Tables of Thermodynamic and Transport Properties

OF

AIR, ARGON, CARBON DIOXIDE, CARBON MONOXIDE, HYDROGEN, NITROGEN, OXYGEN AND STEAM

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of Air, Argon, Carbon Dioxide, Carbon Monoxide, Hydrogen, Nitrogen, Oxygen, and Steam

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PREFACE

Progress in all fields of science and technology rests on a knowledge of the properties of matter. This collection of tables is one of a series of compilations published by the National Bureau of Standards in furtherance of its mission to compile and disseminate data on the physical properties of substances of technical and scientific interest. The advances in high-speed flight -- both in research and engineering--are particularly dependent on precise knowledge of the behavior of materials of construction, of the theory of flight, of the physical and chemical properties of fuels and oxidizers, and of the very atmosphere through which flight is sustained.

The importance of basic thermodynamic and transport data for air and its constituent gases in the conduct of aerodynamic research has long been recognized. In 1948, Raymond J. Seeger, then Chief of the Aeroballistics Research Department, at the Naval Ordnance Laboratory, suggested to Ferdinand G. Brickwedde, Chief of the Heat and Power Division at the National Bureau of Standards, and to Hugh L. Dryden, Director of Research of the National Advisory Committee for Aeronautics, that a program of research and compilation be initiated in this field. After consultation with interested persons, F. G. Brickwedde proposed a program of research and outlined a plan for the compilation of tables of thermodynamic and transport properties of gases. This outline was circulated to a number of research laboratories and independent research workers for comment. As a result, plans for the compilation were improved, the program was formulated, and arrangements were made for a cooperative program with the National Advisory Committee for Aeronautics. The work was organized around members of the Thermodynamics Section of the Heat and Power Division who were at that time engaged in experimental research on the thermodynamic properties of gases. The responsibility for coordinating the efforts of the staff and supervising the work in general was delegated to Joseph Hilsenrath.

A decision was reached to distribute tables initially in looseleaf form in order to gain user reaction and suggestions, to stimulate the receipt of prepublication research results, and to supply research workers with the data without undue delay. The series was called the NBS-NACA Tables of Thermal Properties of Gases. In all, 43 separate tables were prepared and distributed between the inception of the project and October 1951.

The compilation of these tables was greatly facilitated by advances in the mechanization of thermodynamic calculations. From the beginning of this work, the staffs of the NBS Computation Laboratory and the Thermodynamics Section have worked together closely. Valuable assistance was rendered early in the work -- and indeed throughout -- by the hand-computing group of the Computation Laboratory. Later many of the operations involved in the calculation of the tables were performed by the IBM group which handled subtabulations, conversions, numerical integrations, and the automatic-typing, by means of a card-controlled typewriter, of the more than 300 pages of tables presented here.

In the course of the calculation of thermodynamic properties, a number of codes were devised for use on the Bureau of Standards Eastern Automatic Computer (SEAC). Codes are now available for the rapid calculation of: the harmonic-oscillator approximation to the ideal-gas thermodynamic functions; the corrections to the rigid-rotator harmonic-oscillator approximation including non-classical rotation and first-order corrections for rotational stretching, rotation-vibration interaction, and vibrational anharmonicity; and the calculation of tables of compressibility, density, and volume from virial coefficients. The advantage of the use of high-speed electronic computers for the calculation of thermodynamic functions is evidenced by the time -- about 5 minutes -- which was required to compute the some 320 entries in the table of ideal-gas thermal functions for steam (table 9-10).

The following members of the Thermodynamics Section were assigned to the project: William S. Benedict, Harold J. Hoge, Joseph F. Masi, Ralph L. Nuttall, and Harold W. Woolley. The group was joined by Charles W. Beckett in 1950, and by Lilla Fano in 1951. Yeram S. Touloukian, on leave from Purdue University, spent the summers of 1951 and 1952 on the project. The division of responsibility was approximately as follows: Benedict and Hilsenrath correlated the data on air, Beckett and Fano on argon and water, Woolley on hydrogen, nitrogen, and oxygen, Touloukian on carbon monoxide, Masi on carbon dioxide, Hoge correlated the vapor pressure, and Nuttall correlated the thermal conductivities. The viscosity tables were computed by Nuttall, Hilsenrath, and Touloukian.

