport Property Tables to Real Gases., Cryogenics 8, 94 (1968)[44].

On the Selection of the Intermolecular Potential Function: Part 2, From Pair Properties., Trans. Faraday Soc. 64, 2927 (1968)[45].

Discrepancies between Viscosity Data for Simple Gases., Science 159, 1114-7 (1968)[46]. A similar paper is published in the Proc. of the 7th Conference on Thermal Conductivity, Natl. Bur. Standards Special Publication 302, p. 597 (1968).

Density Dependence on Experimental Transport Coefficients of Gases., J. Chem. Phys. 50, 857 (1969)[47].

Dilute Gas Viscosities at Low Temperatures., J. Chem. Phys. 50, 4600 (1969)[48].

Selection of the Intermolecular Potential Function: Part 3, From the Isotopic Thermal Diffusion Factor., J. Chem. Phys. 50, No. 11, 4765-70 (Jun 1969)[49].

The Viscosity and Thermal Conductivity of Dilute Gaseous Hydrogen between 15 and 5000 K., J. Res. Natl. Bur. Standards 74A, 331 (1970)[50].

[†] Principal period of NASA R-46 sponsorship. (The program has been continued with both NASA and OSRD support).

Summary:

The R-46 program was started in December 1965* and continued at about a one and one half man year level of effort until July 1968 and at about one half man year since that date. (See figure 3). Therefore, some of the results described here were not directly produced under R-46 sponsorship. But it is important to stress that the work done for R-46 was the foundation for all our present results and progress.

The object of the program was to clarify the state-of-the-art of transport properties of cryogenic fluids and to provide tables, correlations, and predictive techniques for the transport coefficients.

The initial phase of the program involved studying the literature, collecting data and making preliminary evaluations of the theories and correlation procedures available. It was soon realized that much of the data was erroneous and repetitious, even for simple fluids, and the theoretical status was poor. We decided to approach the program by making a concerted effort to furnish results based on as sound a theoretical and experimental foundation as possible. The program developed into three main areas, all of which were mutually related.

General Studies

We studied first the theory of dilute gases in some detail. The reasons were both practical - since the dilute gas forms the basis for all transport correlations - and theoretical, since a knowledge of the dilute gas leads to an understanding of the intermolecular potential function. The intermolecular potential function is very important. If it is available for a fluid, one can predict transport properties and thermodynamic properties for that fluid. Also systematic errors in data can be checked, and recommendations on accuracy and range of data can be given to the experimental worker. We,therefore, spent time and effort working with the function and obtained useful results [38, 42, 45, 49]. We feel we understand the function with respect to the correlation of data. Further, we now have a reasonable potential function which is a significant improvement over those previously available, yet is simple to apply in practice [58, 60].

To help in our evaluation of data and to develop correlation procedures, we studied several facets of nonequilibrium processes in fluids such as nonequilibrium thermodynamics, statistical mechanics and kinetic theory, and hydrodynamics. The results were published in references [43, 44, 48, 64].

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* About one half professional man year of effort had been expended on this task under NASA Contract R-45 to initiate the study.

Dilute Gas

Tables or correlations were produced for the viscosity and thermal conductivity of dilute argon [39], neon, xenon, and krypton [41], oxygen and nitrogen [40], helium [56], and hydrogen [50]. Our most significant result, however, was that we detected serious discrepancies in experimental dilute gas viscosities at temperatures above room temperatures [46, 59]. The data quoted in the standard reference literature were incorrect. This led to serious errors in experimental and theoretical work. We suggested new values for the viscosities and have collaborated closely with experimental workers to resolve this problem. At present new tables for dilute gas transport properties are in preparation.

Dense Gas and Liquid

We have carefully investigated the theories and correlation procedures available to represent transport properties in the dense fluid. Rigorous theory cannot be used, so one has to turn to a semi-empirical technique. Accordingly, for about two years, we have studied in depth the Enskog theory. Results will soon be published. We have also studied the qualitative features of the experimental data [57].

An interesting investigation started under the R-46 program was our study of the transport first density corrections -- the nonequilibrium analogues of the equilibrium virial coefficients in the equation of state. Theoretical developments since about 1966 suggested that the expansion of transport coefficients in powers of density was, unlike the equation of state virial expansion, very complicated in principle. Doubts were introduced on the whole concept of kinetic theory as used previously and these doubts affected the correlation of data (for instance, the correlation of PVT data would be seriously hampered if we could not use the virial expansion). We investigated the transport density expansion and published results for the first density corrections [47]. Work in this area is now continuing under OSRD* sponsorship.

Conclusion

Overall, we feel that our program has progressed strongly and authorative practical results are now possible. We hope we have cleared up much of the confusion that existed in both theory and experiment. The potential function proposed should be very useful. We now know the qualitative features of transport coefficients over a very wide range of experimental conditions and can represent and predict them, even though we have to use semi-empirical techniques. We are very pleased with the

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* NBS-Office of Standard Reference Data.

extensive collaborations with other workers from NBS, government agencies, universities and industry which have developed along with our progress.

Item F: CORRELATION OF THE THERMODYNAMIC PROPERTIES OF HELIUM

Principal Evaluator: R. D. McCarty

Associates: R. B. Stewart (Project Mgr. Dec. 65 - Sept. 66)
H. M. Roder (Project Mgr. since Sept. 66)
L. A. Hall (Literature Analyst)

Time period: December 1965 - November 1967 and November 1968 to present.

Publications:

Provisional Thermodynamic Functions for Helium 4 for Temperatures from 2 to 1500 K with Pressures to 100 MN/m^2 (1000 atmospheres); NBS Report 9762 (Aug. 1, 1970)[51].

NBS-NSRDS Monograph (in preparation)

Summary:

This task was undertaken by R. D. McCarty at the beginning of the NASA-OART R-46 program for data compilation. The task was pursued at about a one and one-half professional man level of effort except for a one year period from November 1967 to November 1968 when it was inactive. Many of the results of this study are yet unpublished, but this task under the NASA R-46 sponsorship has laid the groundwork for many future publications, has established areas where need for better experimental measurements exists, and has provided an extensive compilation of critically evaluated thermodynamic data.

The object of the program was to study the thermodynamic data available in the world's literature and produce tables of best consistent thermodynamic properties on the basis of these data. This objective was accomplished and the results published in the form of NBS report 9762 [51]. During the course of preparing NBS Report 9762 many important intermediate results were achieved. Three of the most important of these intermediate results merit further comment.

Need for New Experimental Measurements

Early in the preliminary analysis of the existing experimental data, two things became apparent. First, a great deal of experimental measurements of the properties of helium have been made through the years, and second, more measurements of greater accuracy and scope need to be made, at least in specific ranges of pressure and temperature. Before a completely satisfactory thermodynamic correlation can be accomplished it is essential that additional P-V-T, specific heat, and the velocity of sound measurements be made over the temperature range of 2 to 70 K for pressures from .01 to at least 350 atmospheres. The reasons such an experimental program is needed are many, but primarily it is needed because the accuracy of the most important set of data which does exist in this region is in serious doubt and these data do not cover a large enough range of temperature and pressure. In the case of helium it is extremely important to have data from a single source covering as large a range of temperature and pressure as possible. As a result of this study we strongly recommend that an experimental measurement program be undertaken at an early date to provide the range and accuracy of data needed to reduce the present uncertainties and establish a design confidence for this most important region. (See appendix C in section 3.6 for a proposal by D. E. Diller to measure the thermodynamic properties of compressed gases and liquid helium.)

The Temperature Scale at Helium Temperatures

The analysis of the helium experimental thermodynamic data led to two important conclusions. First, for helium experiments, the measurement of temperature should be at least a factor of 70 better than for similar oxygen experiments. One can understand this by comparing the temperature span between the normal boiling point and the critical point for the two fluids.

Second, (until 1968) the absence of an agreed upon IPTS below the oxygen point has led to so many different ways to measure temperature that it is difficult to compare experimental data of multiple source on an equal basis. Indeed, it is very probable that the disagreement in the experimental data for helium is due to inconsistency in temperature scales.

Second Virial Coefficient

A very exhaustive study of the second virial coefficient for helium was made in conjunction with the more general thermodynamic properties correlation. This study has resulted in a knowledge of the second virial coefficient of helium to a greater degree of accuracy and over a larger temperature range than for any other fluid. The details of this study will be published at a future date.

Conclusion

Overall we feel that our helium program has been, and will continue to be for some time in the future, of great benefit to all concerned. We have clarified many of the questions surrounding the existing body of experimental data and pointed the way for future experiments.

Item G: ANNOTATED BIBLIOGRAPHY FOR THE PROPERTIES OF METHANE

Principal Evaluator: L. A. Hall (Chemist)

Associate: H. M. Roder (Project Manager)

Time period: April 1966 to March 1968.

Publication:

A Bibliography of Thermophysical Properties of Methane from 0 to 300 K. NBS Technical Note 367 (May 1968)[52]

Summary:

This task was pursued on a part time basis over a period of nearly two years requiring a total effort of approximately one-half professional man year. The resulting bibliography is one of the most comprehensive classification and listing of references on the properties of methane at low temperatures ever produced.

The Cryogenic Data Center had been monitoring the literature and collecting documents for nearly nine years* before this task was started. To start this task, a mechanized search of the CDC storage and retrieval system was made. The resulting documents were procured and reviewed, including the references cited in each document. Any references that had not appeared in the CDC bibliography were ordered and also reviewed. Since, in addition to the continuous searching of most of the current published literature,the CDC staff also reviews many abstract journals, retrospectively as well as on a current basis, and the government report literature, proceedings of meetings, thesis and dissertations, some company reports, and books, the literature searching for this task was considered to be exhaustive.

Each reference was carefully reviewed and the following items particularly noted for the final bibliography:

1. Author(s)
2. Title (original language) and translated title, if original is in a language other than English.
3. Reference (If the same article is published in more than one place, each reference is cited.)

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* The initial interest started with the preparation of the Compendium of Properties of Materials at Low Temperatures published in 1960 [65].

4. Properties studied for methane, state of substance, temperature and pressure ranges as available.
5. Designation as to primary character of article.
    - a. experimental
    - b. theoretical
    - c. compilation
    - d. correlation
    - e. reference book
6. Form in which data are reported.
    - a. tabular - tables (number of values)
    - b. graphical
    - c. equations
    - d. apparatus, if described or illustrated

The collection was then alphabetized by first author and indexed according to properties with sub-indexes for the state of the substances; i.e., solid, liquid, gas up to 200 K, and gas above 200 K. Also following each citation number in the index, an indication was provided to indicate the type of data such as experimental, theoretical, compilation, correlation, calculation or whether it was a review, discussion or reference work. The following is a list of the properties covered:

1. density, P-V-T data, compressibility factor
2. equation of state, virial coefficients
3. ideal gas property (rotational heat capacities)
4. expansivity and compressibility
5. vapor pressure
6. melting pressure
7. latent heats
8. fixed points (solid transitions, triple point, normal boiling points, critical point)
9. specific heat
10. velocity of sound
11. Joule-Thomson coefficients, inversion curve
12. entropy, enthalpy, internal energy, fugacity, Gibbs function, Helmholtz function
13. thermal conductivity
14. viscosity
15. Prandtl number
16. self-diffusion coefficient

17. surface tension
18. dielectric constant, Clausius-Mossotti function
19. refractive index
20. lattice characteristics (crystal structure, Debye temperature)
21. corresponding states
22. intermolecular potential
23. documents not appearing in the properties index.

The final bibliography contains 660 references, each annotated to indicate the range and type of pertinent data at a glance. It was issued as an NBS Technical Note in May 1968 and has been widely distributed, undoubtedly because of the rising interest in liquid methane and Liquefied Natural Gas (LNG) for use as a propellant and aircraft fuel.

In the normal course of collecting and reviewing literature on properties of materials, it is the standard practice of the Cryogenic Data Center to extract and assemble pertinent data in task notebooks. Much of this was done for the Properties of Methane task during the course of preparing the bibliography. As a result it will be possible to progress rapidly on the evaluation and correlation of the properties of methane whenever this task is reactivated. (The correlation and compilation of the data was to be phase II of this task after completion of the bibliography but was suspended in favor of other tasks).

This bibliographic effort did provide a basis for judgement as to the areas most in need of better experimental measurements [62]. As a result, a modest project in the Cryogenic Properties of Fluids Section has been undertaken to make P-V-T and specific heat measurements under sponsorship of the American Gas Association. The availability of better data will make it possible to critically evaluate and compile better and more extensive tables, charts, and thermofunctions whenever it is possible to reactivate this task.

Item H: ELECTRICAL RESISTIVITY OF METALS

Principal Evaluator: L. A. Hall (Chemist)

Associate: F. E. E. Germann (Physical Chemist)
H. M. Roder (Project Manager)

Time Period: July 1966 to April 1970

Publications:

Survey of Electrical Resistivity Measurements on 16 Pure Metals in the Temperature Range 0 to 273 K; NBS Technical Note 365 (February 1968)[53].

Survey of Electrical Resistivity Measurements on 8 Additional Pure Metals in the Temperature Range 0 to 273 K; NBS Technical Note 365-1 (August 1970)[54].

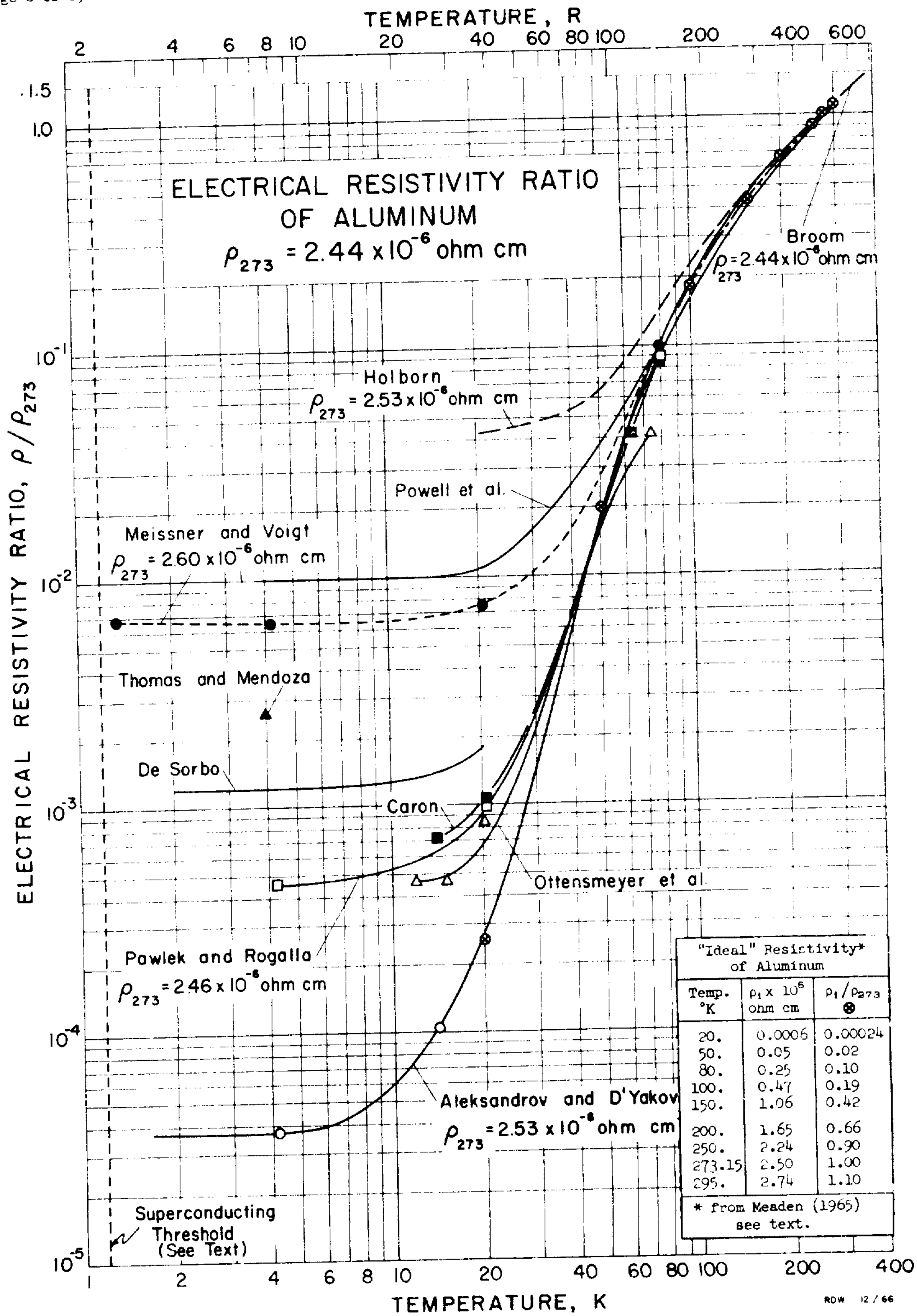
Summary:

In December 1961, the Cryogenic Data Center completed a compendium of the properties of materials at low temperatures (phase II) [66] which included a section on the electrical resistivity of 53 metallic elements. In the succeeding years the Data Center continued to collect the literature in this area and by July of 1966 quite a large number of papers giving new experimental data had been acquired. The task of evaluating the new data and correlating it with that of the earlier publication was then initiated. In this initial effort the evaluation of electrical resistivity data was limited to the following 16 elements:

aluminum
beryllium
cobalt
copper
gold
indium
iron
lead
magnesium
molybdenum
nickel
niobium
platinum
silver
tantalum
tin

The experimental data in the literature were presented in many ways. Many presented results of straight-forward temperature-dependent resistivity measurements on wires or rods of high-purity metals. Some dealt with the effects of irradiation, plastic deformation, magnetic fields, and alloying on resistivity, while others showed the variation in resistivity due to unusual shape of the sample, e.g., whiskers or thin films. In the more recent literature, superconductivity was also studied extensively. Because the amount of literature in this field was so large, the survey was restricted to the temperature-dependent resistivity measurements on very pure metals.

