U.S. Department of Commerce
National Bureau of Standards

Research Paper RP1932
Volume 41, November 1948

Part of the Journal of Research of the National Bureau of Standards

Compilation of Thermal Properties of Hydrogen in Its Various Isotopic and Ortho-Para Modifications

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New developments in science and industry are aided by accurate knowledge of the behavior of important substances. The great abundance of chemical processes and compounds in which hydrogen is involved make it of particular interest. The experimental and derived data presented here for hydrogen extend over a large range of temperature. Low temperatures are required for the liquid and solid, and moderate and high temperatures occur in chemical reactions.

The available thermal data for H_2, HD, and D_2 in solid, liquid, and gaseous states have been brought together, including the distinctive properties of ortho and para forms of H_2 and D_2. Some data not previously published have been added. The thermal data include thermodynamic functions for the ideal gas state, equilibrium constants, data of state, viscosity, and thermal conductivity with dependence on the pressure, vapor pressure, solid-liquid equilibria, specific heats, and latent heats. Values of state derivatives useful in thermodynamic calculations have been given for normal hydrogen, and the related differences between thermodynamic functions for real and ideal gas states have been evaluated. A temperature entropy diagram for normal H_2 in the range of experimental data is also given. The compiled thermal properties of hydrogen are presented in 38 tables, 33 graphs, and numerous equations. The sources of the data have been given in an extensive bibliography.

I. Introduction

It was recommended by the National Research Council Committee on Thermal Data for Chemical Industries [1] [2] and by others that the thermal data on substances of industrial importance should be reexamined with the intention of preparing consistent tables of thermal data of especial interest to chemical engineers and investigators.

In this paper thermal data on hydrogen in its various isotopic and ortho-para modifications are compiled and correlated. Data on properties of the gaseous, liquid, and solid states are presented in tables and graphs, and by use of formulas. Thermodynamic properties are given for the ideal gas state. In addition, tables based on the PVT data for the real gas furnish the additional information required for the calculation of the thermodynamic properties of the real gas. For the condensed phases, directly observable properties are given. Because of the industrial importance of flow and heat-transfer problems, correlations of viscosity and of thermal conductivity are included and their dependence upon pressure discussed briefly. A number of topics are discussed in detail to explain the fundamental principles involved. Most of the data included were taken from published papers. However, a small proportion are based on unpublished measurements made at the Bureau.

The following are the symbols and values of physical constants and conversion factors used in this paper.

1. Symbols

Many symbols that are not used extensively in this paper have been omitted from this list.

A, constant in an equation for a PVT isotherm.

B, second virial coefficient in equation of state of gas.

B_v, rotational spectroscopic constant.

[1] Division of Chemistry and Chemical Technology, National Research Council.

[2] F. Russell Bichowsky, Chairman, 1938 to 1947.

b, b, constant in an equation for a PVT isotherm; also, a constant in an equation of state.

C, C, constant in an equation for a PVT isotherm; also, the Sutherland constant in a viscosity formula.

C', constant in an equation for a PVT isotherm.

C_p°, molar heat capacity (molar specific heat) at constant pressure for ideal gas.

C_s, molar heat capacity (molar specific heat) along a saturation curve.

C_v°, molar heat capacity (molar specific heat) at constant volume for ideal gas.

c, c, velocity of light; also a constant in an equation for a PVT isotherm.

c_2, radiation constant hc/k.

D_v, rotational spectroscopic constant.

E, a thermodynamic function, internal energy per mole.

E°, E for a substance in the ideal gaseous state.

E_0°, E° at the absolute zero of temperature when for each molecule the energy associated with internal degrees of freedom is at its lowest quantized value.

F, a thermodynamic function, molar free energy $F=E+PV-TS$.

F°, F for a substance in the ideal gaseous state at a pressure of 1 atmosphere.

F_v, rotational spectroscopic constant.

$F_{v,J}$, or F, term value.

f, a thermodynamic function, fugacity.

G_v, vibrational term value.

g, statistical weight of a quantum level.

H, a thermodynamic function, molar heat content or enthalpy, $H=E+PV$.

H°, H for a substance in the ideal gaseous state.

H_v, rotational spectroscopic constant.

h, Planck's constant.

i, nuclear spin.

J, rotational quantum number.

K, equilibrium constant.

k, k, Boltzmann constant; also, thermal conductivity.

L_v, latent heat of vaporization.

M, molecular weight.

m, reduced mass for molecule.

N, total number of molecules considered.

N_j, number of molecules in a given quantum level.

N_0, Avogadro's number.

P, pressure.

P_c, pressure at the critical point.

P_0, pressure of 1 standard atmosphere, 1.01325×10^6 dynes cm^{-2} by definition.

p, momentum corresponding to generalized coordinate q.

q, a generalized coordinate.

R, molar gas constant.

r, atomic separation.

r_e, atomic separation r for minimum potential energy.

S, a thermodynamic function, molar entropy.

S°, S for a substance in the ideal gaseous state at a pressure of 1 atmosphere.

T, absolute temperature on the Kelvin scale.

T_c, temperature T at critical point.

T_0, Kelvin temperature T of the ice point, that is, of 0° C.

U, intramolecular potential energy.

U_{11}, ratio of mean free path lengths for diffusion and viscosity.

V, molar volume.

V_c, molar volume at the critical point.

V_0, molar volume of gas at 1-atmosphere pressure and the ice point.

v_0, molar volume of liquid at zero pressure.

v, vibrational quantum number.

Z, abbreviation for PV/RT.

γ, ratio of specific heats, C_p/C_v.

ϵ, energy for a quantum state.

η, viscosity.

Θ, a characteristic Kelvin temperature for a crystal lattice in Debye's theory of specific heats.

Λ, length of mean free path.

μ, Joule-Thomson coefficient.

ξ, fractional increase in atomic separation beyond that for minimum potential energy.