Since a number of the authors have left the National Bureau of Standards, their present addresses are given below: William S. Benedict, Institute for Cooperative Research, Johns Hopkins University, Baltimore, Maryland; Harold J. Hoge, U.S. Army Quartermaster Research and Development Laboratories, Natick, Massachusetts; Joseph F. Masi, Callery Chemical Company, Callery, Pennsylvania; Ralph L. Nuttall, Argonne National Laboratories, Lemont, Illinois; and Yeram S. Touloukian, Department of Mechanical Engineering, Purdue University, Lafayette, Indiana.

The project has had a number of contributors and assistants from time to time. Among the former are: F. Charles Morey, who correlated the viscosity data for air; John Hubbell, who participated in the calculation of the steam data; Robert L. Powell, who correlated the viscosity of oxygen; and Robert Lindsay, who supervised the calculation of some of the air tables. The latter group includes Mary M. Dunlap, H. W. Flieger, F. R. Grover, G. G. King, L. C. Mihaly, J. T. Prather, P. P. Rumps, S. B. Schwartz, M. L. Snow, and Norma Young. One assistant, F. D. Queen, merits special mention. He has the distinction of having served the longest term on the project and for periods of time was indeed the only full-time worker. He was at times computer, draftsman, typist, and literature searcher. His detailed knowledge of the work and its progress was of immeasurable help to the project, and the authors are indeed in his debt.

Most valuable assistance was received from the Division of Applied Mathematics Computation Laboratory Staff under the supervision of Milton Abramowitz and Irene Stegun, and in particular from the IBM group which included L. Gordon, P. J. O'Hara, B. S. Prusch, M. Stein, and Ruth Zucker. The SEAC coding was performed by Ethel C. Marden of the Computation Laboratory. The preparation of the manuscript was expedited by the editorial assistance of Edith N. Reese, and the typescript was prepared by Hattie M. Napier.

A project of this magnitude could not be brought to fruition without the cooperation of many persons within the Bureau and outside. The authors wish particularly to acknowledge the helpful advice or data furnished by the following: N. A. Hall, University of Minnesota; J. O. Hirschfelder, University of Wisconsin; H. L. Johnston, Ohio State University; F. G. Keyes, Massachusetts Institute of Technology; E. J. LeFevre, Mechanical Engineering Research Organization, Scotland; A. Michels, University of Amsterdam; and D. D. Wagman, NBS Thermochemistry Section.

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Extensive checks were incorporated in the machine codes and IBM techniques in an effort to eliminate computational errors in the tables. After the tables were typed, a systematic check was made to eliminate random typographical errors. The authors will appreciate criticism and comments and notification of any error or oversight which the reader may find.

A. V. Astin, Director

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TABLES OF THERMAL PROPERTIES OF GASES

Joseph Hilsenrath, Charles W. Beckett, William S. Benedict, Lilla Fano,
Harold J. Hoge, Joseph F. Masi, Ralph L. Nuttall, Yeram S. Touloukian,
Harold W. Woolley

Tables are given at close temperature intervals for the thermodynamic and transport properties of air, argon, CO_2, CO, H_2, N_2, O_2, and steam. The thermodynamic properties - compressibility factor, density, entropy, enthalpy, specific heat, specific - heat ratio and sound velocity - are tabulated for the real gas at pressures up to 100 atmospheres and to temperatures of 600°K for hydrogen, 1500°K for carbon dioxide, 850°K for steam, and 3000°K for the remainder. The ideal - gas thermodynamic functions are tabulated uniformly to 5000°K. Also tabulated are the vapor pressures and transport properties – thermal conductivity, viscosity, and Prandtl number. These were fitted either semi-theoretically or empirically to the experimental values and are tabulated over the range of the available experimental data. Comparisons of the tabulated values with the existing experimental data are shown in deviation plots which exhibit the range and distribution of the experimental data as well as their agreement with the tabulated values.