A standard format was adopted for presenting the electrical resistivity data and associated documentation for each metal. It consisted of listing a bibliography of the source literature from which data were selected, then listing all other references found. Concise comments were then compiled from the review and evaluation of the data. All of the selected data were listed in tabular form and from all this a



"Ideal" Resistivity* of Aluminum

Temp. °K	$\rho_1 \times 10^6$ ohm cm	ρ_1/ρ_{273} ⊗
20.	0.0006	0.00024
50.	0.05	0.02
80.	0.25	0.10
100.	0.47	0.19
150.	1.06	0.42
200.	1.65	0.66
250.	2.24	0.90
273.15	2.50	1.00
295.	2.74	1.10

* from Meaden (1965) see text.

FIGURE 13. Sample Graph for Electrical Resistivity of Metals

graphical presentation of electrical resistivity ratios was made. For a sample graph see figure 13 which is for the electrical resistivity ratio of Aluminum as presented on page 20 of reference [53]. A separate group of data sheets was prepared for each metal. The aim was to present for the experimentalist a complete picture of what data were already available so that he could plan his work in such a manner as to fill in "gaps" in existing data or to check or "reinforce" existing measurements. Likewise, for the engineer, the aim was to present a method of predicting the electrical behavior of a metallic specimen of known purity.

A general discussion of the electrical resistivity of relatively pure metals at low temperatures was prepared for the user to obtain the maximum benefit from the data presented. For example, according to Matthiessen's rule the total resistivity is derived from a temperature dependent contribution and from a temperature independent contribution. The first is often referred to as the ideal resistivity and the latter as the intrinsic resistivity. Extensive data on the ideal resistivity of metals had been compiled by G. T. Meaden*. Each graph presents these ideal resistivities making it easier to see the effect of the intrinsic resistivity on the total resistivity plotted for each set of experimental values. This method of analysis also provides a means by which the purity of a metal can be estimated. By measuring the residual resistivity at 4.2 K, finding its position on the graph, and referring to the comments section to find statements of purity for curves in the same region of the graph, a fair estimate of probable impurity can be made.

The second phase of this task covered the collection, evaluation, and compilation of the electrical resistivity data on 8 additional metallic elements. These were:

- cadmium
- chromium
- manganese
- titanium
- tungsten
- vanadium
- zinc
- zirconium

The same format was used for presenting the data as in the initial phase of the task, i.e., listing the source literature and other references, discussing the experimental data, presenting tables of selected data and finally the preparation of a graph on the electrical resistivity ratios for the relevant data.

The issuance of the second technical note [54] completed this task for the present time. When there is sufficient need and available data for evaluating the electrical resistivity of additional metals, consideration will be given to the continuation of this effort.

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* Electrical Resistance of Metals by G. T. Meaden, Plenum Press, New York, 1965.

Item I: ANNOTATED BIBLIOGRAPHY OF THE PROPERTIES OF AIR

Principal Evaluator: L. A. Hall (Chemist)

Associate: H. M. Roder (Project Manager)

Time Period: March 1967 to July 1969

Publication:

A Bibliography of Thermophysical Properties of Air from 0 to 300 K, NBS Technical Note 383 (October 1969)[55].

Summary:

This task was pursued on a part-time basis for a period of over two years with a total effort of about 2/3 of a professional man year expended. The object was to assemble a comprehensive annotated bibliography on all of the thermophysical properties of air below room temperature to the lowest temperatures for which data were reported.

The collection of documents for air began over eight years prior to the formal initiation of this task in conjunction with the data compilation presented in the "Compendium." [65]. The initial literature search was conducted by the use of variour abstracting journals, in particular Chemical Abstracts. Copies of the articles were obtained at that time and reviewed for useful data. Since the time of the "Compendium's" publication, the Compilation Unit of the Cryogenic Data Center has actively acquired all articles dealing with the thermophysical properties of air at cryogenic temperatures. These articles were entered into the Storage and Retrieval System together with all the other cryogenically oriented documents that have come to our attention by a systematic scanning of the primary journals, and secondary publications such as Chemical Abstracts, Physics Abstracts, NASA STAR, Nuclear Science Abstracts, DDC TAB, and International Aerospace Abstracts. A computer search of the Storage and Retrieval System was the initial source of references for this task. All pertinent documents from the references listed in this search were reviewed and coded. In addition, other articles, which were referenced in these documents, were also obtained, reviewed, and coded. A final Chemical Abstracts search was conducted back to 1907 to bring to our attention any articles which might have been previously overlooked. (Seventy articles written before 1900, not already in our files, were not ordered because these were believed to be of historical interest only.)

A total of 608 articles were collected and selected for the formal bibliography. Thirteen of these were for oxygen-nitrogen mixtures which presented property values in temperature ranges where experimental data on air were missing. In addition a group of 28 documents dealing with thermophysical properties of air at extremely high temperatures (>1000 K) were also referenced, but separately. These documents came to our attention during the literature search, but because of the high temperature range, they were not included in the main body of the bibliography or indexed. In reviewing the literature each article was classified according to the type of data presented such as experimental, theoretical, compilation, correlation, calculations or whether it was a review, discussion or reference work. The state of the substance such as solid, liquid, gas up to 200 K and gas above 200 K,was indicated. This provided the basis for indexing in the published bibliography. The format used for preparing the citations for the bibliography was as follows:

1. author(s)
2. title (original language) and translated title, if original is in a language other than English
3. reference (if the same article is published in more than one place, each reference is cited)
4. properties studied for air, state of substance, temperature and pressure ranges as available
5. designation as to primary character of article
    a. experimental
    b. theoretical
    c. compilation
    d. correlation
    e. reference book
6. form in which data are reported
    a. tabular - tables (number of values)
    b. graphical
    c. equations
    d. apparatus, if described or illustrated

The citations were arranged alphabetically by first author and numbered. Only information from the article which concerns the properties of air was noted. The temperature and pressure ranges were omitted on references for the critical points and normal boiling points only. Also in many cases the pressures were not stated in the article. This is most often the case in the study of properties near atmospheric pressure that are essentially temperature-dependent only.

The following properties were covered:

1. density, P-V-T data, compressibility factor
2. equation of state, virial coefficients
3. expansivity and compressibility
4. vapor pressure (dew point pressure, bubble point pressure)
5. melting pressure
6. latent heats
7. Solid-solid phase transition, melting range, boiling temperatures, critical points, (plait point, point of contact)
8. specific heat
9. velocity of sound
10. Joule-Thomson coefficients, inversion curve
11. entropy, enthalpy, internal energy, Gibbs function, Helmholtz function
12. thermal conductivity
13. viscosity
14. Prandtl number
15. diffusion coefficient
16. surface tension
17. dielectric constant
18. refractive index
19. corresponding states
20. intermolecular potential
21. documents not appearing in the properties index

The bibliography was published in October 1969 as an NBS Technical Note [55] and has been quite widely distributed by the U. S. Government Printing Office, the Clearinghouse*, and the Cryogenic Data Center. It is the most comprehensive bibliography on the properties of air at low temperatures in existence and can serve as a basis for the evaluation and compilation of thermophysical property data. It can also serve as a basis for determining areas in which more or better experimental measurements are needed; however, critical evaluation of the data is the best means of determining what experimental measurements are most needed.

As in the case of previous tasks for the preparation of bibliographies (such as for oxygen, argon, and methane) much of the data were extracted from the literature as it was reviewed and assembled into task notebooks. Although this task was suspended with the completion of the formal bibliography, the next phase of the task (i. e., the critical evaluation and compilation of the thermal and transport properties) could easily be initiated.

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* Now the Department of Commerce, National Technical Information Service, Operations Division, Springfield, Va. 22151.

Item J: THERMAL CONDUCTIVITY OF METALS, ALLOYS AND NON-METALLIC SOLIDS

Principal Evaluator: G. E. Childs (Physicist)

Associate: R. L. Powell (Supervisory Physicist)

Time Period: November 1967 to November 1969*

Publication:

Thermal Conductivity of Technically Important Solids at Cryogenic Temperatures, G. E. Childs and R. L. Powell, NBS Monograph (in manuscript form).

Summary:

This task was initiated in response to a wide-spread need for low temperature data on the thermal conductivity of metals and alloys at low temperatures. NBS Circular 556 by R. L. Powell and W. A. Blanpied issued in 1954 on this subject was the most recent compilation available but had been out of print and the supply exhausted for several years even though 5000 copies had been printed. Furthermore the circular was out-of-date because of the many new measurements that had been made since 1954,particularly below 1 K and on new materials such as semiconductors. Thus a new review of the thermal conductivity literature was needed to incorporate the great amount of theoretical and experimental information published in the interim.

In March 1967 some NBS reserve funds became available to start this task. The Data Center staff were thus able to do much of the initial literature searching, procure documents not already on hand, and start reviewing pertinent literature. These funds for initiating this task expired at the end of June. However, NASA accepted the sponsorship of the task with Amendment No. 2 to the R-46 contract effective November 1, 1967.

Gregg Childs, under the supervision of R. L. Powell, began work on this task as soon as it became active. Both Childs and Powell realized that the amount of experimental data on the thermal conductivity of materials below 300 K was rather overwhelming. The objective was to compile, review, and critically evaluate all of the experimental data, plot the best and most meaningful data on graphs, and tabulate all of the sources of information. It was felt that to make the final result of greatest value to all scientists and engineers, much effort should also be put into a theoretical discussion of thermal conductivity below room temperature.

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* Period of NASA R-46 Sponsorship.

The bibliography of NBS Circular 556 contained 197 references, which was the total number of critically evaluated papers prior to 1954 that contained experimental thermal conductivity data. In beginning this project, 1200 papers were ordered that were felt to contain pertinent data and information. The papers came from the open literature, (the U. S., Britain, Australia, Canada, Russia, Germany, Czechoslovakia, Poland, Italy, etc.) from company reports, and conference papers. The critical evaluation portion would be significant, because it was felt that the reader would not want to see a compilation containing all the experimental data. For example, on copper the reader would be interested only in data that were original, unique, or significant.

The papers on hand were critically evaluated and a systematic approach to drawing the graphs and preparing the tables began. Log-log graphs were used because of their best representation of the data; temperature ranges were to be 4 to 300 K, 1 to 10 K, and 0.01 to 1 K. Graphs were to be made with a small enough grid so that the reader could read the values to within the experimental error. Tables would accompany each graph for quick reference; they would include the source of the material, its analysis, remarks thought pertinent by both the experimentalists and the authors, and the papers that may have quoted only one value or may be of some special significance, experimental or theoretical, to the thermal conductivity of that material.

The theoretical portion of the project developed into the greatest complement for a review of this type. The authors felt that to include an experimental and theoretical review of each of the papers would be very useful to the field of thermal conductivity. Thus, each paper was coded for experimental characteristics and theoretical discussion. The experimental characteristics include the general methods, types of samples, types of heaters and thermometers and shields, calibrations of thermometers, and estimated inaccuracy; this should be of great use to the user so that he can evaluate the significance of the data without having to look up all of the references. The theoretical coding includes authors that are pertinent for that table; it includes the types of electron-phonon, electron-imperfection, electron-miscellaneous, phonon-phonon, phonon-imperfection, phonon-electron interactions, miscellaneous carriers, and other properties such as electrical resistance, Lorenz ratio, specific heat, etc. All of this coding is also included on the tables with each reference; thus a reader can tell what are the significant effects on the thermal conductivity of a particular material.

The output, in written form now, is nearly ready to be printed. Its final structure is subdivided into the thermal conductivity of several different groups: elements, alloys, semiconductors and semimetals, ionic and valence crystals, disordered dielectrics, and compound crystals. A special section includes experimental and theoretical work below 1 K, including graphs and tables. An additional section, before the complete list of references, presents a thorough discussion of the coding, which is essentially a comprehensive review of thermal conductivity.

There are nearly 600 references used in the document. If an original author discussed essentially the same material in several different sources, we referenced only the one source that would be most accessible. The number of graphs presented total 130.

The funding for two years from contract R-46 greatly advanced the task and made it possible to produce more than just a review of the experimental work on thermal conductivity below room temperature. The resulting monograph is essentially a reference handbook providing a rather complete understanding of thermal conductivity.

2.7 In Conclusion

The foregoing has been a review of 10 major tasks related to the evaluation and compilation of thermophysical property data for industrially important materials at low temperatures which have derived their major support from NASA Contract R-46 for the period from December 1, 1965 to November 1, 1970. Nearly 500 K$ has been expended on this program from which more than 30 publications and reports of a significant nature have been produced. A number of these have been major contributions to NASA's aerospace program and have been widely used throughout the NASA organization and by its contractors. But this is only a part of the benefits derived from this program. Of almost equal value have been the consulting services this program has enabled the NBS to provide to NASA and its contractors. The ready reference material that the conduct of these several tasks has provided has made it possible for the Cryogenic Data Center staff to furnish a wide variety of reliable information to important missions on short notice.

The NASA R-46 sponsorship of the Cryogenic Data Center's data compilation program has made possible a number of other valuable contributions not directly covered in the tasks described. For example, in late 1967 a number of agencies (such as the Compressed Gas Association, the State of California, Division of Weights and Measures, and the Directorate for Air Force Aerospace fuels) appealed to us for a standard set of values for the saturated liquid densities of oxygen, nitrogen, argon, and parahydrogen. These products were being widely distributed to government and commercial users in large quantities yet no standard set of values was being used as a basis for measurement and billing. A standard set of values was prepared by the Cryogenic Data Center staff and issued in January 1968 in NBS Technical Note 361 [61].* The State of California adopted these values in its code, the Compressed Gas Association accepted them as the approved values for its phamplet P-6 and most government agencies and producers of these liquefied gases use these data which were derived from completed or current data compilation tasks largely supported by the NASA R-45 and R-46 contracts.

The National Bureau of Standards and the Cryogenic Data Center staff have been extremely pleased with the type of sponsorship the NASA Office of Advanced Research and Technology (OART) has provided through the tenure of the R-46 contract. The long range goal of the data compilation staff is to produce standard reference data within the framework of the National Standard Reference Data System. It is gratifying that the sponsorship has fully subscribed to this plan and the procedure for producing quality data. It was also pleasing to the authors of the report,described in Item A (section 2.6) on the preparation of the Thermodynamic Property Charts of Saturated Liquid Parahydrogen [22] to have it selected as a Technology Utilization item,† thus giving them additional recognition for their work

2.8 Publications and Reports

A. Documents related to work in progress at the initiation of NASA Contract R-46:

1. Hust, J. G., Stewart, R. B., A Compilation of the Property Differences of Ortho and Para Hydrogen or Mixtures of Ortho and Para Hydrogen., Natl. Bur. Standards, Boulder Labs., Rept. No. 8812 (May 1965).

2. Roder, H. M., Weber, L. A., Goodwin, R. D., Thermodynamic and Related Properties of Parahydrogen from the Triple Point to 100 K at Pressures to 340 Atmospheres., Natl. Bur. Standards Monograph 94 (Aug 1965).

3. Corruccini, R. J., Surface Tensions of Normal and Para Hydrogen., Natl. Bur. Standards Tech. Note No. 322 (Aug 1965).

4. Corruccini, R. J., Refractive Index and Dispersion of Liquid Hydrogen., Natl. Bur. Standards Tech. Note No. 323 (Sep 1965).

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* Also See Appendix D, page 73

† See Appendix E, page 75

5. McCarty, R. D., Thermodynamic Properties of Liquid-Vapor Parahydrogen and Liquid-Vapor Oxygen., Natl. Bur. Standards, Boulder Labs., Rept. No. 8883 (Sep 1965).