ρ, density in Amagat units.

σ, a correlation function for PVT data.

χ, a function in one equation of state.

φ, a correlation function for PVT data.

2. Values Used for Some Physical Constants and Conversion Factors

(Numbers in parentheses refer to the references given below)

c (velocity of light$=2.99776\times 10^{10}$ cm sec^{-1} (1).

c_2 (radiation constant)$=\frac{hc}{k}=\frac{N_0hc}{R}=1.4384$ cm deg (2).

h (Planck's constant$=6.624\times 10^{27}$ cm sec (1).

N_0 (Avogadro number)$=6.0228\times 10^{23}$ mole^{-1} (1).

P_0 (pressure of standard atmosphere)$=1.01325\times 10^6$ dynes cm^{-2} (3).

R (molar gas constant)$=N_0k=8.3144\times 10^7$ erg mole^{-1} deg^{-1} (1).

$=1.98714$ thermochemical cal mole^{-1} deg^{-1} (4).

T_0 (Kelvin temperature of ice point)$=273.16°$ K (5).

Atomic weight of hydrogen (H^1) on chemical scale$=1.000786$ (1).

Atomic weight of deuterium (D or H^2) on chemical scale$=2.01418$ (1).

1 thermochemical calorie$=4.1833$ international joules (5).

1 international joule (NBS)$=1.000165$ absolute joules (6).

(1) Raymond T. Birge, Rev. Modern Phys. **13,** 233 (1941).

(2) Birge's value (Rev. Modern Phys. **13,** 233 (1941)) adjusted for later NBS value of the ratio international coulomb/absolute coulomb$=0.99985$; see also reference (7).

(3) Definition.

(4) Birge's value (Rev. Modern Phys. **13,** 233 (1941)) adjusted to thermochemical calorie and NBS value for ratio international joule/absolute joule.

(5) Definition.

(6) NBS Technical News Bulletin **31,** 49 (1947).

(7) R. W. Curtis, R. L. Driscoll, and C. L. Critchfield, J. Research NBS **28,** 133 (1942).

II. Thermodynamic Properties for the Hydrogens in the Ideal Gas State

1. General Principles of Calculation

For a gas in a state of extreme rarefaction the energy of interaction between molecules forms a minute part of the total energy of the gas. At such low pressures the thermodynamic properties of the gas may be calculated from the spectroscopically determined energies of the single molecules and the general physical constants without considering the energy of interaction of one molecule with another. Some thermodynamic properties, as for example molar entropy and free energy, do not approach a definite value as the pressure of the gas goes to zero. For this reason, values of thermodynamic functions of a gas at low pressure are often indicated by giving values for a pressure of 1 atm for a fictitious ideal gas having in the limit of low pressure the same thermodynamic functions as the actual gas. The result is then said to be for the gas at a pressure of 1 atmosphere in the hypothetical ideal gas state. Data of state may be used to calculate the differences between properties in the real and ideal gas states.

The procedure for calculating the thermodynamic properties of a substance in the ideal gas state has been discussed by many writers [3, 30, 31, 32].[3]

In outline, it involves the following ideas: The average number n_1 of molecules in a quantum state of energy ϵ_1 is related to the average number, n_2 of molecules in another state of energy ϵ_2 by the Boltzmann distribution law

$$n_1/n_2=e^{-\epsilon_1/kT}/e^{-\epsilon_2/kT}=e^{-(\epsilon_1-\epsilon_2)/kT}, \qquad (2.1)$$

where k is the Boltzmann constant, and T is the absolute temperature.

As there are often several states having the same energy, the number of molecules in a given energy level [4] is also proportional to the number of states, g. If N_1, N_2, N_3, . . . are the numbers of molecules in the levels ϵ_1, ϵ_2, ϵ_3, . . ., respectively, the number of molecules in any one level is

$$N_j=\frac{Ng_je^{-\epsilon_j/kT}}{g_1e^{-\epsilon_1/kT}+g_2e^{-\epsilon_2/kT}+\ .\ .\ .}=\frac{Ng_je^{-\epsilon_j/kT}}{\sum_j g_je^{-\epsilon_j/kT}}, \qquad (2.2)$$

where N, the total number of molecules being considered, is equal to ΣN_j. If properties are to be expressed on the basis of 1 mole, N is taken equal to Avogadro's number, N_0.

The quantum states are specified by means of quantum numbers, the integer values which certain natural variables have when a molecule has a stationary value of energy. The magnitude of the energy is generally expressed in terms of these numbers. In diatomic molecules, the quantum numbers of interest are J, the rotational quantum number, K, the rotational quantum number apart from spin, and v, the vibrational quantum number. The electronic state is also similarly quantized, and quantum numbers appropriate to it may likewise be assigned. The nuclear spins of the two constituent atoms are designated by i_1 and i_2. In terms of these numbers, the statistical weight, g, of a level of a diatomic molecule composed of unlike atoms, as for example HD, is $g_e(2i_1+1)(2i_2+1)(2J+1)$, where g_e is the weight of the electronic level of the mole-

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

[4] The term *state* is used in the sense that two states differ if any of *all* the quantum numbers associated with the states are different. The term level is used to express the idea that the energy has a definite value. The statistical weight, g, of a level is the number of states having the energy which define the level. A level with more than one state is said to be degenerate.

cule. The ground electronic level of HD, and of H_2 and D_2, also, is a singlet state, and accordingly g_e is 1.

The proton and deuetron spins are ½ and 1, respectively. For diatomic molecules composed of like atoms, as for example, H_2 and D_2, there is a division of the rotational levels of the molecule into two groups referred to as the ortho and para series, one of which is composed of the even numbered and the other of the odd numbered rotational levels. Ordinarily, transitions between ortho and para levels are relatively rare, so that the gas can be considered as a mixture of two distinct components. The high temperature equilibrium mixture of the two forms is called the normal mixture, and the more abundant component of the normal mixture is called the ortho component. The statistical weights of the two series depends upon the quantum statistics applicable to the nuclei. For H_2 it is the Fermi-Dirac statistics, for D_2 the Bose-Einstein statistics.