CHAPTER 1

INTRODUCTION

The computation of sets of mutually consistent tables of thermodynamic properties of air, argon, carbon dioxide, carbon monoxide, hydrogen, nitrogen, oxygen, and steam has been accomplished through the representation of the pressure-volume-temperature (PVT) data by an equation of state, which was then used to calculate the gas imperfection corrections to the thermodynamic properties of the ideal gas. Since, usually, the experimental PVT data are abundant, cover a wide range of temperatures and pressures, and are precise, the equation of state is an effective and efficient starting point for the calculation of the values of the thermodynamic properties. In representing the PVT data for these tables, the objective was to cover adequately the limited range of pressure from zero to 100 atmospheres and of temperature from 100 to 200°K upward through the experimental range with a suitable extrapolation to higher temperatures. The properties tabulated include, with a few exceptions, the thermodynamic properties of the real gas: compressibility factor, density, entropy, enthalpy, specific heat, specific-heat ratio, and sound velocity at low frequency; the transport properties: viscosity, thermal conductivity, and Prandtl number; the vapor pressure of the liquid and the solid; and, for the ideal gas, the heat capacity, entropy, enthalpy, and free energy function. The vapor pressures and transport properties were correlated independently and are tabulated over the range of the experimental data. The ranges covered in the various tables are shown in the summary table 1-A.

Fundamental Constants

The fundamental constants used in this compilation are those given in NBS Circular 461 [1]*. In the light of more recent information [2,3], these values should be readjusted. Such a readjustment will have no significant effect upon the tables themselves, though it will affect the fifth figure of some of the conversion factors. The values of the gas constant, R, are based on the value 1.98719 cal $mole^{-1}$ $°K^{-1}$, the calorie is the thermochemical calorie defined as 4.1840 absolute joules, and, unless otherwise specified, the mole is the gram-mole. The subscript 0 (except in the symbol E_0^o) is used to denote values at standard conditions (T = 273.16°K and P = 1 atmosphere).

Thermodynamic Properties of the Real Gas

The computation of the thermodynamic properties of the real gases was accomplished through the representation of the data of state (PVT data) by one of a number of equations of state. Except for the data for steam, which were fitted to an empirical equation, the virial equation of state was employed in this compilation. The virial equation expresses the compressibility factor, Z = PV/RT, as an infinite series either in powers of the density or the pressure.

The virial equation, derived from statistical mechanics and confirmed by experiment, can be written either as

$$PV/RT = \sum_{i=0}^{\infty} a_i \rho^i \qquad \text{or} \qquad PV/RT = \sum_{i=0}^{\infty} b_i P^i.$$

These equations represent, respectively, the density and the pressure virial expansions. The virial coefficients, a_i and b_i, can be calculated, in principle, from a knowledge of the intermolecular forces. In most cases, the representation of real-gas properties was accomplished using a three- or four-term virial expansion and the Lennard-Jones intermolecular potential energy:

$$E(r) = 4\epsilon[(r_o/r)^{12} - (r_o/r)^6],$$

where r is the intermolecular distance, ϵ is the maximum binding energy between the molecules, and r_o is the distance at which the attractive and repulsive potentials are equal. The fitting of the virial coefficients to the data of state was facilitated by the use of tabulations of second and third virial coefficient functions for nonpolar gases prepared by Hirschfelder, et al., [4, 5]. The corrections for gas imperfection to the thermodynamic properties were computed from the virial coefficients using the usual thermodynamic relationships. These corrections were combined with the values of the thermodynamic functions for the ideal gas to give the tabulated properties of the real gas over the desired pressure and temperature range.

Experimental measurements of thermodynamic properties such as the specific heat, Joule-Thomson coefficient, sound velocity, etc., were considered to varying degrees for each gas in choosing the force constants. It should be emphasized, however, that the values tabulated here for derived thermodynamic properties were obtained through the thermodynamic relationships from the equations of state. This method ensures a set of mutually consistent tables. The concordance of these derived properties with the scanty experimental data is, in general, quite good as is illustrated by the deviation plots.

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*Numbers in brackets indicate references listed at the end of the chapter.

The values of sound velocity at low frequency, given in dimensionless form as a/a_0, are obtained from the usual thermodynamic relations involving the specific heat, the compressibility, and its derivatives. The tabulated sound velocities are for equilibrium conditions involving excitation of vibrational and rotational energies. Hence, the tables apply only at low frequency.

The special problems presented by the available data for each gas dictated certain modifications in the correlating and calculating procedures from gas to gas. A full account of these details is beyond the scope of this volume. Discussions of the general and particular methods used are to be found in the literature or in National Advisory Committee for Aeronautics technical reports cited later.