6. Hust, J. G., Stewart, R. B., Thermodynamic Property Computations for Systems Analysis., ASHRAE Journal Vol. 8, No. 2, 64-68 (Feb 1966).

7. Boyd, M. E., Larsen, S. Y., Quantum Mechanical Calculations of the Second Virial Coefficients for Hydrogen., Natl. Bur. Standards Tech. Note 412 (Apr 1967).

8. McCarty, R. D., Weekley, R. D., Temperature-Entropy Chart for Parahydrogen., Natl. Bur. Standards, Cryogenic Lab., Thermodynamic Chart D-20 (1965).

9. McCarty, R. D., Weekley, R. D., Enthalpy-Entropy Chart for Parahydrogen., Natl. Bur. Standards, Cryogenic Lab., Thermodynamic Chart D-22 (1965).

10. Hust, J. G., Wallace, L. D., Crim, J. A., Hall, L. A., Stewart, R. B., A Bibliography of the Thermophysical Properties of Oxygen at Low Temperatures., Natl. Bur. Standards Tech. Note 137 (Feb 1962).

11. Stewart, R. B., Hust, J. G., McCarty, R. D., Interim Thermodynamic Properties for Gaseous and Liquid Oxygen at Temperatures from 55 to 300 K and Pressures to 300 Atm., Natl. Bur. Standards Rept. No. 7922 (Oct 1963).

12. Hust, J. G., Stewart, R. B., A Vapor Pressure Equation for Oxygen., Natl. Bur. Standards Rept. No. 8753 (Feb 1965).

13. Hall, L. A., Hust, J. G., Gosman, A. L., A Bibliography of Thermophysical Properties of Argon from 0 to 300 K., Natl. Bur. Standards Tech. Note No. 217 (Jun 1964).

14. Gosman, A. L., Thermodynamic Properties of Argon in the Liquid and Gaseous State for Temperatures from the Triple Point to 300 K with Pressures to 1000 Atmospheres., Iowa Univ., Iowa City, Ph.D. Thesis (Aug 1965).

15. Johnson, V. J., Stewart, R. B., Olien, N. A., First Quarterly Progress Report on Cryogenic Data Center Activities for the Period Ending March 31, 1965., Natl. Bur. Standards Rept. No. 8788 (Mar 1965).

16. Johnson, V. J., Stewart, R. B., Olien, N. A., Second Quarterly Progress Report on Cryogenic Data Center Activities for the Period Ending June 30, 1965., Natl. Bur. Standards Rept. No. 8838 (Jun 1965).

17. Johnson, V. J., Stewart, R. B., Olien, N. A., The Third Quarterly Progress Report on Cryogenic Data Center Activities for the Period Ending September 30, 1965., Natl. Bur. Standards Rept. No. 9105 (Sep 1965).

18. Johnson, V. J., Stewart, R. B., Olien, N. A., Fourth Quarterly Progress Report on Cryogenic Data Center Activities for the Period Ending December 31, 1965., Natl. Bur. Standards Rept. No. 9156 (Dec 1965).

19. Johnson, V. J., Stewart, R. B., Olien, N. A., Semi-annual Progress Report on Cryogenic Data Center Activities for the Period of January 1 Through June 30, 1966., Natl. Bur. Standards Rept. No. 9254 (Jun 1966).

20. Johnson, V. J., Olien, N. A., Roder, H. M., Semi-annual Progress Report on Cryogenic Data Center Activities for the Period of July 1 through December 31, 1966., Natl. Bur. Standards Rept. 9271 (Dec 1966).

21. Stewart, R. B., Hust, J. G., Hanley, H. J. M., McCarty, R. D., Hall, L. A., Childs, G. E., Germann, F. E. E., Gosman, A. L., Johnson, V. J., Cryogenic Propellant Fluid Properties; Final Report for Data Evaluation Program on Government Order H-76797., Natl. Bur. Standards Rept. No. 9198 (Feb 1966).

B. Publications and reports resulting directly from NASA Contract R-46 Sponsorship:

22. McCarty, R. D., Roder, H. M., Thermodynamic Property Charts of Saturated Liquid Parahydrogen in British Units., Natl. Bur. Standards, Boulder Labs., Rept. No. 9263 (Nov 1966).

23. Hust, J. G., McCarty, R. D., Fortran Package for Least Squares Curve Fitting and the Solution of Simultaneous Equations., Natl. Bur. Standards Rept. No. 9258 (Oct 1966).

24. Hust, J. G., McCarty, R. B., Curve-Fitting Techniques and Applications to Thermodynamics., Cryogenics 7, No. 4, 200-6 (Aug 1967).

25. Hust, J. G., A Compilation and Historical Review of Temperature Scale Differences., Cryogenics 9, No. 6, 443-55 (Dec 1969).

26. Stewart, R. B., Thermodynamic Properties of Oxygen., University of Iowa, Mechanical Engineering Dept., Iowa City, Ph.D. Thesis (Jun 1966).

27. Stewart, R. B., Temperature-Entropy Chart for Oxygen., Natl. Bur. Standards, Cryogenic Lab., Thermodynamic Chart D-56 (1966).

28. Stewart, R. B., Compressibility Factor Chart for Oxygen., Natl. Bur. Standards, Cryogenic Lab., Thermodynamic Chart D-57 (1966).

29. Gosman, A. L., McCarty, R. D., Hust, J. G., Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres., NSRDS-NBS 27 (Mar 1969).

30. Gosman, A. L., McCarty, R. D., Hust, J. G., Temperature Entropy Chart for Argon., Natl. Bur. Standards, Cryogenic Division, Thermodynamic Chart D-61 (1969).

31. Gosman, A. L., McCarty, R. D., Hust, J. G., Compressibility Factor Chart for Argon., Natl. Bur. Standards, Cryogenic Division, Thermodynamic Chart D-62 (1969).

32. Prydz, R., The Thermodynamic Properties of Deuterium., Univ. of Colo; Chem. Engrg. Dept., Boulder, Master of Science Thesis (1967).

33. Prydz, R., The Thermodynamic Properties of Deuterium., Natl. Bur. Standards Rept. No. 9276 (Apr 1967).

34. Prydz, R., Temperature-Entropy Chart for Deuterium (20 to 100 K)., Natl. Bur. Standards, Cryogenic Division, Thermodynamic Chart D-58 (1967).

35. Prydz, R., Temperature-Entropy Chart for Deuterium (80 to 300 K)., Natl. Bur. Standards, Cryogenic Division, Thermodynamic Chart D-59 (1967).

36. Prydz, R., Compressibility Factor Chart for Deuterium., Natl. Bur. Standards, Cryogenic Division, Thermodynamic Chart D-60 (1967).

37. Prydz, R., Timmerhaus, K. D., Stewart, R. B., The Thermodynamic Properties of Deuterium., Paper F-5, Published in Advances in Cryogenic Engineering, Vol. 13, 384-96 Plenum Press, N. Y. (1968).

38. Hanley, H. J. M., Comparison of the Lennard-Jones, exp-6, and Kihara Potential Functions from Viscosity Data of Dilute Argon., J. Chem. Phys. 44, No. 11, 4219-22 (Jun 1966).

39. Hanley, H. J. M., The Viscosity and Thermal Conductivity Coefficients of Dilute Argon between 100 and 2000 K., Natl. Bur. Standards Tech. Note 333 (Mar 1966).

40. Childs, G. E., Hanley, H. J. M., The Viscosity and Thermal Conductivity Coefficients of Dilute Nitrogen and Oxygen., Natl. Bur. Standards Tech.Note 350 (Oct 1966).

41. Hanley, H. J. M., Childs, G. E., The Viscosity and Thermal Conductivity Coefficients of Dilute Neon, Krypton, and Xenon., Natl. Bur. Standards Tech. Note 352 (Mar 1967).

42. Hanley, H. J. M., Klein, M., On the Selection of the Intermolecular Potential Function: Application of Statistical Mechanical Theory to Experiment., Natl. Bur. Standards Tech. Note 360 (Nov 1967).

43. Hanley, H. J. M., Thermodynamics of Transport Phenomena in Membrane Systems., J. Chem. Educ. 44, No. 12, 717-23 (Dec 1967).

44. Childs, G. E., Hanley, H. J. M., Applicability of Dilute Gas Transport Property Tables to Real Gases., Cryogenics 8, 94-7 (Apr 1968).

45. Klein, M., Hanley, H. J. M., Selection of the Intermolecular Potential, Part 2. From Data of State and Transport Properties Taken in Pairs., Trans. Faraday Soc. 64, No. 551, Pt 11, 2927-38 (Nov 1968).

46. Hanley, H. J. M., Childs, G. E., Discrepancies between Viscosity Data for Simple Gases., Science 159, 1114-7 (1968). A similar paper is published in the Proc. of 7th Conference on Thermal Conductivity, Gaithersburg, Md., Nov 13-17, 1967. Natl. Bur. Standards Spec. Publ. 302 (Sep 1968).

47. Hanley, H. J. M., McCarty, R. D., Density Dependence of Experimental Transport Coefficients of Gases., J. Chem. Phys. 50, No. 2, 857-70 (Jan 1969).

48. Hanley, H. J. M., Childs, G. E., Dilute Gas Viscosities at Low Temperatures, J. Chem. Phys. 50, No. 10, 4600-01 (May 1969).

49. Hanley, H. J. M., Klein, M., Selection of the Intermolecular Potential Function. Part 3. From the Isotopic Thermal Diffusion Factor., J. Chem. Phys. 50, No. 11, 4765-70 (Jun 1969).

50. Hanley, H. J. M., McCarty, R. D., Intemann, H., The Viscosity and Thermal Conductivity of Dilute Gaseous Hydrogen between 15 and 5000 K., J. Res. Natl. Bur. Standards 74A, No. 3, 331-53 (May-Jun 1970).

51. McCarty, R. D., Provisional Thermodynamic Functions for Helium 4 for Temperatures from 2 to 1500 K with Pressures to 100 MN/m^2 (1000 Atmospheres)., Natl. Bur. Standards Rept. No. 9762 (Aug 1970).

52. Hall, L. A., A Bibliography of Thermophysical Properties of Methane from 0 to 300 K., Natl. Bur. Standards Tech. Note No. 367 (May 1968).

53. Hall, L. A., Survey of Electrical Resistivity Measurements on 16 Pure Metals in the Temperature Range 0 to 273 K., Natl. Bur. Standards Tech. Note No. 365 (Feb 1968).

54. Hall, L. A., Germann, F. E. E., Survey of Electrical Resistivity Measurements on 8 Additional Pure Metals in the Temperature Range 0 to 273 K., Natl. Bur. Standards Tech. Note No. 365-1 (Aug 1970).

55. Hall, L. A., A Bibliography of Thermophysical Properties of Air from 0 to 300 K., Natl. Bur. Standards Tech. Note No. 383 (Oct 1969).

C. Publications resulting from associate sponsorship of NASA Contract R-46 tasks:

56. Hanley, H. J. M., Childs, G. E., Interim Values for the Viscosity and Thermal Conductivity Coefficients of Fluid He^4 between 2 and 50 K., Cryogenics 9, No. 2, 106-11 (Apr 1969).

57. Diller, D. E., Hanley, H. J. M., Roder, H. M., The Density and Temperature Dependence of the Viscosity and Thermal Conductivity of Dense Simple Fluids., Cryogenics 10, No. 4, 286-94 (Aug 1970).

58. Klein, M., Hanley, H. J. M., The m-6-8 Potential Function., J. Chem. Phys. (Dec 1970).

59. Guevara, F. A., Hanley, H. J. M., McInteer, B. B., Otteman, D., Viscosities at High Temperatures., Phys. Fluids (to be published).

60. Klein, M., Hanley, H. J. M., Smith, F. J., Holland, P. M., Collision Integrals for the m-6-8 Potential., (to be published as an NSRD Monograph).

61. Roder, H. M., McCarty, R. D., Johnson, V. J., Saturated Liquid Densities of Oxygen, Nitrogen, Argon, and Parahydrogen., Natl. Bur. Standards Tech. Note No. 361 (Jan 1969).

62. Mann, D. B., Roder, H. M., Liquefied Natural Gas as a Cryogenic Fluid--Instrumentation and Properties., Proceedings Transmission Conference of A.G.A. Operating Section, T-98--T-106., American Gas Association, Arlington, Va. (1970). Also: Cryogenic Ind. Gases 5, No. 7, 23-9 (Jul-Aug 1970).

63. Roder, H. M., Correlation of the Thermodynamic Properties of Methane in the Immediate Vicinity of the Triple Point., Part II of Slush and Boiling Methane Characterization by Sindt, C. F., Ludtke, P. R., Roder, H. M., Natl. Bur. Standards Rept. No. 9758, 41-69 (July 1970).

D. Other related publications:

64. Hanley, H. J. M., Transport Phenomena in Fluids., BOOK, Marcel Dekker, Publisher (Jul 1969).

65. Johnson, V. J., Editor, A Compendium of the Properties of Materials at Low Temperature (Phase I), Part I. Properties of Fluids., Natl. Bur. Standards, Cryogenic Eng. Lab., WADD Tech. Rept. 60-56 (1960) Contr. No. AF 33(616)58-4.

66. Stewart, R. B., Johnson, V. J., Editors., A Compendium of the Properties of Materials at Low Temperatures (Phase II)., Natl. Bur. Standards, Cryogenic Eng. Lab., WADD Tech. Rept. 60-56 (1960) Contr. No. AF 33(616)58-4.

3.0 DETERMINATION OF THE THERMOPHYSICAL PROPERTIES OF COMPRESSED GASEOUS AND LIQUID OXYGEN AND HELIUM

3.1 Introduction

Since November 1966 the NASA Office of Advanced Research and Technology has invested approximately $300,000 with the Properties of Cryogenic Fluids Section, NBS Cryogenics Division for the purpose of determining the thermophysical properties of compressed gaseous and liquid oxygen. During this period, Drs. L. A. Weber, R. D. Goodwin, B. A. Younglove and G. C. Straty have completed an extensive program of precision measurements, mathematical representation of data, computation of derived properties, and publication of technical papers. Accurate measurements of the densities, specific heats (C_{sat} and C_v), sound velocities and dielectric constants were performed at closely spaced intervals throughout a wide range of temperatures (55-300 K) and at pressures to 330 atm. From the measurements, many important thermodynamic properties such as internal energies, entropies, enthalpies, heats of vaporization, specific heats at constant pressure (C_p), and specific heat inputs were derived. It is believed that the quality of these data is such that it will be recognized as definitive or standard for all foreseeable engineering calculations at cryogenic temperatures and high pressures. The PVT data have recently been selected by the International Union of Pure and Applied Chemistry as the basis for its International Thermodynamic Property Tables Project on oxygen.

Throughout the period of the contract, the NBS Cryogenics Division has provided the NASA and its subcontractors with quarterly progress reports, data tables, interpolation formulas, property charts, and extensive consulting services. A list of reports and publications produced by this contract is attached to the end of this summary. Selected pages from publications [4] and [7] are also reproduced here. (See Appendices A and B). NBS Report 9710, "Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 330 Atmospheres," is perhaps the single most significant and comprehensive publication produced and as such has been widely distributed throughout the NASA organization since June 1968. It contains one of the most extensive sets of thermophysical property measurements and thermodynamic property computations ever performed by a single laboratory on any substance. (Estimated to be 80% of the World's experimental data for the region covered.)

The primary purpose of this program was to provide NASA engineers with accurate, wide-range fluid property data so that processes involving the storage, transport, and pumping of compressed gaseous and liquid oxygen could be designed reliably, safely, and economically. Many informal contacts with NASA aerospace engineers suggest that this general purpose has been accomplished. A specific example of the value of these data to NASA's programs concerns the recent failure of the oxygen storage tank on the Apollo 13 lunar mission. The NBS Cryogenics Division was able to make an important contribution to the analysis of this failure because sufficient knowledge of the thermophysical properties of oxygen was available when it was needed. This knowledge established the general features of the tank failure and assisted in deducing the series of unfortunate events preceding the failure. It has subsequently provided the basis for a safe and reliable redesign of this system.

NASA has recently formed a new group called ASRDI (Aerospace Safety Research and Data Institute) for anticipating and dealing with the potentially hazardous aspects of aerospace missions. One of their tasks is to provide for safety in the use of cryogenic fluids such as oxygen. The NBS Cryogenics Division has been selected to provide ASRDI with comprehensive information on the problems associated with the safe use of this fluid. The basic nucleus of the physical property data on oxygen assembled for this purpose will be derived from the projects previously completed for the Office of Advanced Research and Technology.