Fermi-Dirac statistics:

$$\left.\begin{aligned} &g\ (\text{para series, even } J\text{'s}) = \\ &g_e\ (2i+1)i(2J+1) \\ &\\ &g\ (\text{ortho series, odd } J\text{'s}) = \\ &g_e\ (2i+1)(i+1)(2J+1) \end{aligned}\right\} \quad (2.3)$$

Bose-Einstein statistics:

$$\left.\begin{aligned} &g\ (\text{ortho series, even } J\text{'s}) = \\ &g_e\ (2i+1)(i+1)(2J+1) \\ &\\ &g\ (\text{para series, odd } J\text{'s}) = \\ &g_e\ (2i+1)i(2J+1) \end{aligned}\right\} \quad (2.4)$$

The energy per mole due to molecular rotation and intramolecular vibration is

$$E_{v+r}=\Sigma N_j\epsilon_j=\frac{N_0\Sigma g_j\epsilon_j e^{-\epsilon_j/kT}}{\Sigma g_j e^{-\epsilon_j/kT}}, \quad (2.5)$$

where the ϵ's are the energies of the rotational-vibrational levels relative to the lowest energy level of the molecule. The translational energy, $3/2\ N_0kT$ or $3/2\ RT$, is added to this to get $E^\circ-E_0^\circ$, the total internal energy per mole for the ideal gas above the chosen zero in which there would be no translational energy and each molecule would be in the lowest energy state available to any form of the molecule.[5]

$$E^\circ-E_0^\circ=3/2\ RT+N_0\frac{\sum_j g_j\epsilon_j e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}}. \quad (2.6)$$

The superscript zero is used to indicate the ideal gas state.

The enthalpy H°, the specific heats C_v° and C_p°, the entropy S°, and the free energy F° for the ideal gas state are derivable in accordance with familiar methods of thermodynamics from (1) the internal energy $E^\circ-E_0^\circ$, (2) the equation of state $PV=RT$, and (3) the *translational* entropy S_t° of an ideal gas of molecular weight M. The equations for these properties as functions of (ϵ_j/kT) are

$$\frac{E^\circ-E_0^\circ}{RT}=\frac{\sum_j g_j(\epsilon_j/kT)e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}}+\frac{3}{2}. \quad (2.7)$$

$$\frac{H^\circ-E_0^\circ}{RT}=\frac{E^\circ-E_0^\circ}{RT}+1. \quad (2.8)$$

$$\frac{C_v^\circ}{R}=\frac{\sum_j g_j(\epsilon_j/kT)^2e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}}-\left(\frac{\sum_j g_j(\epsilon_j/kT)e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon_j/kT}}\right)^2+\frac{3}{2}. \quad (2.9)$$

$$\frac{C_p^\circ}{R}=\frac{C_v^\circ}{R}+1. \quad (2.10)$$

$$\frac{S^\circ}{R}=\ln\sum_j g_j e^{-\epsilon_j/kT}+\frac{\sum_j g_j(\epsilon_j/kT)e^{-\epsilon_j/kT}}{\sum_j g_j e^{-\epsilon/kT}}+\frac{S_t^\circ}{R}. \quad (2.11)$$

$$\frac{S_t^\circ}{R}=\frac{5}{2}\ln T+3/2\ln M-\ln(P/P_0)+\ln\frac{(2\pi)^{3/2}R^{5/2}}{h^3N_0^4P_0}+\frac{5}{2}. \quad (2.12)$$

$$\frac{S_t^\circ}{R}=\frac{3}{2}\ln T+3/2\ln M+\ln V+\ln\frac{(2\pi R)^{3/2}}{h^3N_0^4}+\frac{5}{2}. \quad (2.13)$$

$$\frac{F^\circ-E_0^\circ}{RT}=\frac{H^\circ-E_0^\circ-TS^\circ}{RT}=-\ln\sum_j g_j e^{-\epsilon_j/kT}+\frac{5}{2}-\frac{S_t^\circ}{R}. \quad (2.14)$$

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[5] Accordingly for orthohydrogen and paradeuterium E_0° is not the internal energy at 0° K. For these substances at 0° K the internal energy above the chosen zero ($J=0$, $v=0$) is the rotational energy per mole of molecules in the rotational level $J=1$. At 0° K internal energies of normal hydrogen and normal deuterium are respectively three-fourths the internal energy of orthohydrogen and one-third the internal energy of paradeuterium.

In eq 2.12, P and P_0 are the pressure of the gas and standard atmospheric pressure, respectively, with both expressed in dynes cm^{-2}. The ratio P/P_0 is the pressure expressed in atmospheres.

For a monatomic gas in which the ground state is so far below the others in energy that it alone makes appreciable contribution to the state-sum, $\sum_j g_j e^{-\epsilon_j/kT}$, eq 2.7 to 2.14 are simplified considerably. With ϵ_1, the energy of the ground state, taken as zero, the state-sum reduces to the constant g_1

As a result, $(E^\circ - E_0^\circ)/RT = 3/2$; $(H^\circ - E_0^\circ)/RT = 5/2$; $C_v^\circ/R = 3/2$; $C_p^\circ/R = 5/2$; $S^\circ/R = \ln g_1 + S_t^\circ/R$, and $(F^\circ - E_0^\circ)/RT = -\ln g_1 + 5/2 - S_t^\circ/R$. When the nuclear spin is included, g_1 contains $(2i+1)$ as a factor.