Thermodynamic Properties of the Ideal Gas

The values of the ideal-gas thermodynamic properties of the molecular and atomic species tabulated herein were computed from spectroscopic data using statistical mechanical formulas. The details of the computation are given in references cited here [6, 7, 8, 9] and in the succeeding chapters. The values of the functions have been tabulated in dimensionless form as follows: C_p^o/R, S^o/R, $(H^o - E_0^o)/RT_0$, and $(F^o - E_0^o)/RT$. The zero reference point of the enthalpy and free energy function is taken as the internal energy, E_0^o, of the ideal gas at absolute zero. The enthalpy function is divided here by a constant RT_0, where $T_0 = 273.16°K\,(491.688°R)$. The values tabulated are for the normal isotopic composition for all gases. The values of S^o/R and $(F^o - E_0^o)/RT$ are for the ideal gas at one atmosphere pressure. The effect of nuclear spin and isotopic mixing have not been included. The entropy of mixing for the constituent gases has been included in the tables for air.

The Transport Properties

The transport properties, values of which are tabulated in dimensionless form in this work, are the absolute viscosity, η/η_0, the thermal conductivity, k/k_0, and the Prandtl number, $N_{Pr} = \eta C_p/k$. The viscosities of the nonpolar gases at low pressures were calculated on the basis of the Lennard-Jones 6-12 intermolecular potential, for which Hirschfelder, Bird, and Spotz [10, 11] have calculated the collision integrals given by Chapman and Cowling [12]. The force parameters for the Lennard-Jones potential were fitted to the experimental viscosity data. The remainder of the viscosity tables were calculated from empirical formulas (see summary table 1-B) which had been fitted to the experimental data. For nitrogen and steam, where the pressure dependence of the viscosity has been investigated over a range of pressure and temperature, the tables are based on the Enskog theory [13]. The values of the thermal conductivity are tabulated at atmospheric pressure except in the case of steam. The tables were computed from empirical formulas (see summary table 1-C) fitted to the experimental data. The Prandtl numbers were computed directly from the tabulated viscosity, thermal conductivity, and specific heat.

Vapor Pressures

The tables of vapor pressures were prepared from experimental data by the use of empirical equations. In some cases, an equation of the form $\log_{10}P = A + B/T$ was adequate, but, generally, the equation contained an additional term or terms to give a closer fit. Deviations from the equation were plotted; a smooth curve was drawn through the deviations; and values read from this smooth curve were added to the equation to give the values tabulated. Mathematical smoothing procedures were used, where necessary, to avoid small irregularities in the tabulated values. Since the differences in reported values of vapor pressures seem to be more the result of uncertainties in the temperature measurement than anything else, the deviation plots for the vapor-pressure tables have been prepared in terms of temperature deviations.

The Effect of Dissociation on the Thermodynamic Properties

The effect of dissociation has been included only in the tables for air. The tables for the other gases have been extended to high temperatures without considering dissociation effects, so that these tables might serve as building-blocks from which properties of equilibrium mixtures at high temperatures can be computed by methods given in standard works [7, 14, 15]. A discussion of the effects of dissociation on the thermodynamic properties of pure diatomic gaseous substances is given by Woolley [16]. For the simple case of the diatomic gaseous elements, a graphical method of calculation is presented in reference 16 together with results of its application to H_2, O_2, and N_2. These results are presented in figures 6b, 6c, 7e, 7f, 8e, and 8f for the entropy, enthalpy, and compressibility factor.

Relaxation Phenomena in Gases

The thermodynamic properties tabulated here are based on the assumption that thermodynamic equilibrium exists in the gas. This is a valid assumption for many research and engineering applications. In hypersonic wind tunnels, however, the instantaneous equipartition of energy among the degrees of freedom in a molecule cannot be taken for granted. This delay in the redistribution of energy between the vibrational and translational degrees of freedom is a relaxation phenomenon and has been the subject of investigation by Griffiths [17], Kantrowitz [18], Huber and Kantrowitz [19], Walker [20], and others.

The Consistency and Reliability of the Tables

As indicated earlier, the internal or mutual consistency of the tables of thermodynamic properties was achieved through the application of the thermodynamic identities which relate the properties of both the real and ideal gas. Although direct measurements of Joule-Thomson coefficients, heat capacity, etc., were given weight in the course of correlation for various gases, the resulting tables depend very largely for their reliability and consistency on the accuracy of the data of state and the ideal-gas thermodynamic functions.