In the November 69 - November 70 contract period (as the measurements program for the Thermodynamic Properties of Oxygen was nearing completion) funding was provided to initiate a measurements program for the Thermodynamic Properties of Helium. A new cryostat is being completed and general procedures established to measure the P-V-T and calorimetric values for helium sufficiently accurate to resolve much of the uncertainty of existing data as determined by R. D. McCarty in his data evaluation program as described in Section 2.6 item F. Work on this helium properties measurements program is being suspended, however, for lack of continued funding. A proposal for continuing the program is included at the end of this report which details the need for better data and efforts that have been made to secure support. (See Appendix C, Section 3.6).

3.2 Historical Highlights of Research Completed for NASA Contract R-46

A. Preceding the R-46 Contract in November 1966, we completed extensive PVT measurements on compressed gaseous and liquid oxygen. (Supported by SNPO Contract R-45).

B. Between November 1967 and November 1968 we completed wide-range specific heat measurements on oxygen.

C. Between November 1968 and November 1969 we completed the calculation of the thermodynamic properties of oxygen and measurement of the dielectric constants of oxygen.

D. Between November 1969 and November 1970 we repeated the dielectric constant measurements on oxygen with a new capacitance cell, we completed wide-range sound velocity measurements on oxygen, and we began assembling apparatus for PVT measurements on gaseous and liquid helium. Preparations for PVT measurements on helium are continuing (see appended funding proposal). Figure 14 (page 56) illustrates the chronology of the experimental measurements program for the NASA R-46 Contract.

3.3 Work in Progress

A. Publication of measurements of the dielectric constant of oxygen.

B. Analysis and publication of measurements of the sound velocity in compressed gaseous and liquid oxygen.

C. Assembly of new apparatus for wide-range PVT measurements on gaseous and liquid helium (2-70 K at pressures to 340 atm). Most of the necessary instrumentation for precision thermometry and pressure measurements has been purchased. A helium cryostat is about 50% complete.

3.4 Work for which Additional Funding is Sought

A. Completion of PVT and specific heat (C_v) measurements on gaseous and liquid helium. (See appended funding proposal).

B. The viscosity of saturated liquid oxygen will be measured this year as part of a project on the viscosity of gaseous and liquid fluorine. (Currently funded by NBS).

C. Measurements of the thermal conductivity of gaseous and liquid oxygen with emphasis on the critical region (140-170 K at pressures between 45 and 60 atm). (Funding being sought from NASA-Lewis Research Center.)

D. Publication of an NBS Technical Note containing extensive tables of the thermodynamic properties of oxygen.

E. Extrapolation of the thermodynamic properties of oxygen to higher pressures (800 atm). (Funding being sought from NASA Marshall Spaceflight Center.)

3.5 Publications and Reports on the Thermophysical Properties of Gaseous and Liquid Oxygen (from the Properties of Cryogenic Fluids Section)

1. Weber, L. A., Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 330 Atmospheres., NBS Report 9710, June 20, 1968; and Supplement A (British Units), NBS Report 9710A, August 29, 1968.

2. Weber, L. A., The Specific Heat Input, $\rho(\partial H/\partial \rho)$, of Oxygen, NBS Report 9718, November 1, 1968.

3. Goodwin, R. D., and Weber, L. A., Specific Heats of Oxygen at Coexistence., J. Res. Natl. Bur. Standards, 73A, 1 (1969).

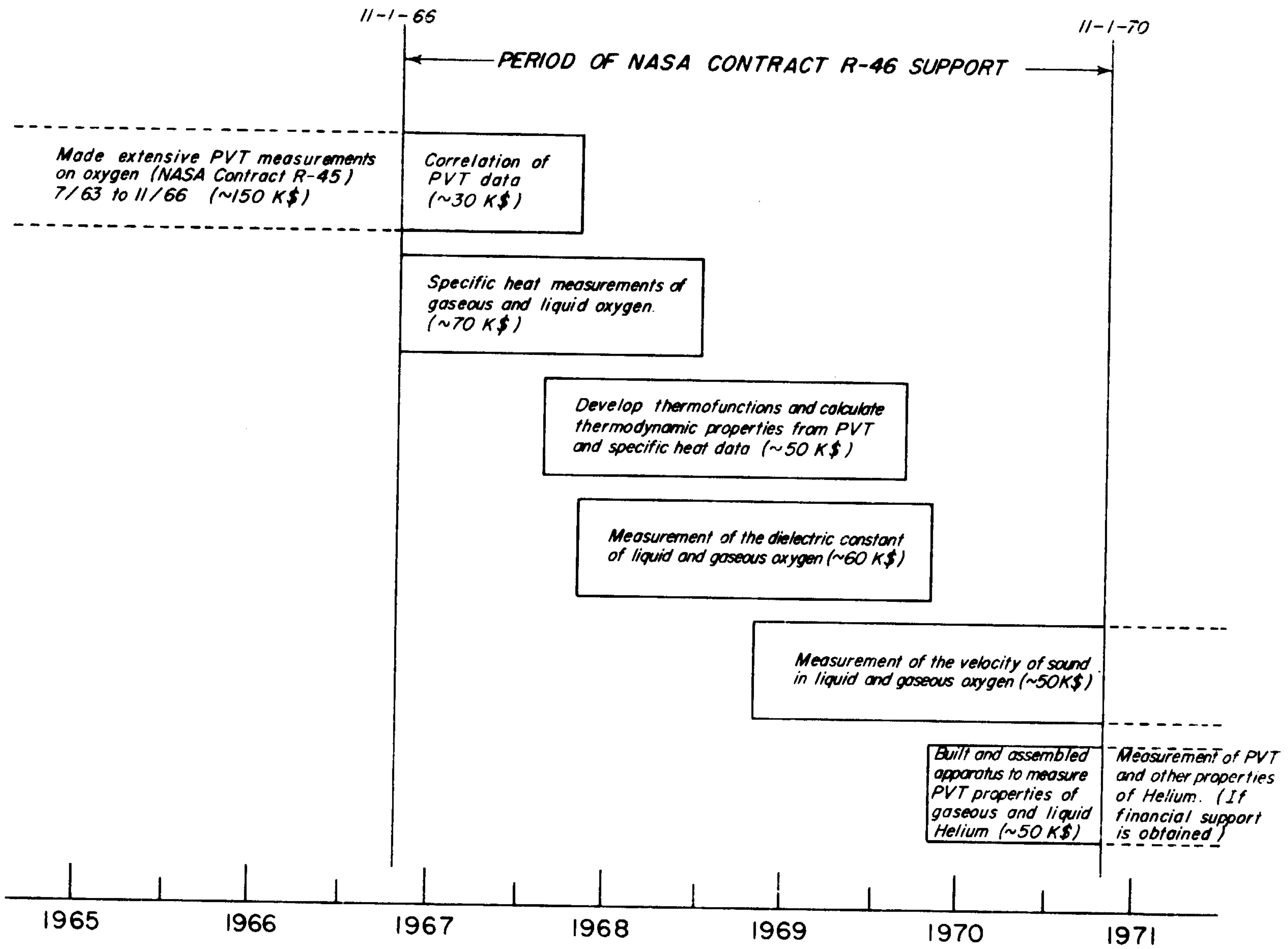

FIGURE 14. Chronology of THERMOPHYSICAL PROPERTIES MEASUREMENT PROGRAM

4. Goodwin, R. D. and Weber, L. A., Specific Heats C_v of Fluid Oxygen from the Triple Point to 300 K at Pressures to 350 Atmospheres, J. Res. Natl. Bur. Standards, 73A, 15, (1969). (See excerpts, Sect. 3.6 Appendix A).

5. Goodwin, R. D., Thermodynamic Properties of Fluid Oxygen at Temperatures to 250 K and Pressures to 350 Atmospheres on Isochores at 1.3 to 3.0 Times Critical Density, J. Res. Natl. Bur. Standards, 73A, 25, (1969).

6. Goodwin, R. D., Nonanalytic Vapor Pressure Equation with Data for Nitrogen and Oxygen, J. Res. Natl. Bur. Standards, 73A, 487, (1969).

7. Weber, L. A., P-V-T Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 33 MN/m^2, J. Res. Natl. Bur. Standards, 74A, 93, (1970). (See excerpts, Sect. 3.6 Appendix B).

8. Goodwin, R. D., Estimation of Critical Constants T_c, ρ_c From the $\rho(T)$ and $T(\rho)$ Relations at Coexistence, J. Res. Natl. Bur. Standards, 74A, 221 (1970).

9. Weber, L. A., Saturation Densities of Oxygen in the Critical Region, Physics Letters, 30A, 390 (1969).

10. Weber, L. A., The P-V-T Surface of Oxygen in the Critical Region: Densities of Saturated Liquid and Vapor, Advances in Cryogenic Engineering, 15, 50, (1970).

11. Weber, L. A., Density and Compressibility of Oxygen in the Critical Region, Phys. Rev. A (December 1970).

12. Younglove, B. A., and Straty, G. C., A Capacitor for Accurate Wide-Range Dielectric Constant Measurements on Compressed Fluids, Rev. Sci. Inst. 41, 1087, (1970).

13. Younglove, B. A., Measurements of the Dielectric Constant of Saturated Liquid Oxygen, Advances in Cryogenic Engineering, 15, 70, (1970).

14. Younglove, B. A., Dielectric Constant of Liquid and Gaseous Oxygen, submitted to J. of Chemical Physics, (1970).

4. 0 APPENDICES

Appendix A: Excerpts from Reference [4] Section 3. 5

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Specific Heats C_v of Fluid Oxygen from the Triple Point to 300 K at Pressures to 350 Atmospheres*

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(August 15, 1968)

Experimental specific heats at constant volume for oxygen in single phase domains are reported from the triple point to 300 K at pressures to 350 atmospheres. An empirical equation with seven constants describes these specific heats over the entire domain of ρ-T coordinates to within the experimental accuracy of 1 to 2 percent. Values for the terminal slopes of PVT isochores at the coexistence boundary, $(\partial P/\partial T)_v$, are derived for the liquid.

Key Words: Compressed liquid; heat capacities; liquid; oxygen; specific heats; thermodynamic properties.

List of Symbols

C_b	heat capacity of empty calorimeter bomb.
$C_v(\rho, T)$	specific heat of the sample.
$C_v^\circ(T)$	specific heat in ideal gas states.
C_V	adjustment for bomb expansion.
J	the joule.
k	conversion factor, 0.101325 J/cm^3 atm.
L	the liter, 1,000 cm^3.
N	total moles of fluid in bomb plus capillary tube.
N_b	moles of fluid in the bomb.
N_c	moles of fluid in the capillary tube.
P	pressure. 1 atm = 0.101325 MN/m^2.
Q	calorimetric heat input.
$Q/\Delta T$	gross heat capacity.
ρ	density.
ρ_c	critical density, 13.62 mol/l.
σ	density reduced at the critical point.
t	time.
T	temperature, Kelvin, NBS 1955 scale.
T_1, T_2	temperature at start and end of heating interval.
T_c	critical-point temperature, 154.77 K.
$\Delta T \equiv T_2 - T_1$	calorimetric temperature increment.
v	molal volume, $1/\rho$.
V_b	volume of the calorimeter bomb.
x	temperature reduced at the critical point.

1. Introduction

Specific heats are basic data for the computation of thermodynamic properties in the compressed liquid domain, yet for oxygen these data apparently never have been measured [1].[1] In the present report we give our results for C_v over the entire fluid domain below 300 K and below 350 atm. Many details of the experimental work are given in our companion publication on specific heats along the liquid-vapor coexistence path [2]. In forthcoming reports we give thermodynamic properties based on the current measurements.

2. Experimental Method

The calorimeter and cryostat are the same as used for the two-phase observations [2]. Briefly, the calorimeter is a spherical shell of stainless steel, 2 in in diameter, surrounded by adiabatic shields maintained at the calorimeter temperature by automatic controls. The amount of sample is determined from an observed temperature T and pressure P in a single-phase domain; from the bomb volume at this T, P; and from the fluid density derived from an equation of state [1]. The method for measuring calorimetric heat is identical with that of [2] as is the tare heat capacity of the empty calorimeter bomb. The computational method of adjusting for expansion of the bomb during a heating interval also is the same except that the required pressure increase in the bomb is estimated.

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[*] This work was carried out at the National Bureau of Standards under the sponsorship of the National Aeronautics and Space Administration Fund Transfer R–06–006–046.

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

3. Calculation of C_v From Laboratory Observations

To adjust for expansion of the bomb we estimate the pressure at T_1 and at T_2. An iterative method minimizes the difference $|\rho-\rho_e|$ where density ρ is obtained from contents and volume of the bomb,

$$\rho=[N-N_c(P,T)]/V_b(P,T), \tag{1}$$

and density ρ_e is used in the equation of state $P(\rho_e, T)$ to obtain the pressure. For the capillary tube we obtain $N_c(P, T)$ by summing over both liquid and gaseous phases whenever a meniscus exists in this tube. The capillary volume is about $0.0002 \cdot V_b$.

The densities ρ_1, ρ_2 obtained in this way at T_1, T_2 already recognize fluid in the capillary tube. We therefore use them in the adjustment C_x for bomb expansion as follows (appendix I),

$$\Delta v \equiv 1/\rho_2 - 1/\rho_1,$$

$$C_x \equiv k \cdot [T_2 \cdot (\partial P/\partial T)_2 - \Delta P/2] \cdot \Delta_v/\Delta T. \tag{2}$$

Our experimental data thus are reduced by the equation,

$$C_v = [Q/\Delta T - C_b]/N_b - C_x \tag{3}$$

with no curvature adjustments [2]. Only for datum No. 225 near critical is the adjustment significant: this datum should be reduced to 46.4 J/mol-K in table 2. The maximum uncertainties (errors) in C_v are calculated as in [2], using the same estimates for uncertainty of individual variables.

4. Experimental Results

The locus of each specific heat observation is given by figure 1 in density-temperature coordinates. The observations extend from the coexistence envelope at low temperatures to the 350-atm boundary of pressure at high temperatures. The amount of sample for each experimental run (horizontal line on fig. 1) is calculated from the loading conditions of table 1. The total number of moles N given in the last column includes a few ten thousandths in the capillary tube.

Table 2 gives experimental results. Identification in the first column is the run number followed by two digits for the point of that run. Next are the observed temperature, the estimated pressure, and the calculated density at this pressure. The bomb volume V, BMB and DV/DT for the bomb are calculated at T, P as in [2]. The seventh column DEL T is the experimental temperature increment, ΔT. Following columns are the gross heat capacity $Q/\Delta T$, the tare heat capacity of the empty calorimeter, and the adjusted specific heat of the oxygen sample computed

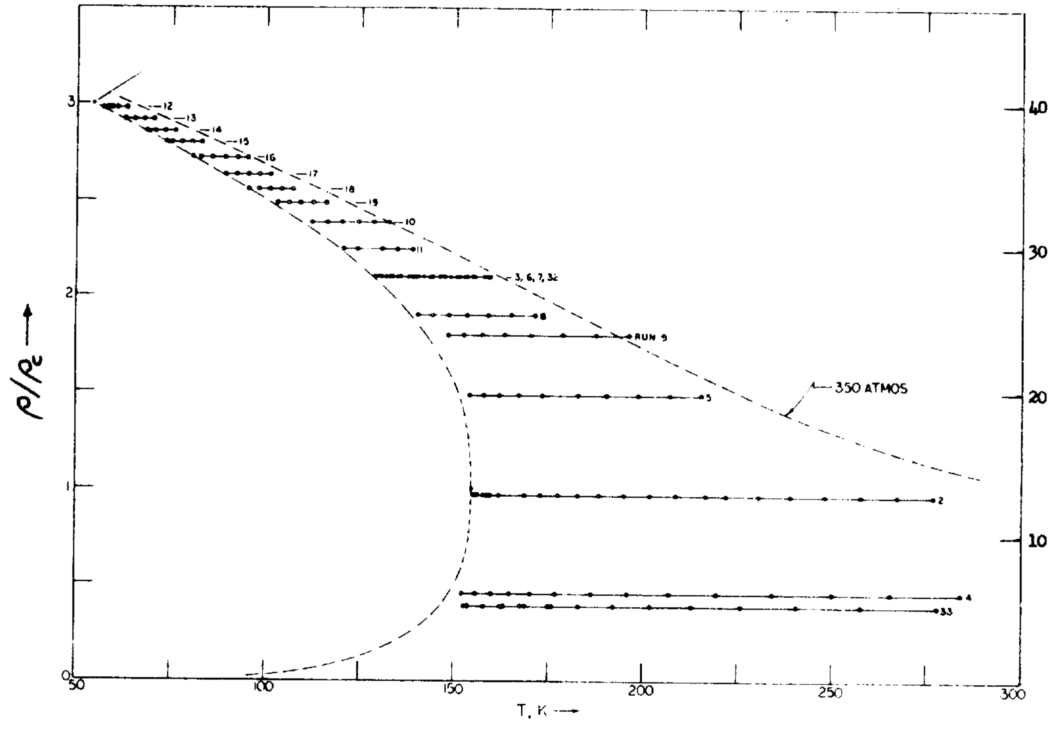

FIGURE 1. *Locus of C_v data in ρ – T coordinates.*

by eq (3). The last column is estimated maximum relative uncertainty (error), in percent. This increases rapidly with diminishing interval ΔT and with diminishing amount of sample. A comparison of runs 3, 6, 7, 32, all at the same density, shows that these estimates of error are realistic.