Normal hydrogen is a mixture 75 percent of orthohydrogen and 25 percent of parahydrogen, and normal deuterium 66⅔ percent of orthodeuterium, and 33⅓ percent of paradeuterium. The molar entropy and free energy of a mixture of ideal gases present in the mole fractions x_1, x_2, . . . are

$$S_{\text{mixture}} = \sum_j x_j S^\circ{}_j - R\sum_j x_j \ln x_j \tag{2.15}$$

$$F_{\text{mixture}} = \sum_j x_j F^\circ{}_j + RT\sum_j x_j \ln x_j, \tag{2.16}$$

where $S^\circ{}_j$ and $F^\circ{}_j$, the molar entropy and free energy of the ideal gas j in a pure state at the pressure of the mixture, are given by eq 2.11 and 2.14, using eq 2.12 for the evaluation of $S^\circ{}_t$. The summation $-R\sum x_j \ln x_j$ is called the entropy of mixing. Using eq 2.13 for the evaluation of S_t, and setting V equal to the molar volume of the constituent, that is, the volume of the mixture divided by the moles of constituent present, is equivalent to using partial pressures in eq 2.12, in which case the entropy and free energy of the mixture are equal simply to $\sum x_j S^\circ{}_j$ and $\sum x_j F^\circ{}_j$.

2. Energy Values From Spectroscopic Data

The values of ϵ_j to be used in evaluating the equations of the preceding section are derived from analysis of molecular spectra. In general, banded electronic absorption and emission spectra, infrared, rotation-vibration absorption spectra, and Raman spectra are considered. But as the H_2 and D_2 molecules have no electric dipole moments in their normal states, they have no rotation-vibration absorption spectra. Similarly, no such spectra have been observed for HD, although lack of symmetry permits it to have a very weak dipole moment.

The spectroscopic energy level data for hydrogen are represented by a series in which the energies of the levels relative to the ground level, $v=0$, $J=0$, divided by hc are expressed as a function of the rotational and vibrational quantum numbers J and v, see eq 2.17. The quantity ϵ_j/hc is called the *term value* of the level and is designated by the symbol F. Term values are determined experimentally from differences between the wave numbers of spectrum lines and are expressed in terms of reciprocal centimeters as a unit. Here $F_{v,J}$ is the term value for the level v, J; $F_{0,0}$ for the ground state being zero.

Up to 25,000 cm^{-1}, the term values on which tables 4, 7, and 8 are based, can be represented by

$$F_{v,J} = G_v - G_0 + B_v J(J+1) + D_v J^2(J+1)^2 + F_v J^3(J+1)^3 + H_v J^4(J+1)^4 + \frac{(H_v J^4(J+1)^4)^2}{F_v J^3(J+1)^3 - H_v J^4(J+1)^4}, \tag{2.17}$$

where the subscripts used indicate the quantum numbers on which the different symbols depend for their values.

The functions G_v, B_v, D_v, F_v, and H_v for H_2, HD and D_2 are as follows:

For H_2:

$$\left.\begin{aligned}
G_v &= 4405.3(v+\tfrac{1}{2}) - 125.325(v+\tfrac{1}{2})^2 + 1.9473(v+\tfrac{1}{2})^3 - 0.11265(v+\tfrac{1}{2})^4 \\
B_v &= 60.8483 - 3.06635(v+\tfrac{1}{2}) + 0.068361(v+\tfrac{1}{2})^2 - 0.0065(v+\tfrac{1}{2})^3 \\
D_v &= -0.046435 + 0.0014904(v+\tfrac{1}{2}) - 0.000063648(v+\tfrac{1}{2})^2 \\
F_v &= 4.93203\times 10^{-5} + 0.02800\times 10^{-5}(v+\tfrac{1}{2}) \\
H_v &= -6.7217\times 10^{-8}
\end{aligned}\right\} \quad 2.18$$

For HD:

$$\left.\begin{aligned}
G_v&=3817.09(v+\tfrac{1}{2})-94.958(v+\tfrac{1}{2})^2+1.4569(v+\tfrac{1}{2})^3-0.07665(v+\tfrac{1}{2})^4\\
B_v&=45.6549-1.992721(v+\tfrac{1}{2})+0.038482(v+\tfrac{1}{2})^2-0.00316885(v+\tfrac{1}{2})^3\\
D_v&=-0.026136+0.00072661(v+\tfrac{1}{2})-0.0000268773(v+\tfrac{1}{2})^2\\
F_v&=2.0827\times10^{-5}+0.01024\times10^{-5}(v+\tfrac{1}{2})\\
H_v&=-2.1295\times10^{-8}
\end{aligned}\right\}\quad 2.19$$

For D_2:

$$\left.\begin{aligned}
G_v&=3118.46(v+\tfrac{1}{2})-64.10(v+\tfrac{1}{2})^2+1.2514(v+\tfrac{1}{2})^3-0.10612(v+\tfrac{1}{2})^4+0.00034(v+\tfrac{1}{2})^5\\
B_v&=30.4286-1.04917(v+\tfrac{1}{2})+0.0057934(v+\tfrac{1}{2})^2-0.00027486(v+\tfrac{1}{2})^3\\
D_v&=-0.011586+0.000151(v+\tfrac{1}{2})+0.000058(v+\tfrac{1}{2})^2\\
F_v&=6.22\times10^{-6}+0.105\times10^{-6}(v+\tfrac{1}{2})\\
H_v&=-0.442\times10^{-8}
\end{aligned}\right\}\quad 2.20$$

The numerical values of the coefficients in eq 2.18 to 2.20 are based on the latest available spectroscopic measurements due principally to Rasetti [2], Hyman [5, 6], Jeppesen [6, 7, 12, 15, 24], Beutler [20, 21], and Teal and Mac Wood [22]. The data of Fujioka and Wada [23] were not used and the data of Mie [16] on HD only through its influence on the formula for G_v. The equations G_v for H_2 and HD are those given by Teal and Mac Wood [22], and that for D_2 by Jeppesen [24]. The equations for B_v are essentially Jeppesen's [12, 24] equations expressed for use with $J(J+1)$. The constants in the equations for D_v, F_v, and H_v were obtained from theory using the equations for G_v and B_v and the formulas of Dunham [10] without his correction terms.