A precise indication of the uncertainties of the tabulated values is difficult to achieve for the data of state outside of the experimental range and for the derived properties over the entire range. The uncertainties can be ascribed to two major causes: the uncertainties in the values of the ideal-gas properties and those in the corrections for the gas imperfection. It has been found convenient to express these uncertainties separately. Approximate uncertainties for the ideal-gas properties are given in the summary table 1-D. The uncertainties in the corrections for gas imperfection are given in each chapter together with the deviation plots for the experimental range. The magnitude of the corrections for gas imperfection $(Z - 1)$, $(C_p - C_p^o)$, etc., can be found simply by subtraction of the tabulated values, except for the entropy where the effect of $\ln P$ on the tabulated entropy must be taken into account.

The specified reliabilities of the tables have been arrived at in two general ways. Where tables have been computed from empirical or semi-theoretical equations fitted directly to the experimental data, the departures of the experimental data from the tabulation form the basis for the estimate of reliability. Such tables include compressibility, density, viscosity, and thermal conductivity. The remaining tables - entropy, enthalpy, specific heat, specific-heat ratio, and sound velocity at low frequency - having been computed through the thermodynamic relationships from the equation of state, depend for their reliability on the accuracy and extent of the data of state and the validity of the numerical differentiations involved, and not solely on the agreement with the direct experimental data. The deviation plots for the derived properties serve to corroborate the verity of the tabulation.

The degree to which the adopted equations of state fit the experimental data varies with the gas. For argon, for example, the data are abundant and accurate and they are fitted to within a few hundredths of 1 percent in PV/RT; whereas the data for carbon monoxide are fitted to a few tenths of 1 percent. The reliability of the data of state tables in the extrapolated region and the reliability of the pressure corrections to the thermodynamic properties over the entire range are further dependent upon the temperature range covered by the experimental data and upon the mode of calculation. The corrections for nonideality which depend on the derivatives of the virial coefficients are less precise than the corresponding corrections for the data of state. Thus, in the case of entropy and enthalpy, where the nonideality correction depends on the first derivative of the virial coefficients, the uncertainty in this correction may be twice as large as in the case of the data of state; whereas, in the case of heat capacity, it may be three to five times as large. The above uncertainties are only rough estimates and are independent of the uncertainties of the ideal-gas values. For economy in machine tabulation, more decimal places are tabulated in some regions than is warranted by the correlation. The reader should consult the deviation plots and statements of reliability before using the tabulated values.

Conversion Factors

The compressibility factor is dimensionless. Values of the gas constant R are listed for each gas in the frequently used units in order to facilitate the use of the tables in calculating, by means of the equation $Z = PV/RT$, the pressure P, the volume V (or the density), or the temperature T, when any two of these are known. The rest of the tables also are given in dimensionless form. Conversion factors for frequently used units are given in each chapter immediately preceding the tables of thermal properties for each gas.

Interpolation

The ease with which interpolations may be made is an important factor in the practical use of a table. Seldom is it possible to avoid interpolation altogether. Since linear interpolation is relatively simple and rapid as compared with higher-order interpolation, even when tables of interpolation coefficients are at hand, the goal has been to subtabulate to the point where linear interpolation yields valid results. Although this objective was achieved in the direction of temperature, the pressure entries had to be curtailed to keep the tables within a manageable size. The tabulations in pressure were therefore arranged to permit a four-point Lagrangian interpolation formula to be used where the precision of the table justified it. It is for this reason that entries are found for the pressures 1,4,7,10,40,70,100 atmospheres, etc. In the tables for vapor pressure, with the exception of those for steam, the logarithms of the pressures have been included to facilitate interpolation. A convenient rule of thumb for determining the adequacy of linear interpolation is the following: "The maximum error introduced in linear interpolation is approximately 1/8 of the second difference." Where this error greatly exceeds the uncertainty in the table, Lagrangian or other forms of interpolation should be used.. For the convenience of the user, first differences have been tabulated in smaller type in the temperature direction.

References

The references consulted in the course of the work have been listed at the end of each chapter, generally in the order cited, and numbered consecutively starting with 1 in each chapter. In some instances, references to works considered in the figures and deviation plots were not cited in the text; in such cases, they have been included in the reference lists at the end of each chapter. It is not intended, however, that these lists be considered complete bibliographies.