TABLE 1. *Loading conditions for the samples*

Run	*T*, *K*	*P*, ATM	*V*, cm^3	*D*, Mol/l	*N*, Mol
2	197.279	131.432	73.133	13.128	0.9602
3	139.255	129.352	72.950	28.679	2.0924
4	200.125	76.159	73.086	6.110	0.4467
5	173.070	129.980	73.054	20.223	1.4775
6	139.083	128.514	72.949	28.696	2.0936
7	138.976	127.012	72.948	28.688	2.0929
8	148.103	96.998	72.947	25.893	1.8890
9	173.955	187.207	73.112	23.090	1.6884
10	116.705	125.967	72.884	32.557	2 3731
11	131.071	159.226	72.953	30.621	2 2341
12	59.069	122.822	72.754	40.632	2.9565
13	65.450	120.256	72.763	39.783	2.8950
14	71.341	114.230	72.769	38.974	2.8364
15	76.877	108.612	72.775	38.202	2.7805
16	85.691	138.618	72.817	37.157	2.7060
17	94.357	145.740	72.843	36.010	2.6234
18	102.979	156.273	72.873	34 875	2.5417
19	109.048	141.669	72.877	33.884	2.4696
32	137.181	106.345	72.934	28.633	2.0882
33	207.639	71.974	73.106	5.253	0.3841

The behavior of these specific heats is illustrated in figure 2 by plots of selected runs (isochores). For a wide range of densities about the critical density the specific heat increases sharply as temperature diminishes toward the coexistence envelope. At densities far removed from critical, however, the temperature dependence is relatively weak.

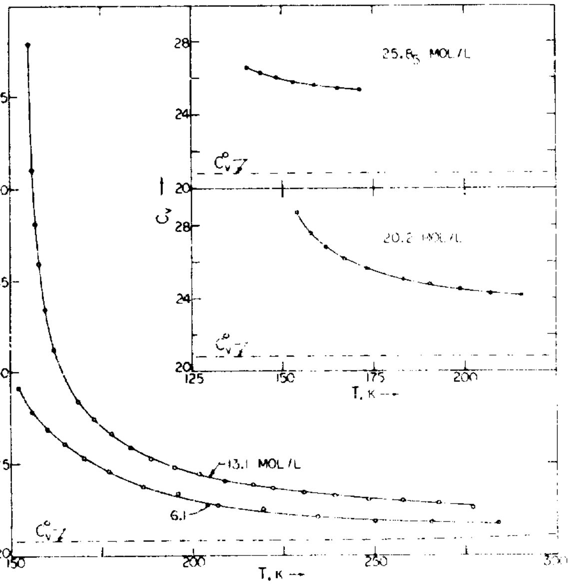

FIGURE 2. *Selected isochores of C_v data.*

TABLE 2. *Experimental specific heats*

ID	*T*, K	*P*, atm	Dens. mol/l	*V*, bmb cm^3	DV_b/DT cm^3/deg	Del *T* K	*DQ/DT* J/deg	Tare J/deg	C_v J/M-K	Error percent
225	155.297	51.144	13.166	72.925	0.0047	0.764	112.656	66.536	47.883	2.077
226	155.970	52.427	13.166	72.928	.0047	0.812	106.171	66.679	40.978	2.173
227	156.753	53.920	13.165	72.932	.0047	0.830	103.576	66.844	38.103	2.237
228	157.829	55.971	13.164	72.937	.0047	1.414	101.692	67.069	35.905	1.592
229	159.558	59.267	13.163	72.945	.0047	2.106	99.644	67.423	33.402	1.311
230	162.067	64.054	13.160	72.957	.0048	2.991	98.042	67.923	31.208	1.145
231	168.678	76.686	13.154	72.989	.0049	3.947	96.558	69.170	28.354	1.090
232	172.876	84.734	13.151	73.010	.0049	4.554	96.375	69.912	27.385	1.061
233	177.619	93.820	13.146	73.033	.0050	5.036	96.396	70.709	26.571	1.051
234	182.951	104.018	13.141	73.060	.0050	5.737	96.521	71.556	25.811	1.034
235	188.633	114.906	13.136	73.089	.0051	6.284	96.805	72.407	25.213	1.029
236	195.116	127.315	13.130	73.122	.0052	6.853	97.260	73.319	24.729	1.025
237	201.815	140.083	13.124	73.157	.0052	6.741	97.840	74.202	24.404	1.048
238	208.788	153.339	13.117	73.193	.0053	7.397	98.351	75.065	24.028	1.040
239	216.716	168.371	13.109	73.235	.0054	8.697	99.094	75.984	23.835	1.012
240	222.219	178.853	13.104	73.265	.0054	8.676	99.500	76.588	23.621	1.025
241	230.717	194.880	13.096	73.311	.0055	8.624	100.165	77.471	23.384	1.043
242	239.156	210.642	13.087	73.357	.0055	9.367	100.833	78.295	23.211	1.036
243	248.314	227.681	13.078	73.408	.0056	9.298	101.488	79.138	23.003	1.053
244	257.729	245.185	13.069	73.461	.0056	9.901	102.259	79.955	22.943	1.048
245	267.382	263.047	13.059	73.515	.0057	9.883	102.936	80.749	22.810	1.061
246	276.983	280.719	13.049	73.570	.0057	9.810	103.453	81.497	22.557	1.079
317	130.692	45.629	28.719	72.852	.0115	4.180	117.358	60.316	26.501	0.710
318	134.835	86.416	28.700	72.899	.0117	4.155	118.134	61.515	26.279	.722
319	138.945	126.677	28.680	72.947	.0119	4.115	119.032	62.638	26.149	.734
320	143.490	169.947	28.659	73.000	.0121	4.071	120.315	63.808	26.181	.745

TABLE 2. *Experimental specific heats*—Continued

ID	T, K	P, atm	Dens. mol/l	V, bmb cm^3	DV_b/DT cm^3/deg	Del T K	DQ/DT J/deg	Tare J/deg	C_V J/M·K	Error percent
321	147.531	208.734	28.640	73.048	.0122	4.065	121.052	64.790	26.045	.754
322	151.493	246.338	28.621	73.096	.0123	4.038	121.854	65.703	25.975	.762
323	155.489	283.838	28.602	73.144	.0123	4.010	122.640	66.577	25.917	.771
324	159.453	320.561	28.583	73.191	.0124	3.987	123.419	67.402	25.881	.779
401	152.179	42.261	6.126	72.908	.0035	3.667	78.902	65.856	29.116	1.842
402	155.794	44.979	6.124	72.921	.0036	3.654	79.105	66.642	27.809	1.932
403	160.002	48.086	6.123	72.936	.0036	4.858	79.536	67.512	26.825	1.784
404	164.797	51.575	6.122	72.954	.0036	4.830	80.129	68.450	26.050	1.851
405	170.195	55.441	6.120	72.973	.0037	6.065	80.766	69.443	25.253	1.770
406	176.883	60.164	6.118	72.998	.0037	7.453	81.616	70.588	24.586	1.719
407	186.560	66.896	6.115	73.034	.0038	8.851	82.742	72.102	23.712	1.720
408	196.057	73.392	6.112	73.070	.0038	10.315	83.926	73.446	23.349	1.704
409	207.059	80.831	6.108	73.113	.0039	11.906	85.051	74.856	22.704	1.718
410	219.594	89.217	6.104	73.162	.0040	14.076	86.411	76.303	22.502	1.703
411	234.502	99.074	6.099	73.222	.0040	16.083	87.771	77.847	22.080	1.721
412	250.222	109.382	6.093	73.285	.0041	15.818	89.133	79.307	21.849	1.768
413	265.673	119.428	6.088	73.348	.0041	15.564	90.424	80.611	21.810	1.801
414	284.186	131.436	6.082	73.425	.0042	22.098	91.825	82.036	21.743	1.743
516	154.095	54.534	20.260	72.925	.0065	3.557	109.070	66.277	28.687	0.861
517	157.860	69.185	20.253	72.950	.0066	4.052	108.211	67.075	27.548	.841
518	162.027	85.593	20.245	72.978	.0068	4.604	107.931	67.915	26.773	.821
519	167.104	105.862	20.235	73.012	.0069	5.636	108.019	68.882	26.160	.784
520	173.286	130.879	20.222	73.056	.0071	6.818	108.375	69.983	25.635	.758
521	182.885	169.899	20.203	73.125	.0073	7.424	109.089	71.546	25.030	.762
522	190.402	200.537	20.187	73.180	.0074	8.030	109.875	72.662	24.786	.759
523	198.662	233.997	20.170	73.242	.0076	8.631	110.597	73.793	24.489	.759
524	207.168	268.288	20.152	73.306	.0077	8.559	111.373	74.869	24.263	.773
525	215.586	301.941	20.134	73.371	.0078	8.488	112.233	75.857	24.159	.784
601	129.811	37.509	28.740	72.842	.0115	3.266	117.622	60.052	26.746	.776
602	133.528	74.090	28.722	72.885	.0117	4.191	118.258	61.144	26.503	.715
603	137.687	114.969	28.703	72.933	.0119	4.158	119.135	62.301	26.348	.727
604	141.772	154.822	28.683	72.981	.0120	4.123	119.959	63.374	26.208	.738
605	146.114	196.833	28.663	73.032	.0121	4.601	120.928	64.452	26.134	.718
606	150.669	239.909	28.641	73.087	.0123	4.556	121.869	65.517	26.071	.728
607	154.966	279.917	28.621	73.138	.0124	4.084	122.699	66.465	25.983	.764
608	159.013	317.536	28.601	73.187	.0124	4.056	123.490	67.312	25.941	.772
706	128.832	27.695	28.736	72.831	.0114	1.235	116.949	59.755	26.563	1.311
701	130.025	39.312	28.730	72.844	.0115	3.309	117.328	60.116	26.580	0.774
702	134.223	80.690	28.710	72.893	.0117	5.111	118.134	61.342	26.354	.672
703	139.804	135.185	28.684	72.957	.0119	6.140	119.373	62.864	26.197	.647
704	146.427	198.814	28.653	73.036	.0121	7.147	120.813	64.527	26.058	.633
705	153.498	265.658	28.619	73.120	.0123	7.036	122.247	66.147	25.940	.645
801	140.433	41.159	25.920	72.874	.0094	3.443	114.237	63.029	26.569	.800
802	144.299	69.148	25.906	72.911	.0096	4.335	114.672	64.009	26.260	.743
803	148.597	100.417	25.891	72.952	.0097	4.315	115.265	65.040	26.003	.755
804	153.298	134.674	25.874	72.998	.0099	5.247	115.933	66.103	25.769	.717
805	159.026	176.397	25.854	73.054	.0101	6.277	116.864	67.315	25.593	.690
806	165.241	221.439	25.831	73.117	.0103	6.228	117.775	68.534	25.404	.702
807	171.390	265.204	25.809	73.179	.0104	6.159	118.795	69.654	25.335	.712
901	148.563	49.065	23.158	72.904	.0078	3.472	111.380	65.032	27.063	.836
902	152.486	70.121	23.148	72.935	.0079	4.430	111.376	65.924	26.510	.775
903	157.402	96.826	23.135	72.974	.0081	5.460	111.703	66.980	26.056	.736
904	163.303	128.912	23.119	73.023	.0083	6.544	112.244	68.164	25.651	.711
905	170.379	167.584	23.100	73.082	.0085	7.701	113.034	69.475	25.311	.695
906	178.665	212.816	23.077	73.153	.0087	8.963	113.961	70.879	25.001	.684
907	187.541	261.017	23.052	73.231	.0089	8.897	114.947	72.247	24.743	.698
908	196.331	308.226	23.027	73.308	.0090	8.810	115.944	73.483	24.579	.710
1001	108.879	10.276	32.611	72.766	0.0154	2.682	144.011	52.706	37.350	0.691
1002	112.214	60.010	32.588	72.816	.0154	3.998	122.680	54.028	27.778	.670
1003	116.182	118.880	32.560	72.875	.0155	3.956	123.831	55.520	27.617	.683
1004	120.105	175.140	32.533	72.934	.0157	3.913	125.072	56.916	27.568	.695
1005	124.452	236.551	32.503	73.000	.0159	4.807	126.438	58.374	27.472	.658
1006	128.570	293.382	32.475	73.064	.0159	3.930	127.509	59.674	27.404	.711
1007	132.456	345.654	32.449	73.123	.0159	3.884	128.793	60.835	27.405	.720

TABLE 2. *Experimental specific heats* – Continued

ID	T, K	P, atm	Dens. mol/l	V, bmb cm^3	DV_b/DT cm^3/deg	Del T K	DQ/DT J/deg	Tare J/deg	C_v J/M-K	Error percent
1101	120.598	34.060	30.681	72.814	.0134	3.252	119.834	57.086	27.145	.756
1102	124.251	77.714	30.660	72.862	.0134	4.078	120.649	58.308	26.970	.696
1103	130.736	155.031	30.623	72.949	.0137	4.093	122.320	60.329	26.782	.710
1104	134.797	202.264	30.600	73.003	.0138	4.062	123.406	61.504	26.702	.720
1105	138.824	249.075	30.577	73.057	.0139	4.026	124.403	62.605	26.638	.730
1201	56.368	31.319	40.670	72.689	.0266	2.189	136.052	22.495	36.444	.660
1202	58.917	116.769	40.634	72.751	.0268	2.909	133.675	24.309	35.190	.602
1203	57.897	82.169	40.649	72.726	.0267	2.561	133.302	23.565	35.202	.629
1204	60.442	169.884	40.612	72.787	.0269	2.535	134.526	25.387	34.989	.642
1205	62.967	251.014	40.578	72.849	.0271	2.530	135.948	27.159	34.995	.652
1301	62.590	31.232	39.821	72.697	.0253	2.525	135.336	26.896	35.516	.640
1302	65.138	109.378	39.787	72.756	.0255	2.576	132.643	28.668	34.171	.652
1303	67.705	186.200	39.754	72.815	.0256	2.566	132.990	30.429	33.533	.665
1304	70.233	262.996	39.721	72.874	.0257	2.528	134.959	32.130	33.603	.677
1401	68.303	20.551	39.015	72.698	.0241	2.453	139.280	30.699	36.401	.654
1402	70.626	94.552	38.983	72.753	.0242	2.604	131.137	32.391	32.993	.667
1403	73.222	166.234	38.951	72.811	.0243	2.597	132.251	34.092	32.902	.678
1404	75.794	235.407	38.921	72.868	.0244	2.555	133.549	35.733	32.638	.692
1501	72.907	3.541	38.249	72.691	.0229	1.469	148.023	33.888	39.092	.840
1502	74.969	58.588	38.221	72.735	.0229	2.665	129.376	35.211	32.211	.674
1503	77.616	126.868	38.194	72.791	.0230	2.641	130.468	36.867	31.904	.687
1504	80.237	195.252	38.164	72.847	.0231	2.614	131.740	38.458	31.779	.699
1505	82.813	261.059	38.134	72.902	.0232	2.585	133.216	39.975	31.748	.710
1601	80.108	5.857	37.217	72.705	.0214	2.010	146.516	38.381	38.279	.732
1602	82.640	67.258	37.189	72.756	.0214	3.064	128.741	39.872	31.172	.659
1603	85.671	137.879	37.158	72.816	.0215	3.029	130.090	41.596	31.124	.671
1604	89.014	214.296	37.123	72.883	.0216	3.673	131.574	43.420	30.882	.634
1605	92.303	287.554	37.089	72.949	.0217	2.922	132.853	45.136	30.812	.702
1606	95.052	346.307	37.061	73.005	.0218	2.593	133.954	46.516	30.599	.747
1701	89.205	38.784	36.059	72.747	.0198	3.071	127.701	43.522	30.522	.673
1702	92.249	102.328	36.030	72.803	.0198	3.024	128.105	45.110	30.173	.689
1703	95.257	163.556	36.002	72.859	.0199	2.998	129.212	46.617	29.942	.701
1704	98.232	224.501	35.973	72.915	.0200	2.969	130.292	48.047	29.792	.715
1705	100.982	279.569	35.947	72.967	.0200	2.540	131.390	49.318	29.718	.770
1801	95.085	9.674	34.943	72.736	.0182	2.325	143.109	46.532	36.569	.729
1802	97.805	60.228	34.920	72.783	.0183	3.124	125.443	47.845	29.177	.697
1803	100.912	117.381	34.893	72.837	.0183	3.096	126.360	49.286	28.914	.709
1804	103.990	174.180	34.867	72.890	.0184	3.067	127.467	50.653	28.800	.721
1805	107.030	229.235	34.841	72.944	.0185	3.036	128.575	51.946	28.708	.732
1901	102.977	40.081	33.932	72.778	.0170	3.112	124.268	50.210	28.681	.711
1902	106.074	93.034	33.907	72.828	.0170	3.092	124.934	51.546	28.423	.723
1903	109.146	143.256	33.883	72.878	.0171	3.060	126.022	52.814	28.395	.734
1904	112.406	195.782	33.858	72.932	.0172	3.488	127.224	54.102	28.282	.705
1905	115.869	252.214	33.831	72.989	.0174	3.451	128.404	55.406	28.202	.717
3215	129.470	31.078	28.669	72.836	.0114	1.904	117.407	59.949	26.757	1.007
3216	132.006	55.993	28.657	72.865	.0115	3.216	117.856	60.704	26.613	0.788
3217	135.669	91.698	28.639	72.906	.0117	4.166	118.642	61.748	26.466	.721
3218	140.018	134.022	28.619	72.957	.0119	4.589	119.623	62.920	26.350	.706
3219	144.268	175.030	28.599	73.007	.0120	4.567	120.439	64.001	26.202	.716
3220	148.803	217.859	28.578	73.060	.0121	4.566	121.420	65.088	26.146	.724
3221	153.319	259.958	28.556	73.114	.0123	4.528	122.265	66.108	26.029	.734
3222	157.769	301.385	28.535	73.168	.0123	4.456	123.186	67.056	25.998	.744
3301	153.683	40.658	5.268	72.911	.0034	3.974	76.126	66.188	25.789	2.225
3302	157.856	43.222	5.267	72.925	.0035	4.481	76.804	67.074	25.242	2.177
3303	162.538	46.053	5.265	72.942	.0035	5.023	77.530	68.015	24.681	2.146
3304	167.824	49.204	5.264	72.960	.0035	5.670	78.393	69.015	24.324	2.104
3305	175.869	53.924	5.262	72.989	.0036	6.997	79.464	70.420	23.450	2.060
3306	183.525	58.348	5.260	73.016	.0036	8.471	80.576	71.644	23.154	2.000
3307	192.262	63.335	5.257	73.048	.0037	9.183	81.705	72.924	22.756	2.018
3308	292.057	68.848	5.255	73.085	.0037	10.605	82.915	74.233	22.494	1.999
3309	213.082	74.992	5.252	73.126	.0038	12.226	84.166	75.570	22.262	1.986