In the case of hydrogen as for many other substances, extrapolations of spectroscopic formulas have to be made into regions of large rotational quantum numbers for which no wavelength measurements are available in order to obtain values for the energies ϵ_j of the higher quantum states. The energy values for large rotational and vibrational quantum numbers are influenced by the law of internuclear force of the molecule for large separations of the nuclei. Special consideration has been given to this point in the present work and two methods were developed whereby more reliable values of the energies of the unobserved higher rotational levels were obtained.

The first improvement was the addition of the final term in eq 2.17, $[H_vJ^4(J+1)^4]^2/[(F_vJ^3(J+1)^3-H_vJ^4(J+1)^4)]$. Without the final term, eq 2.17 is of the form in which spectroscopic data have heretofore been represented, but in that form it is not a good approximation for large values of J. The third, fourth, fifth, and sixth terms of eq 2.17 are of alternate sign and for H_2 the third, fourth, and fifth terms are approximately equal for $J=28$. This suggested that the series be extended with successive terms in constant ratio. The final term of eq 2.17 is the sum of the geometric series of added terms in which the term to term ratio is that between the fifth and sixth terms of eq 2.17.

This change in the formula for the energies of the rotational-vibrational levels of the normal ($1s^1\Sigma$) electronic state of hydrogen has only a small effect on the energy values of the observed spectrum lines. Thus the mean difference between Jeppesen's [12] observed and calculated term values for the $2p^1\Sigma-1s^1\Sigma$ band for H_2 was 1.032 cm^{-1}, whereas using eq 2.17 in place of Jeppesen's equation for the $1s^1\Sigma$ state the mean difference between observed and calculated values is 1.030 cm^{-1}.

As a second improvement, for the calculation of thermodynamic properties above 2,000° K, an alternative determination of the highest rotational levels was made. Instead of using the power series eq 2.17, the energies corresponding to any degree of rotation and vibration were determined from the potential energy. This was

carried out in effect by (1) determining the potential energy U of the nonrotating H_2 molecule as a function of the internuclear separation, (2) adding the rotational energy $h^2J(J+1)/8\pi^2I_e(r/r_e)^2$ to U to obtain an effective potential energy, U', for a molecule with rotational quantum number J, and (3) using the quantum condition $\oint pdq=\int(2m)^{1/2}(\epsilon_{v,J}-U')^{1/2}dr=(v+1/2)h$ to determine the energy $\epsilon_{v,J}$ of the quantum state v, J.

The coefficients of a power series used to represent the molecular potential energy were evaluated for the H_2 molecule using Dunham's [10] theoretical relations and the rotational and vibrational data for H_2:

$$U=79734\xi^2(1-1.6082\xi+1.8598\xi^2-1.8882\xi^3+1.7118\xi^4-1.450\xi^5+1.421\xi^6), \tag{2.21}$$

where ξ is $(r-r_e)/r_e$, r_e being the equilibrium value of the internuclear separation, and U is expressed in reciprocal centimeters. Although this series is a poor representation of U for internuclear separations twice the equilibrium value (i. e., at $\xi=1$), it is very good for small values of ξ. Therefore, this series was not used for the potential energy function finally accepted for internuclear separations much greater than the equilibrium value, but it was used for internuclear separations less than the equilibrium value. At dissociation the minimum value of r for classical motion is more than half of r_e (i. e., $|\xi|<0.5$), and the series determines the inner portion of the potential energy curve with sufficient reliability for the present purposes.

The ranges of internuclear oscillation, $\xi_{max}-\xi_{min}$, for different values of the energy needed to fix the outer portion of the potential energy curve, were determined from (1) the vibrational levels of the nonrotating molecule, symbolized by G_v in eq 2.17 to eq 2.20, which have been accurately measured to within 140 cm^{-1} of dissociation [5, 12, 20, 21] and (2) the quantum condition.

$$\oint pdq=(2mr_e^2hc)^{1/2}\oint(G_v-U)^{1/2}d\xi=(v+1/2)h. \tag{2.22}$$

The method used to obtain $(\xi_{max}-\xi_{min})$ by satisfying eq 2.22 was essentially that of Rydberg [8] and Klein [9]. Calculated values of the potential energy U in wave numbers are given in table 1.

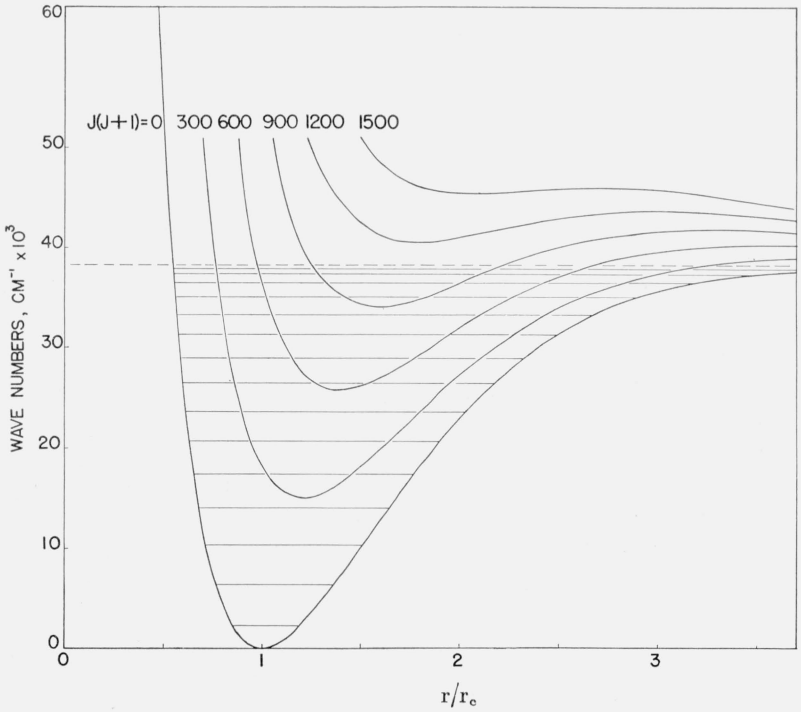

FIGURE 1. *Potential-energy curves for* H_2.

TABLE 1. *Molecular potential energy U for H_2 as a function of $\xi=(r-r_e)/r_e$, the change in internuclear separation*

ξ	U	ξ	U	ξ	U
	cm^{-1}		*cm*$^{-1}$		*cm*$^{-1}$
−0.5	53,648	0.9	20,540	2.3	36,828
−.4	27,150	1.0	22,822	2.4	37,100
−.3	12,338	1.1	24,915	2.5	37,322
−.2	4,511	1.2	26,810	2.6	37,503
−.1	942	1.3	28,505	2.7	37,650
0	0	1.4	30,009	2.8	37,770
.1	683	1.5	31,329	2.9	37,867
.2	2,360	1.6	32,472	3.0	37,946
.3	4,628	1.7	33,454	3.1	38,009
.4	7,223	1.8	34,292	3.2	38,061
.5	9,968	1.9	35,001	3.3	38,102
.6	12,744	2.0	35,599	3.4	38,136
.7	15,466	2.1	36,092	3.5	38,163
.8	18,079	2.2	36,496	∞	38,296
$r_e=0.7414\times10^{-8}$cm					

The effective potential energy curves for rotating molecules obtained by adding to U for the nonrotating molecule the energy of rotation, $J(J+1)B_e/(1+\xi)^2$, in cm^{-1}, are illustrated in figure 1. By applying the quantum integral,

$$\oint pdq=(2mr_e^2hc)^{1/2}\oint (F-U')^{1/2}d\xi=(v+1/2)h, \tag{2.23}$$

to the effective potential energy curves, U', a set of corresponding values of energy (F) and vibrational quantum number was determined for each

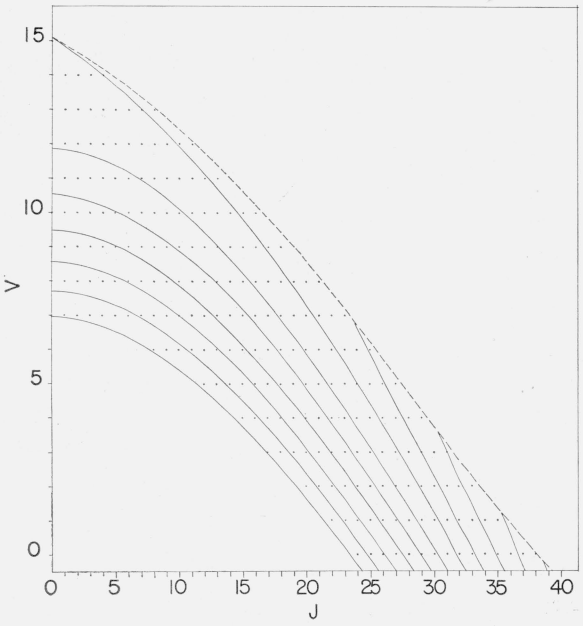

FIGURE 2. *Energy contour diagram for H_2.*

of a few large values of the rotational quantum number. In table 2 these corresponding values are given together with the maximum and minimum values of the energy (F) for different values of $J(J+1)$. The data were used to determine the constant energy lines in the v versus J diagram in figure 2.

TABLE 2. *Corresponding values of v, $J(J+1)$, and F obtained by evaluating $\oint pdq=(v+1/2)h$*

[The values of v and J are not integral and so do not represent stationary states, yet the table values indicate how F depends on v and J over a range including many stationary states.]

F (above U at $\xi=0$)	$J(J+1)$	v
cm^{-1}		
38,269	300	8.8483
34,269	300	6.2874
30,269	300	4.5015
26,269	300	2.9881
22,269	300	1.6461
38,269	600	4.8378
34,269	600	2.7292
30,269	600	1.0757
38,269	900	1.4032
42,269	1,200	0.4845
Maximum values of F and v for given values of $J(J+1)$		
38,288	0	15.053
39,098	300	9.919
40,323	600	6.615
41,858	900	3.929
43,712	1,200	1.703
45,989	1,500	−0.072
Minimum values of F and v for given values of $J(J+1)$		
0	0	−0.5
15,027	300	−.5
25,847	600	−.5
34,111	900	−.5
40,606	1,200	−.5
45,601	1,500	−.5

Table 3 shows that over a wide range of J values the results of the numerical integration just described are in good agreement with the rotational energy formula (eq 2.17) when the last term, corresponding to a geometric series continuation, is included. For the larger values of J there are appreciable differences; yet, when it

is observed how large the final term of eq 2.17 is in these cases, it seems surprising that the discrepancies between F (table 2) and F (eq 2.17 are as small as they are. In another publication [27] a more rapidly converging series representing $J\ (J+1)$ as a function of the rotational energy has been suggested.