Appendix B: Excerpts from Reference [7] Section 3.5

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P–V–T, Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 33 MN/m²[*]

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The results of new experimental pressure-volume-temperature measurements on oxygen are presented. The data range in temperature from 54 to 300 K and in pressure from 0.1 to about 33 MN/m². The following properties are tabulated for selected isobars: molar volume, $(\partial P/\partial \rho)_T$, $(\partial P/\partial T)_\rho$, internal energy, enthalpy, entropy, specific heats at constant volume and at constant pressure, and the velocity of sound. Additional tables present the above properties for saturated liquid and vapor, the freezing liquid P–V–T relationship, and the derived Joule-Thomson inversion curve. New values for the critical density and triple point density are presented, and the second and third virial coefficients are tabulated.

Key words: Density; enthalpy; entropy; equation of state; fixed points (PVT); Joule-Thomson; latent heat; melting curve; oxygen; properties of fluids; saturated liquid and vapor; specific heat; vapor pressure; velocity of sound.

List of Symbols and Units

The symbols and units used here are listed below. Values of fixed points and other quantities used here are given where applicable.

R = gas constant; 8.3147 N-m/mol-K (Note: this value differs by less than 1/20000 from the currently accepted best value.)
P = pressure, MN/m².
P_{sat} = vapor pressure.
P_{melt} = melting pressure.
P_c = critical pressure, 5.043 ± .002 MN/m².
P_t = triple point pressure, 152 ± 6 N/m².
V = molar volume, cm³/mol.
T = absolute temperature, Kelvins International Practical Temperature Scale of 1948 where the triple point of water is 273.16 K; below the oxygen boiling point the NBS 1955 temperature scale is used.
T_c = critical temperature, 154.576 ± .010 K.
T_t = triple point temperature, 54.3507 ± .0010K
T_b = boiling point temperature, 90.18 K (90.188 K on the IPTS 1968 scale).
ρ = density, mol/cm³ = 1/V.
ρ_c = critical density, 0.01363 ± .00002 mol/cm³.
ρ_t = liquid triple point density, 0.04083 ± .00004 mol/cm³.
$\rho_{sat\,L}$ = saturated liquid density.
$\rho_{sat\,G}$ = saturated vapor density.
$\rho_{melt\,L}$ = density of the liquid along the liquid-solid boundary.
ρ_1 = a selected density in the compressed liquid, 0.028687 mol/cm³.
A_i = generalized coefficients in approximating equations; numerical values given in tables.
$B(T)$ = second virial coefficient, cm³/mol.
$C(T)$ = third virial coefficient, (cm³/mol)².
$C_v(T, \rho)$ = heat capacity at constant volume, J/mol K $C_v^\circ(T)$ heat capacity of the ideal gas.
$C_p(T, \rho)$ = heat capacity at constant pressure, J/mol K.
C_{sat} = heat capacity of the saturated liquid, J/mol K.
$S(T, \rho)$ = entropy, J/mol K.
$H(T, \rho)$ = enthalpy, J/mol.
$U(T, \rho)$ = internal energy, J/mol.
W = velocity of sound, m/s.
Molecular Weight = 31.9988 g.

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1. Introduction

The importance of oxygen in the U.S. space program and the lack of comprehensive and accurate data for many of its physical properties have led to an extensive research program at the NBS Institute for Basic Standards. The results of part of that program are presented here in the form of extensive tables of P–V–T data and derived thermodynamic properties.

Prior to 1960 there were relatively few measurements of the P–V–T properties of oxygen at low temperatures. This condition was especially true for the compressed liquid. In 1960 and 1961 Timrot and Borisoglebskii [1, 2][1] and Van Itterbeek and Verbeke [3, 4] published new P–V–T results for the liquid. However, these results were limited in scope and there was disagreement in the region in which they overlapped.

The results of the present investigation consist of approximately 1500 P–V–T points at 111 different densities varying from 0.0047 to 3 times the critical density. This constitutes approximately two-thirds of all the P–V–T data published for oxygen.

The data range from the triple point temperature to 300 K for the high densities and from 85 K to 300 K for the low (subcritical) density points. The data range in pressure up to about 33 MN/m^2.

The highest and lowest density data were represented by two analytic surfaces while the intermediate densities were fitted to a large number of isotherm polynomials. Second and third virial coefficients were extracted from the low density data.

This representation of the P–V–T surface together with the specific heat of the ideal gas [5] allowed the calculation of thermodynamic properties of the gas at temperatures below critical and of all densities at temperatures above critical. Thermodynamic calculations for the compressed liquid at subcritical temperatures made use of additional data in the form of new experimental determinations of the heat capacity at constant volume [6] and heat capacity of the saturated liquid [7] from this laboratory.

The properties calculated using this smoothed surface are compared with some of the P–V–T and thermodynamic property data from the literature.

Due to limitations of space only skeleton tables of thermodynamic properties are presented here. A more complete set of tables will be issued as NBS Tech. Note 384.

2. Experimental P–V–T Measurements

2.1. Apparatus

The cryostat designed and described by Goodwin [8] was used with minor modifications. These modifications are listed below in terms of the nomenclature used in reference [8]. Early vapor pressure measurements yielded results which were lower than published values by 4000 to 6000 N/m^2, indicating the presence of a cold spot in the stainless steel transition capillary which connects the sample holder to the top of the cryostat. Jacketing the capillary with $\frac{1}{8}$ in OD copper tubing removed this difficulty. For the high temperature ($T > 150$ K) portion of the measurements the shield, shown in figure 2 of reference [8], was replaced with one that completely surrounded the sample holder thereby reducing heat losses to the cold wall. For measurements above 200 K the only refrigerant used was the liquid nitrogen in the open dewar surrounding the cryostat. The oil operated dead-weight gage pressure measuring system was modified, as shown in figure 1 here, for safety. Two null pressure detectors were used. The first separated the oil in the gage from an intermediate nitrogen gas system. The second separated the nitrogen from the oxygen sample. Thus in the event of a diaphragm failure there was no chance of high pressure oxygen coming in contact with the oil.

With practice the two-diaphragm system could be operated with as much sensitivity as the one diaphragm system in reference [8]. All external capillary lines, valves, and gages were cleaned by flushing with liquid Freon. Repairs to several of the glass flasks in the gasometer system necessitated recalibration of these volumes. The 1-liter flask, which was the primary standard of volume, was calibrated by weighing with water and agreed with the original calibration by Goodwin [8] to within 0.02 percent. The 2- and 6-liter flasks were calibrated by both water weighing and by gas expansion from the 1-liter flask. These two independent determinations agreed to better than one part in ten thousand in each case. The 21-liter flask was calibrated by gas expansion only, with an estimated uncertainty of 0.04 percent. The volume of the sample holder was recalibrated by gas expansion into the 1- and 2-liter flasks. The volume obtained was 25.852 ± 0.015 cm^3 in good agreement with the earlier measurements, by weighing with water, of reference [8].

The relationship used to calculate the elastic stretching of the sample holder due to pressure was modified to correspond more closely to experimental results on similar thick walled vessels [9]. Thus, eq (5.2–7) of reference [8] was modified to become

$$V/V_o = 1 + a\,[1 + 4.35 \cdot 10^{-4}\,T] \cdot P, \qquad (1)$$

with $a = 2.3 \times 10^{-5}$ m^2/MN. This modification changed the calculated densities by 0.04 percent at 30 MN/m^2. A quartz bourdon gage with a sensitivity of 7 N/m^2 was used to measure the pressure in the gasometer flasks for the density determinations.

The estimated relative error in the measured pressures is 0.01 percent, increasing somewhat at the lower pressures. Corrections were made for the hydrostatic pressure of the oxygen in the capillaries, which often amounted to several thousandths of a MN/m^2. Temperature readings may deviate from the thermometer calibration by 2 millidegrees at 50 K, increasing to 28 millidegrees at 300 K, due to the specifications of the potentiometer used. The uncertainty of the calibration itself is probably less than 0.002 K. To this must be added the deviations of the International Practical

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

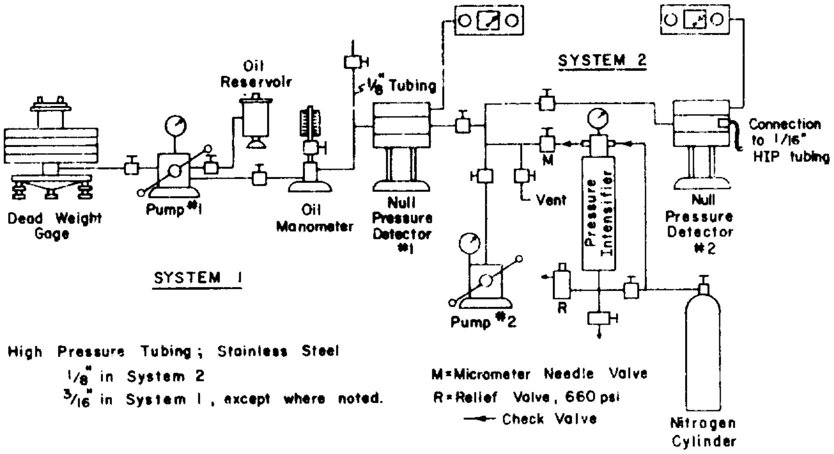

FIGURE 1. *Dead weight gage pressure measuring system.*

Temperature Scale (1948) from the thermodynamic temperature scale, perhaps as much as 0.04 K. With this apparatus, however, temperatures are reproducible to within 1 millidegree. Uncertainty in the density determinations is estimated at 0.1 percent for low pressures, increasing to 0.14 percent at the highest pressures. A precision of the order of 0.025 percent in density has been realized.

The samples used came from commercially available cylinders of ultra pure oxygen with a nominal purity of 99.99 percent and were passed through a molecular sieve trap at 76 K to remove water.

2.2 The Data

The measuring technique used here is the modified Reichsanstalt method described by Goodwin [8]. The data were taken along experimental pseudo-isochores, hereafter referred to as runs. Due to the precisely reproducible nature of the temperature control system, data on the various runs were measured at the same temperatures and therefore, could be rearranged into isotherms at the conclusion of the experimental work. Data were taken at integral temperatures with 2 K spacing from 56 K to 160 K, 5 K spacing from 160 K to 200 K, and 10 K spacing from 200 K to 300 K. In the low density gas phase a 5 K spacing was used between 85 K and 150 K.

For convenience the data may be divided chronologically into four series. Table 1 shows the distribution of the data between the series. Between Series I and II certain changes were made in the apparatus which necessitated recalibration of some of the volumes external to the cryostat. Between Series II and III the apparatus was moved to a new building and most of the external volumes were rebuilt. Series IV differed from the others by the way in which the density and pressure were determined.

The data were checked for systematic deviations between Series I, II, and III in the following way. Isotherm polynomials were fitted to the data in the regions where the data of different series overlapped. The deviations of all points in a series, expressed as percent error in density, were averaged. The results showed that the internal precision within each series was good (0.015 to 0.025 percent). However, while Series I and III were in agreement, the data of Series II differed systematically by an average of 0.066 percent in density. The origin of this difference is not clear. However, since the smoothness of the P–V–T surface is of utmost importance in the calculation of thermodynamic properties, the densities of the data of Series II were arbitrarily multiplied by 1.00066. This difference falls within the estimated overall uncertainty of the data.

TABLE 1. *Four series of experimental runs*

Series	No. of data points	Run No.
I	239	33–51
II	922	53–108
III	275	109–137
IV	67	138–145

Series IV consisted of data in the very low density ($0.0047 \leq \rho/\rho_c \leq 0.14$) gas phase between 85 K and 150 K. Pressures were measured with a quartz bourdon gage. Densities were too low for the use of the gasometer and were extracted from the measured pressure at 160 K, using virial coefficients obtained from the data of Series II and III.

The single-phase experimental P–V–T data are presented in table 2. The column labeled "IDENT" contains the identification number of each point. The first two or three digits are the number of the run or experimental isochore and the last two are the number of the point. The entries in runs 132 and 133 which contain no value for the density are pressures measured on the melting curve. In addition some pressures were measured along the vapor pressure curve. They are given in table 3 and were used mainly as a check on the vapor pressure curve taken from the literature. Because of the rather large vertical dimensions of the apparatus no attempt was made to take data in close proximity to the critical point.

$$H(T,\rho)=H(T,\rho_1)+\int_{\rho_1}^{\rho}[P-T(\partial P/\partial T)_\rho]/\rho^2 d\rho$$
$$+P(T,\rho)/\rho-P(T,\rho_1)/\rho_1, \qquad (20)$$

$$S(T,\rho)=S(T,\rho_1)-\int_{\rho_1}^{\rho}[(\partial P/\partial T)_\rho/\rho^2]d\rho, \qquad (21)$$

$$C_v(T,\rho)=C_v(T,\rho_1)-T\int_{\rho_1}^{\rho}[(\partial^2 P/\partial T^2)_\rho/\rho^2]d\rho. \qquad (22)$$

For the compressed liquid at temperatures less than 128 K the properties of the saturated liquid at 128 K ($\rho=\rho_1$) serve as the starting point. First the changes with temperature are computed along the saturation line:

$$H(T,\rho_{\mathrm{sat}L})=H(128,\rho_{\mathrm{sat}L})$$
$$+\int_{128}^{T}C_{\mathrm{sat}}dT+\int_{P_{\mathrm{sat}}(128)}^{P_{\mathrm{sat}}(T)}(1/\rho_{\mathrm{sat}L})dP, \qquad (23)$$

$$S(T,\rho_{\mathrm{sat}L})=S(128,\rho_{\mathrm{sat}L})+\int_{128}^{T}(C_{\mathrm{sat}}/T)dT, \qquad (24)$$

and

$$C_v(T,\rho_{\mathrm{sat}L})=C_{\mathrm{sat}}(T)+\frac{T}{\rho^2_{\mathrm{sat}L}}\left(\frac{d\rho_{\mathrm{sat}L}}{dT}\right)\left(\frac{\partial P}{\partial T}\right)_\rho. \qquad (25)$$

Next the isothermal changes are computed using eqs (20, 21, 22) and substituting $\rho_{\mathrm{sat}L}(T)$ in place of ρ_1.