TABLE 3. *Comparison of rotational-vibrational energies F from table 2 and from equation 2.17*

$J\ (J+1)$	v	F (table 2)	F (table 2) $-F$ (eq 2.17)	Final term of eq 2.17
		cm $^{-1}$	*cm* $^{-1}$	*cm* $^{-1}$
300	4.5015	30,269	−54	155
300	6.2874	34,269	−34	154
600	1.0757	30,269	−78	3,904
900	1.4032	38,269	−300	24,192
1,200	0.4845	42,269	761	86,345

3. Details of the Calculations and Results

In the evaluation of the series of section II, 1 for the calculation of the thermal properties, direct summation was employed for temperatures below 2,000° K. The resulting values to 2,000° K for the various thermodynamic functions $S°$, $H°-E_0°$, $-(F°-E_0°)/T$, and $C_p°$ for the ideal gas state at one atmosphere pressure are tabulated in tables 4, 5, and 6, for H_2, HD, and D_2. For n-H_2 for temperatures above 2,000° K, the contributions due to levels below 25,000 cm^{-1} were calculated by direct summation, whereas for levels above 25,000 cm^{-1} a less laborious method was used involving the determination of the number of levels within successive equal steps of 2,000 cm^{-1} in the rotational vibrational energy, using the results of the calculations of the last section which led to figures 1 and 2. For these

TABLE 4. *Thermodynamic functions for* H_2 *in the ideal gaseous state*

Values for $S°$ and $-(F°-E_0°)/T$ include nuclear spin

Temperature	$S°$, cal mole $^{-1}$ deg $^{-1}$			$H°-E_0°$, cal mole $^{-1}$			$-\frac{F°-E_0°}{T}$, cal mole $^{-1}$ deg $^{-1}$			$C_p°$ cal mole $^{-1}$ deg $^{-1}$		
	p-H_2	o-H_2	n-H_2	p-H_2	o-H_2	n-H_2	p-H_2	o-H_2	n-H_2	p-H_2	o-H_2	n-H_2
°*K*												
10	11.215	15.581	15.607	49.6785	388.327	303.665	6.247	−23.252	−14.760	4.968	4.968	4.968
20	14.658	19.024	19.050	99.357	438.006	353.344	9.690	−2.876	1.382	4.968	4.968	4.968
20.39	14.754	19.120	19.146	101.295	439.943	355.281	9.786	−2.457	1.721	4.968	4.968	4.968
30	16.672	21.039	21.064	149.036	487.684	403.022	11.705	4.783	7.630	4.968	4.968	4.968
33.1	17.161	21.527	21.553	164.437	503.085	418.423	12.193	6.328	8.911	4.968	4.968	4.968
40	18.102	22.468	22.494	198.729	537.363	452.705	13.134	9.034	11.176	4.973	4.968	4.969
50	19.214	23.576	23.603	248.581	587.041	502.426	14.243	11.836	13.554	5.007	4.968	4.978
60	20.135	24.492	24.513	299.106	636.722	552.318	15.150	13.870	15.307	5.115	4.969	5.005
70	20.938	25.248	25.288	351.222	686.422	602.622	15.921	15.442	16.679	5.330	4.972	5.061
80	21.669	25.913	25.969	406.015	736.179	653.638	16.594	16.710	17.799	5.646	5.982	5.148
90	22.356	26.500	26.581	464.385	786.085	705.660	17.197	17.766	18.741	6.036	5.003	5.261
100	23.014	27.029	27.142	526.837	836.277	758.916	17.745	18.667	19.554	6.455	5.039	5.393
120	24.259	27.959	28.151	663.752	938.227	869.609	18.729	20.140	20.904	7.204	5.170	5.678
150	25.945	29.143	29.461	890.605	1,097.78	1,045.99	20.007	21.825	22.488	7.807	5.487	6.067
200	28.202	30.808	31.275	1,282.70	1,387.90	1,361.61	21.788	23.869	24.466	7.742	6.110	6.518
250	29.889	32.225	32.758	1,660.49	1,705.80	1,694.47	23.246	25.402	25.981	7.380	6.565	6.770
298.16	31.168	33.404	33.963	2,009.99	2,028.34	2,023.75	24.426	26.602	27.175	7.158	6.803	6.891
300	31.212	33.446	34.005	2,023.16	2,040.87	2,036.44	24.468	26.643	27.217	7.152	6.809	6.894
350	32.306	34.505	35.073	2,377.84	2,384.39	2,382.75	25.512	27.693	28.265	7.049	6.917	6.951
400	33.244	35.432	36.003	2,729.19	2,731.54	2,730.95	26.421	28.603	29.175	7.010	6.963	6.975
500	34.806	36.990	37.561	3,429.24	3,429.53	3,429.46	27.948	30.131	30.702	6.998	6.992	6.993
600	36.083	38.266	38.838	4,129.48	4,129.52	4,129.51	29.200	31.383	31.955	7.010	7.009	7.009
700	37.165	39.348	39.920	4,831.65	4,831.66	4,831.66	30.263	32.446	33.018	7.037	7.036	7.036
1,000	39.701	41.884	42.455	------	----------	6,966.23	32.735	34.918	35.490	-----	---------	7.219
1,500	42.720	44.903	45.475	------	----------	10,697.20	35.589	37.770	38.343	-----	---------	7.720
2,000	45.007	47.190	47.762	------	----------	14,679.2	37.668	39.851	40.422	-----	---------	8.195
3,000	------	------	51.221	------	----------	23,230.9	------	--------	43.478	-----	---------	8.859
4,000	------	------	53.839	------	----------	32,345.	------	--------	45.753	-----	---------	9.342
5,000	------	------	55.969	------	----------	41,895.	------	--------	47.590	-----	---------	9.748