The internal energy and heat capacity at constant pressure are computed from

$$U(T,\rho)=H(T,\rho)-P/\rho, \qquad (26)$$

and

$$C_p(T,\rho)=C_v(T,\rho)+(T/\rho^2)(\partial P/\partial T)^2_\rho/(\partial P/\partial\rho)_T. \qquad (27)$$

Two other quantities have been calculated. The velocity of sound, W, is given by the relation

$$W=((C_p/C_v)(\partial P/\partial\rho)_T)^{1/2}, \qquad (28)$$

and the Joule-Thomson inversion curve may be defined by the locus of points where

$$T(\partial P/\partial T)_\rho=\rho(\partial P/\partial\rho)_T. \qquad (29)$$

3.2. Results

Tables 13 and 14 present the results of all calculations on the saturation boundary and on selected isobars respectively. The terms isochore and isotherm derivative refer to $(\partial P/\partial T)_\rho$ and $(\partial P/\partial\rho)_T$ respectively.

The derived Joule-Thomson inversion curve is given in table 15, where δP is the uncertainty in the inversion pressure calculated from an assumed 1 percent error in either the isotherm or the isochore derivative.

Figure 5 illustrates the variation of C_p with temperature along several isobars, and Figure 6 shows the variation of C_v with density along several isotherms.

3.3. Estimate of Uncertainties in the Derived Properties

Probably the best estimate of the uncertainties in the derived properties is obtained through comparisons with experimental values for these properties published in the literature. Unfortunately, these measurements are often either nonexistent or limited in scope.

Because of the rather roundabout process, detailed in section 3.1, used to obtain the enthalpy of the liquid, it is desirable to make a comparison with liquid enthalpies obtained by other methods. This is best done by comparing heats of vaporization from various sources, in table 16. Here the second column is the difference between the enthalpies of the vapor and liquid states taken from table 13, while column four contains the change in enthalpy calculated using the Clapeyron equation. The values from reference [11]

TABLE 13. *Thermodynamic properties of oxygen on the saturation boundaries.**

T	P	V	$\left(\frac{\partial P}{\partial\rho}\right)_T$	$\left(\frac{\partial P}{\partial T}\right)_\rho$	Internal Energy	Enthalpy	Entropy	C_v	C_p	Vel. of Sound
K	MN/m²	cm³/mol	J/mol	MN/m²-K	J/mol	J/mol	J/mol-K	J/mol K	J/mol-K	m/s
54.3507	0.00015	24.49	28792	3.945	-6189.6	-6189.6	67.00	35.65	53.27	1159
54.3507	0.00015	2974819.07	452	0.000	1120.0	1571.8	209.44	20.81	29.13	141
56	0.00025	24.63	28001	3.849	-6101.7	-6101.7	68.59	35.29	53.26	1149
56	0.00025	1876345.27	465	0.0000	1154.2	1619.7	206.23	20.81	29.13	143
58	0.00043	24.80	27058	3.736	-5995.2	-5995.2	70.46	34.86	53.25	1136
58	0.00043	1111925.72	482	0.0000	1195.6	1677.6	202.60	20.81	29.14	145
60	0.00073	24.97	26134	3.624	-5888.7	-5888.7	72.27	34.45	53.25	1124
60	0.00073	683074.11	498	0.0000	1237.0	1735.5	199.26	20.81	29.15	148
62	0.00119	25.14	25228	3.516	-5782.2	-5782.2	74.01	34.06	53.26	1110
62	0.00119	433699.56	514	0.0000	1278.2	1793.2	196.16	20.82	29.16	150
64	0.00187	25.32	24341	3.410	-5675.7	-5675.6	75.70	33.67	53.27	1097
64	0.00187	283821.73	530	0.0000	1319.3	1850.6	193.29	20.82	29.18	152

TABLE 13. *Thermodynamic properties of oxygen on the saturation boundaries.*[a] — Continued

T K	P MN/m²	V cm³/mol	$\left(\frac{\partial P}{\partial \rho}\right)_T$ J/mol	$\left(\frac{\partial P}{\partial T}\right)_\rho$ MN/m²-K	Internal Energy J/mol	Enthalpy J/mol	Entropy J/mol-K	C_v J/mol-K	C_p J/mol-K	Vel. of Sound m/s
66	0.00287	25.50	23471	3.306	-5569.1	-5569.0	77.34	33.30	53.29	1083
66	0.00287	190960.14	546	0.0000	1360.2	1907.7	190.63	20.83	29.21	155
68	0.00428	25.69	22619	3.205	-5462.5	-5462.4	78.94	32.94	53.31	1070
68	0.00428	131788.10	562	0.0001	1400.9	1964.5	188.16	20.84	29.25	157
70	0.00623	25.87	21784	3.106	-5355.9	-5355.7	80.48	32.59	53.34	1056
70	0.00623	93094.99	577	0.0001	1441.2	2020.9	185.87	20.85	29.30	159
72	0.00886	26.07	20966	3.009	-5249.2	-5248.9	81.98	32.26	53.38	1041
72	0.00886	67181.69	592	0.0001	1481.2	2076.6	183.73	20.87	29.35	161
74	0.01236	26.26	20164	2.914	-5142.4	-5142.0	83.45	31.93	53.43	1027
74	0.01236	49440.13	607	0.0002	1520.8	2131.8	181.74	20.89	29.43	163
76	0.01691	26.47	19379	2.822	-5035.5	-5035.0	84.87	31.61	53.49	1012
76	0.01691	37043.15	621	0.0002	1560.0	2186.2	179.86	20.91	29.51	165
78	0.02273	26.67	18610	2.732	-4928.5	-4927.9	86.26	31.31	53.56	997
78	0.02273	28215.79	634	0.0003	1598.5	2239.8	178.14	20.95	29.62	167
80	0.03006	26.88	17857	2.644	-4821.3	-4820.5	87.62	31.01	53.64	982
80	0.03006	21819.46	647	0.0004	1636.5	2292.5	176.51	20.98	29.74	169
82	0.03918	27.10	17119	2.557	-4714.0	-4713.0	88.94	30.73	53.73	967
82	0.03918	17109.05	659	0.0005	1673.8	2344.1	174.98	21.03	29.89	171
84	0.05036	27.32	16397	2.473	-4606.6	-4605.2	90.24	30.45	53.84	952
84	0.05036	13587.75	670	0.0006	1710.3	2394.5	173.54	21.08	30.06	173
86	0.06391	27.55	15689	2.391	-4498.9	-4497.1	91.50	30.18	53.96	936
86	0.06391	10918.43	680	0.0008	1745.9	2443.7	172.18	21.13	30.25	174
88	0.08015	27.78	14997	2.311	-4391.0	-4388.8	92.74	29.92	54.10	921
88	0.08015	8868.59	690	0.0010	1780.7	2491.5	170.90	21.20	30.49	176
90	0.09943	28.02	14319	2.232	-4282.8	-4280.1	93.96	29.67	54.26	905
90	0.09943	7275.38	698	0.0012	1814.5	2537.9	169.68	21.28	30.74	178
92	0.12210	28.27	13655	2.156	-4174.4	-4171.0	95.15	29.42	54.44	889
92	0.12210	6023.11	706	0.0014	1847.2	2582.6	168.53	21.36	31.04	179
94	0.14852	28.52	13005	2.081	-4065.7	-4061.4	96.32	29.18	54.64	872
94	0.14852	5028.47	712	0.0017	1878.8	2625.6	167.43	21.45	31.37	180
96	0.17909	28.79	12370	2.008	-3956.6	-3951.4	97.47	28.95	54.87	856
96	0.17909	4230.71	717	0.0021	1909.2	2666.8	166.38	21.56	31.73	182
98	0.21420	29.06	11748	1.936	-3847.1	-3840.9	98.60	28.73	55.13	839
98	0.21420	3585.00	721	0.0024	1938.2	2706.2	165.38	21.68	32.14	183
100	0.25425	29.34	11139	1.866	-3737.2	3729.7	99.71	28.51	55.42	823
100	0.25425	3057.86	723	0.0029	1966.0	2743.4	164.42	21.80	32.60	184
102	0.29965	29.63	10544	1.797	-3626.8	-3617.9	100.81	28.30	55.74	806
102	0.29965	2624.08	724	0.0034	1992.3	2778.6	163.49	21.94	33.11	185
104	0.35083	29.93	9961	1.731	-3515.8	-3505.3	101.88	28.10	56.10	788
104	0.35083	2264.42	724	0.0040	2017.1	2811.5	162.60	22.09	33.68	186
106	0.40822	30.24	9392	1.665	-3404.3	-3392.0	102.95	27.90	56.51	771
106	0.40822	1964.12	722	0.0046	2040.3	2842.1	161.74	22.26	34.30	187
108	0.47226	30.57	8836	1.601	-3292.1	-3277.7	104.00	27.71	56.96	753
108	0.47226	1711.70	719	0.0053	2061.8	2870.1	160.91	22.44	34.99	187
110	0.54339	30.90	8292	1.538	-3179.2	-3162.4	105.03	27.52	57.47	736
110	0.54339	1498.21	714	0.0062	2081.5	2895.6	160.10	22.63	35.76	188

TABLE 13. *Thermodynamic properties of oxygen on the saturation boundaries.** – Continued

T K	P MN/m^2	V cm^3/mol	$\left(\frac{\partial P}{\partial \rho}\right)_T$ J/mol	$\left(\frac{\partial P}{\partial T}\right)_\rho$ MN/m^2-K	Internal Energy J/mol	Enthalpy J/mol	Entropy J/mol-K	C_v J/mol-K	C_p J/mol-K	Vel. of Sound m/s
112	0.62207	31.26	7761	1.476	-3065.5	-3046.0	106.06	27.34	58.05	718
112	0.62207	1316.57	708	0.0071	2099.4	2918.4	159.31	22.83	36.61	188
114	0.70876	31.63	7242	1.415	-2950.9	-2928.5	107.08	27.16	58.70	699
114	0.70876	1161.16	700	0.0081	2115.2	2938.2	158.53	23.05	37.55	189
116	0.80391	32.02	6736	1.356	-2835.2	-2809.5	108.09	26.99	59.43	681
116	0.80391	1027.49	690	0.0093	2129.0	2955.0	157.78	23.28	38.59	189
118	0.90801	32.42	6242	1.297	-2718.5	-2689.1	109.09	26.83	60.25	662
118	0.90801	911.95	678	0.0106	2140.6	2968.6	157.03	23.52	39.75	189
120	1.0215	32.85	5760	1.239	-2600.5	-2566.9	110.08	26.67	61.19	643
120	1.0215	811.59	664	0.0120	2149.8	2978.8	156.30	23.78	41.04	189
122	1.1450	33.31	5292	1.182	-2481.1	-2442.9	111.07	26.53	62.27	623
122	1.1450	724.02	649	0.0137	2156.4	2985.4	155.57	24.06	42.49	189
124	1.2788	33.79	4836	1.126	-2360.1	-2316.8	112.06	26.39	63.49	603
124	1.2788	647.27	631	0.0155	2160.3	2988.0	154.85	24.35	44.13	189
126	1.4236	34.31	4394	1.070	-2237.3	-2188.4	113.05	26.26	64.91	583
126	1.4236	579.72	612	0.0176	2161.2	2986.4	154.12	24.65	45.99	189
128	1.5797	34.86	3965	1.015	-2112.4	-2057.3	114.04	26.15	66.56	562
128	1.5797	520.03	590	0.0199	2158.8	2980.3	153.40	24.97	48.12	188
130	1.7478	35.45	3688	0.987	-1984.8	-1922.9	115.03	26.60	69.77	550
130	1.7478	467.05	565	0.0224	2153.0	2969.3	152.68	25.31	50.60	188
132	1.9284	36.09	3314	0.924	-1853.9	-1784.3	116.04	26.48	70.79	526
132	1.9284	419.84	538	0.0254	2143.1	2952.7	151.94	25.68	53.48	187
134	2.1219	36.79	2849	0.868	-1719.9	-1641.8	117.06	26.37	74.38	501
134	2.1219	377.60	509	0.0287	2128.8	2930.0	151.19	26.06	56.90	186
136	2.3291	37.55	2472	0.811	-1582.5	-1495.0	118.09	26.30	77.32	477
136	2.3291	339.63	478	0.0324	2109.4	2900.5	150.42	26.47	61.03	186
138	2.5504	38.40	2100	0.752	-1441.1	-1343.2	119.14	26.30	81.14	450
138	2.5504	305.34	443	0.0368	2084.2	2862.9	149.63	26.90	66.14	185
140	2.7866	39.35	1745	0.696	-1295.0	-1185.4	120.21	26.38	86.51	423
140	2.7866	274.21	406	0.0418	2052.0	2816.1	148.80	27.38	72.63	183
142	3.0383	40.43	1419	0.640	-1143.0	-1020.1	121.31	26.52	93.59	396
142	3.0383	245.75	365	0.0476	2011.3	2757.9	147.92	27.89	81.18	182
144	3.3064	41.68	1124	0.589	-983.4	-845.6	122.45	26.73	103.86	369
144	3.3064	219.53	320	0.0545	1959.8	2685.6	146.98	28.48	93.04	181
146	3.5918	43.17	875	0.532	-813.9	-658.9	123.66	27.06	114.99	341
146	3.5918	195.08	270	0.0630	1894.0	2594.7	145.95	29.14	110.71	179
148	3.8955	44.99	613	0.476	-630.4	-455.2	124.95	27.54	138.37	310
148	3.8955	171.89	215	0.0737	1807.8	2477.4	144.77	29.95	140.18	177
150	4.2190	47.38	391	0.419	-425.1	-225.2	126.39	28.28	179.31	278
150	4.2190	149.13	153	0.0881	1688.2	2317.4	143.35	31.01	200.53	176
152	4.5638	50.90	194	0.353	-179.5	52.7	128.12	29.94	283.23	240
152	4.5638	126.20	84	0.109	1512.3	2088.2	141.52	33.36	373.23	171
154	4.9320	58.46	26	0.267	200.0	488.4	130.84	33.30	1478.52	190
154	4.9320	97.80	17	0.149	1165.1	1647.5	138.37	37.02	1962.81	167
154.576	5.0427	73.37		0.200	662.3	1032.2	134.32			
154.576	5.0427	73.37		0.200	662.3	1032.2	134.32			

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*The first entry for each temperature refers to the liquid phase.

TABLE 14. *Thermodynamic properties of oxygen.* – Continued

30 MN/m² Isobar

T K	V cm³/mol	$\left(\frac{\partial P}{\partial \rho}\right)_T$ J/mol	$\left(\frac{\partial P}{\partial T}\right)_\rho$ MN/m²·K	Internal Energy J/mol	Enthalpy J/mol	Entropy J/mol·K	C_v J/mol·K	C_p J/mol·K	Vel. of Sound m/s
*57.720	24.17	32404	3.970	-6135.9	-5410.8	67.88	35.87	52.27	1215
58	24.19	32280	3.955	-6121.8	-5396.2	68.13	35.82	52.26	1213
60	24.33	31406	3.847	-6021.7	-5291.7	69.90	35.45	52.19	1202
62	24.48	30551	3.742	-5921.8	-5187.4	71.61	35.09	52.12	1191
64	24.63	29714	3.640	-5822.0	-5083.2	73.26	34.75	52.05	1179
66	24.78	28897	3.540	-5722.4	-4979.2	74.86	34.42	51.99	1168
68	24.93	28096	3.442	-5623.1	-4875.3	76.41	34.11	51.92	1156
70	25.08	27316	3.347	-5523.9	-4771.5	77.92	33.80	51.86	1144
72	25.24	26553	3.255	-5424.9	-4667.8	79.38	33.51	51.80	1133
74	25.39	25807	3.165	-5326.0	-4564.3	80.80	33.22	51.74	1121
76	25.55	25078	3.077	-5227.4	-4460.8	82.18	32.95	51.68	1109
78	25.71	24365	2.991	-5128.9	-4357.5	83.52	32.68	51.62	1097
80	25.88	23670	2.908	-5030.6	-4254.3	84.82	32.43	51.56	1085
82	26.04	22991	2.827	-4932.5	-4151.2	86.10	32.18	51.51	1072
84	26.21	22327	2.748	-4834.6	-4048.3	87.34	31.94	51.45	1060
86	26.38	21680	2.671	-4736.8	-3945.4	88.55	31.71	51.40	1048
88	26.55	21047	2.597	-4639.2	-3842.6	89.73	31.48	51.36	1036
90	26.73	20430	2.524	-4541.8	-3739.9	90.88	31.26	51.31	1024
92	26.91	19820	2.454	-4444.5	-3637.3	92.01	31.04	51.26	1012
94	27.09	19240	2.385	-4347.4	-3534.8	93.11	30.83	51.22	999
96	27.27	18667	2.319	-4250.5	-3432.4	94.19	30.62	51.18	987
98	27.46	18108	2.254	-4153.7	-3330.1	95.25	30.42	51.15	975
100	27.64	17562	2.191	-4057.1	-3227.8	96.28	30.21	51.11	964
102	27.84	17030	2.131	-3960.7	-3125.6	97.29	30.01	51.08	952
104	28.03	16511	2.072	-3864.4	-3023.5	98.28	29.81	51.05	940
106	28.23	16005	2.014	-3768.3	-2921.4	99.26	29.61	51.02	926
108	28.43	15512	1.959	-3672.4	-2819.4	100.21	29.40	51.00	917
110	28.64	15031	1.905	-3576.6	-2717.4	101.14	29.19	50.98	906
112	28.85	14562	1.853	-3481.0	-2615.5	102.06	28.97	50.95	895
114	29.06	14105	1.803	-3385.5	-2513.6	102.97	28.75	50.93	884
116	29.28	13660	1.754	-3290.2	-2411.7	103.85	28.52	50.91	873
118	29.50	13227	1.706	-3195.0	-2309.9	104.72	28.29	50.90	862
120	29.73	12804	1.660	-3100.0	-2208.1	105.58	28.04	50.88	852
122	29.96	12393	1.616	-3005.2	-2106.3	106.42	27.77	50.86	842
124	30.20	11992	1.573	-2910.5	-2004.5	107.25	27.50	50.83	832
126	30.44	11602	1.532	-2816.0	-1902.7	108.06	27.21	50.81	823
128	30.69	11223	1.491	-2721.6	-1801.0	108.86	26.90	50.79	814
130	30.94	10917	1.450	-2626.1	-1697.9	109.66	27.43	51.41	800
132	31.20	10519	1.407	-2530.7	-1594.8	110.45	27.35	51.53	787
134	31.46	10272	1.389	-2434.4	-1490.5	111.23	27.26	52.19	784
136	31.73	9873	1.337	-2338.9	-1387.0	112.00	27.17	51.96	768
138	32.01	9515	1.297	-2243.3	-1283.1	112.76	27.07	52.08	756
140	32.29	9174	1.263	-2147.5	-1178.8	113.51	26.97	52.34	746
142	32.58	8878	1.233	-2051.3	-1073.8	114.25	26.86	52.69	738
144	32.87	8523	1.168	-1956.3	-970.1	114.98	26.76	51.68	717
146	33.18	8180	1.158	-1860.2	-864.9	115.70	26.64	52.98	713
148	33.49	7933	1.127	-1763.9	-759.1	116.42	26.52	53.10	705
150	33.82	7660	1.090	-1668.0	653.5	117.13	26.40	53.03	693
152	34.14	7398	1.053	-1572.4	-548.1	117.83	26.27	52.82	682
154	34.48	7145	1.035	-1476.4	-441.9	118.52	26.14	53.59	677
156	34.83	6844	0.9967	-1380.8	-336.0	119.21	26.01	53.48	663
158	35.18	6674	0.9615	-1285.2	-229.7	119.88	25.90	52.99	653
160	35.54	6372	0.9238	-1190.3	-124.1	120.55	26.41	53.47	635
165	36.49	5863	0.8693	-948.6	146.3	122.21	25.99	54.32	619
170	37.51	5402	0.8055	-707.3	418.0	123.83	25.86	54.59	597
175	38.59	4974	0.7465	-466.3	691.5	125.42	25.79	54.98	576
180	39.74	4569	0.6894	-226.1	966.1	126.97	25.69	55.26	554
185	40.97	4233	0.6380	13.3	1242.3	128.48	25.54	55.40	536
190	42.27	3927	0.5910	251.2	1519.3	129.96	25.34	55.54	519
195	43.65	3665	0.5471	486.6	1796.1	131.40	25.10	55.44	503
200	45.11	3431	0.5076	718.8	2072.2	132.79	24.81	55.38	489
210	48.26	3096	0.4379	1172.7	2620.6	135.47	24.31	54.60	466
220	51.66	2888	0.3794	1610.2	3160.0	137.98	23.98	53.24	448
230	55.28	2741	0.3333	2029.0	3687.4	140.32	23.68	52.16	434
240	59.05	2693	0.2948	2429.8	4201.2	142.51	23.45	50.46	426
250	62.88	2692	0.2627	2809.8	4696.3	144.53	23.22	48.56	420
260	66.77	2701	0.2367	3170.8	5173.8	146.41	22.97	47.02	416
270	70.67	2745	0.2148	3514.9	5635.0	148.15	22.71	45.37	414
280	74.57	2816	0.1970	3844.3	6081.3	149.77	22.46	43.93	415
290	78.44	2908	0.1819	4160.3	6513.6	151.29	22.23	42.53	417
300	82.28	3005	0.1690	4464.0	6932.3	152.71	22.00	41.30	420

*Two-phase boundary.

APPENDIX C: Preliminary Proposal: Thermodynamic Property Measurements on Compressed Gaseous and Liquid Helium

Helium is a fluid with physical properties such as a very low boiling point and low solubility in other fluids which make it unique for many aerospace applications. There is also a promising future for devices and systems which operate at low temperatures attainable with helium refrigeration. The acceptance of applications involving helium is currently limited more by economic considerations rather than technical practicality. One of the most important factors in achieving a more favorable economic situation is the availability of accurate wide-range engineering design data for compressed gaseous and liquid helium. It is apparent that there are serious uncertainties in the best available thermodynamic property data for helium† and that these uncertainties must be significantly reduced to obtain optimum efficiency and economy required for anticipated developments in helium technology.

Extensive thermodynamic property data for compressed gaseous and liquid helium-4 were first computed by D. B. Mann of the NBS Cryogenics Division in 1962 [1,2]. He tabulated derived values of the density, enthalpy, entropy and internal energy at temperatures between 3 and 300 K and pressures to 100 atm. R. D. McCarty of the NBS Cryogenics Division has recently completed a more extensive and accurate correlation of helium thermodynamic property data in the temperature range 2-1500 K at pressures to 1000 atm [3]. McCarty's report includes tabulations of the specific heats and sound velocities as well as properties of the liquid and vapor at equilibrium. His work incorporates significant improvements in equation of state and property data analysis in addition to several important sets of property measurements which have become available since D. B. Mann's report. The PVT data of Hill and Lounasmaa [4] are the basis for both correlations in the compressed fluid region.

McCarty's property tables are limited by some important remaining gaps and inconsistencies in the measurements. Among the most important of these are:

1) uncertainties in the temperature scale: Most previous measurements have been made on poorly documented temperature scales or on the erroneous helium vapor pressure scale which extends only to helium critical temperature.
2) irreconcilable inconsistencies between the PVT data of Hill and Lounasmaa [4] and the liquid-vapor equilibrium property data of all other workers.
3) irreconcilable inconsistencies between the compressed fluid PVT data of Hill and Lounasmaa and the compressed fluid PVT data of Glassford and Smith [5] in

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† See "Need for New Experimental Measurements" in Section 2.6 Item F describing the task on "Correlation of the Thermodynamic Properties of Helium".

the region of overlap.

4) a complete gap in the existing data at temperatures between 20 and 70 K at pressures to 1000 atm.

In 1970 the NBS Cryogenics Division initiated an experimental program to remedy all of the most important deficiencies noted above. The goal of this program is to provide the accurate closely-spaced PVT and specific heat (C_v) measurements needed for engineering design calculations in the most important temperature and pressure ranges (2-70 K at pressures to 350 atm). This is a particularly opportune time to perform such measurements because of the following factors:

1. The availability of germanium and platinum resistance thermometers calibrated on the new NBS acoustical thermometer scale [6] at temperatures below 20 K and on the IPTS-68 scale [7] at temperatures above 13.8 K. These scales are now well documented and are much closer to the "thermodynamic temperature scale" than previous practical temperature scales.
2. Extensive development of methods for accurate property measurements and thermodynamic property analysis at the NBS Cryogenics and Heat Divisions [8-13].

This program was supported initially by a one year contract with the NASA Office of Advanced Research and Technology (R-46 Contract). OART support for this undertaking expired November 1, 1970. During the year, financial support was sought from a number of agencies:

1. The NASA centers, particularly Marshall Spaceflight Center and Lewis Research Center.
2. The National Bureau of Standards.
3. The Helium Society and several industrial helium producers.
4. The Atomic Energy Commission was carefully considered but not formally approached.

Funds have not been forthcoming from any of these agencies. It is hoped that NASA-OART support will be reconsidered to enable continuation of this most important program.

References

1. Mann, D. B., The Thermodynamic Properties of Helium from 3 to 300 K Between 0.5 and 100 Atmospheres, NBS Technical Note 154 (January 1962).

2. Mann, D. B., Properties of Helium, Chapter 2 in Technology of Liquid Helium, NBS Monograph 111 (October 1968).

3. McCarty, R. D., Provisional Thermodynamic Properties of Helium-4 at Temperatures from 2 to 1500 K and Pressures to 100 MN/m^2 (1000 atm), NBS Report 9762 to NASA (to appear late 1970).

4. Hill, R. W., and Lounasmaa, O. V., The Thermodynamic Properties of Fluid Helium, Trans. Roy Soc. (London) 252A, 357 (1960).

5. Glassford, A. P. M., and Smith, J. L. Jr., Pressure-Volume-Temperature and Internal Energy Data for Helium from 4.2 to 20 K between 100 and 1300 atm, Cryogenics, 6, 193 (1966).

6. Plumb, H. and Cataland, G., Acoustical Thermometer and the NBS Provisional Temperature Scale, Metrologia 2, 127 (1966).

7. The International Practical Temperature Scale of 1968, Metrologia 5, 35 (1969).

8. Roder, H. M., Weber, L. A., and Goodwin, R. D., Thermodynamic and Related Properties of Parahydrogen from the Triple Point to 100 K at Pressures to 340 Atm, NBS Monograph 94 (1965).

9. Weber, L. A., PVT, Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 33 MN/m^2, J. Res. Natl. Bur. Standards 74A, 93 (1970).

10. Prydz, R. and Straty, G. C., Thermodynamic Properties of Compressed Gaseous and Liquid Fluorine, NBS Technical Note 392 (in press 1970).

11. Gosman, A. L., McCarty, R. D., and Hust, J. G., Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres, NSRDS Monograph 27 (1969).

12. Vincenti-Missoni, M., Levelt Sengers, J. M. H., and Green, M. S., Scaling Analysis of Thermodynamic Properties on the Critical Region of Fluids, J. Res. Natl. Bur. Standards 73A, 563 (1969).

13. Boyd, M. E., Larsen, S. Y., and Plumb, H., Second Virial Coefficient of Helium^4 in the Temperature Range from 2 to 20 K, J. Res. Natl. Bur. Standards 72A, 155 (1968).

September 1970

Brief 70-10333

AEC-NASA TECH BRIEF

AEC-NASA Tech Briefs announce new technology derived from the research and development program of the U.S. AEC or from AEC-NASA interagency efforts. They are issued to encourage commercial application. Tech Briefs are available on a subscription basis from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151. Requests for individual copies or questions relating to the Tech Brief program may be directed to the Technology Utilization Division, NASA, Code UT, Washington, D.C. 20546.

Uniform Data System Standardizes Technical Computations and the Purchasing of Commercially Important Gases

Commercial and Government users of oxygen, nitrogen, argon and parahydrogen have encountered difficulties in costing, billing, and ordering these commercially important gases because different suppliers use slightly different values for the physical properties of the gases. Integrated tables of pressure, volume, and temperature for the saturated liquid, from the triple point to the critical point of the gases, have now been developed from sources which are considered to be the best available today. The tables should benefit both suppliers and purchasers, engineers and scientists.

Earlier efforts to standardize values for the physical properties of these gases included values of pressure, temperature, density for the normal boiling point (NBP), and standard temperature and pressure. The new tables also include a definition of the saturated liquid curve. Numerical values differ from the earlier selections by as much as 0.1%.

The tables include entries of integral values of temperature (in both degrees Kelvin (K) and degrees Rankine (R)), and pressure in both atmospheres and psia. Volumes and densities in three different units and a density ratio are tabulated for each entry. Estimates of the uncertainty of the tabulated data are given. Values are presented both in metric and practical units. The principal tables are merged into tables containing even values of pressure in both atmospheres and psia and even values of temperature in both K and R. The values of density in these tables are also presented in terms of (specific) volume and in terms of a ratio referred to the density at the NBP. Supplemental tables give values of density or volume at one atmosphere near room temperature. A third set of tables gives the uncertainties in the data. The parts of the tables which lie in the practical range of pressures for liquid transfer are also illustrated in convenient graphical form. In addition, sample problems are worked out to demonstrate the ease in computing billings.

The advantages in using the new tables include the following:

1. Each of the compilations selected presents a consistent set of values from a single source for each fluid.
2. All available data, in particular the correlation of the single phase pressure-volume-temperature data with the saturation boundaries and the vapor pressure curve, have been considered, not only the value of the NBP.
3. The equations of state, in the form of computer programs, allow determination of values, both at liquid temperatures and at room temperatures.
4. The equations of state used present a consistent set of values for the saturation boundary as well as for the compressed fluid states. As flowmeter technology improves, an extension to the compressed fluid state will become imperative. Such a change can be accomplished without a further adjustment in the numerical values.

Note:

Requests for further information may be directed to:

Technology Utilization Officer
AEC-NASA Space Nuclear Propulsion Office
U.S. Atomic Energy Commission
Washington, D.C. 20545
Reference: B70-10333

[illegible]

Patent status:

No patent action is contemplated by NASA.

Source: H. M. Roder, R. D. McCarty and
V. J. Johnson
U.S. Department of Commerce
National Bureau of Standards
(NUC-10549)

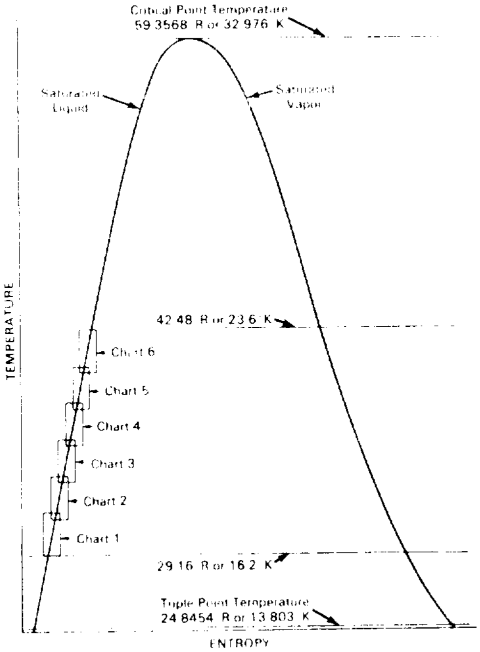
September 1967

Brief 67-10346

AEC-NASA TECH BRIEF

AEC-NASA Tech Briefs describe innovations resulting from the research and development program of the U.S. AEC or from AEC-NASA interagency efforts. They are issued to encourage commercial application. Tech Briefs are published by NASA and may be purchased, at 15 cents each, from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151.

Thermodynamic Properties of Saturated Liquid Parahydrogen Charted for Important Temperature Range



Existing temperature-entropy diagrams for parahydrogen in or near the saturated liquid state, specifically between 29.16° and 42.48°R, were not adequate for some applications. At this state the pressure, density, enthalpy, and quality curves ran so close together on a normal scale of plotting that it was impractical to distinguish one curve from another. Therefore, to obtain reasonable accuracy in this range, it was necessary to expand these scale onto large charts.

Data on parahydrogen were developed previously by the National Bureau of Standards, from the Triple Point to 100° K at pressures to 340 atmospheres. These data have now been reprocessed, refined, and expanded to create six new entropy diagrams which cover the temperature range from 29.16° to 42.48°R

(continued overleaf)

(16.2° to 23.6°K), with pressures to 100 psia (6.8046 atm) and mixtures of the liquid and vapor phases to 0.003 quality.

The six entropy diagrams are contained in: *Thermodynamic Charts of Saturated Liquid Parahydrogen in British Units*, by R. D. McCarty and H. M. Roder, NBS Report 9263, Nov. 1966. Copies of this report are available from:

Technology Utilization Officer
AEC NASA Space Nuclear Propulsion Office
U.S. Atomic Energy Commission
Washington, D.C. 20545
Reference: B67-10346

Notes:

1. The diagrams are printed in color, are 19×30 inches in size, and are suitable for wall mounting.
2. This information is of particular significance in the design, analysis, and operation of laboratory and large-scale commercial apparatus using near-saturated liquid hydrogen.

Patent status:

No patent action is contemplated by AEC or NASA.

Source: R. D. McCarty and H. M. Roder
of the National Bureau of Standards
under contract to
AEC NASA Space Nuclear Propulsion Office
(NUC-10018)