TABLE 5. *Thermodynamic functions for HD in the ideal gas state*

Values for S° and $-(F^\circ-E_0^\circ)/T$ include nuclear spin

Temperature	S_0	$H^\circ-E_0^\circ$	$-\frac{F^\circ-E_0^\circ}{T}$	C_p°
°K	*cal mole*$^{-1}$ *deg*$^{-1}$	*cal mole*$^{-1}$	*cal mole*$^{-1}$ *deg*$^{-1}$	*cal mol*$^{-1}$ *deg*$^{-1}$
10	15.982	49.681	11.014	4.971
20	19.497	100.600	14.468	5.365
22.13	20.050	112.234	14.979	5.564
30	21.861	159.230	16.553	6.367
40	23.792	226.510	18.129	6.991
50	25.375	297.472	19.425	7.149
60	26.680	368.910	20.531	7.126
70	27.772	439.914	21.488	7.076
80	28.714	510.464	22.333	7.037
90	29.542	580.708	23.089	7.013
100	30.279	650.733	23.772	6.999
120	31.554	790.592	24.966	6.985
150	33.112	1,002.02	26.445	6.978
200	35.119	1,348.82	28.375	6.975
250	36.676	1,697.62	29.885	6.977
298.16	37.905	2,033.66	31.084	6.979
300	37.948	2,046.50	31.126	6.979
400	39.957	2,744.72	33.095	6.986
500	41.517	3,443.85	34.629	6.999
600	42.795	4,144.90	35.886	7.025
700	43.881	4,849.60	36.953	7.072
1,000	46.443	7,007.50	39.436	7.339
1,500	49.527	10,821.2	42.313	7.909
2,000	51.871	14,898.4	44.421	8.376

higher levels having characteristic temperatures above 36,000° K, the exact placement of each individual level is not important for calculations up to 5,000° K.

Figure 1 shows that the effective potential energy curves for rotational quantum numbers other than 0 have broad potential energy barriers above the minimum dissociation energy, 38,296 cm^{-1}, for $J=0$. As a result there are above 38,296 cm^{-1}, the minimum dissociation energy, quantized rotational-vibrational levels belonging to the sequences of levels below 38,296 cm^{-1}. These states are represented by the points in figure 2 between the dashed curve and the full line dissociation energy curve passing through ($J=0$, $v=15.1$) and ($J=32.5$, $v=-\frac{1}{2}$).

It seemed proper to include in the calculations of the thermal properties of hydrogen above 2,000° K these quantized or partially quantized rotational-vibrational states. The values of the thermodynamic functions for n-H_2 from 2,000° to 5,000° K in table 4 are based on this convention.

The effect of the quantized rotational-vibrational levels above the minimum dissociation energy of H_2 on the most sensitive of the functions calculated, namely the molecular heat capacity, is represented in figure 3. Curve A represents the

TABLE 6. *Thermodynamic functions for* D_2 *in the ideal gaseous state*

Values for S° and $-(F^\circ-E_0^\circ)/T$ include nuclear spin

Temperature	S°, cal mole^{-1} deg^{-1}			$H^\circ-E_0^\circ$, cal mole^{-1}			$-\frac{F^\circ-E_0^\circ}{T}$, cal mole^{-1} deg^{-1}			C_p°, cal mole^{-1} deg^{-1}		
	p-D_2	o-D_2	n-D_2	p-D_2	o-D_2	n-D_2	p-D_2	o-D_2	n-D_2	p-D_2	o-D_2	n-D_2
°K												
10	17.645	16.839	18.372	220.505	49.679	106.621	−4.406	11.871	7.710	4.968	4.968	4.968
20	21.088	20.283	21.816	270.183	99.364	156.303	7.579	15.315	14.001	4.968	4.972	4.971
23.57	21.904	21.101	22.633	287.918	117.139	174.065	9.689	16.131	15.248	4.968	4.989	4.982
30	23.102	22.315	23.842	319.863	149.514	206.297	12.440	17.331	16.965	4.968	5.105	5.059
40	24.533	23.843	25.338	369.584	202.775	258.378	15.293	18.774	18.879	4.980	5.617	5.404
50	25.649	25.180	26.600	419.599	262.811	315.048	17.257	19.923	20.299	5.033	6.412	5.952
60	26.576	26.418	27.736	470.480	330.843	377.389	18.734	20.904	21.446	5.156	7.163	6.495
70	27.384	27.563	28.768	522.948	405.192	444.444	19.913	21.775	22.419	5.348	7.656	6.887
80	28.114	28.601	29.704	577.589	482.997	514.528	20.893	22.564	23.272	5.586	7.862	7.103
90	28.786	29.527	30.545	634.706	561.671	586.016	21.734	23.287	24.035	5.838	7.860	7.187
100	29.414	30.353	31.304	694.306	639.875	658.018	22.471	23.954	24.724	6.079	7.751	7.193
120	30.559	31.739	32.611	819.996	791.908	801.270	23.725	25.139	25.933	6.466	7.454	7.125
150	32.041	33.366	34.189	1,019.52	1,010.37	1,013.42	25.244	26.629	27.432	6.790	7.149	7.029
200	34.023	35.395	36.202	1,364.06	1,362.90	1,363.29	27.202	28.580	29.386	6.947	6.996	6.980
298.16	36.805	38.182	38.988	2,048.10	2,048.08	2,048.09	29.936	31.313	32.119	6.977	6.978	6.978
300	36.848	38.225	39.031	2,060.93	2,060.92	2,060.92	29.978	31.355	32.161	6.977	6.978	6.978
400	38.857	40.234	41.040	--------	--------	2,759.18	31.959	33.336	34.142	-----	-----	6.989
500	40.419	41.796	42.602	--------	--------	3,459.38	33.500	34.877	35.683	-----	-----	7.019
600	41.704	43.081	43.887	--------	--------	4,164.03	34.763	36.141	36.946	-----	-----	7.079
700	42.802	44.179	44.985	--------	--------	4,876.39	35.835	37.212	38.018	-----	-----	7.173
1,000	45.422	46.800	47.605	--------	--------	7,084.30	38.338	39.716	40.521	-----	-----	7.562
1,500	48.611	49.989	50.794	--------	--------	11,027.3	41.259	42.637	43.442	-----	-----	8.178
2,000	51.027	52.405	53.210	--------	--------	15,229	43.411	44.789	45.594	-----	-----	8.598

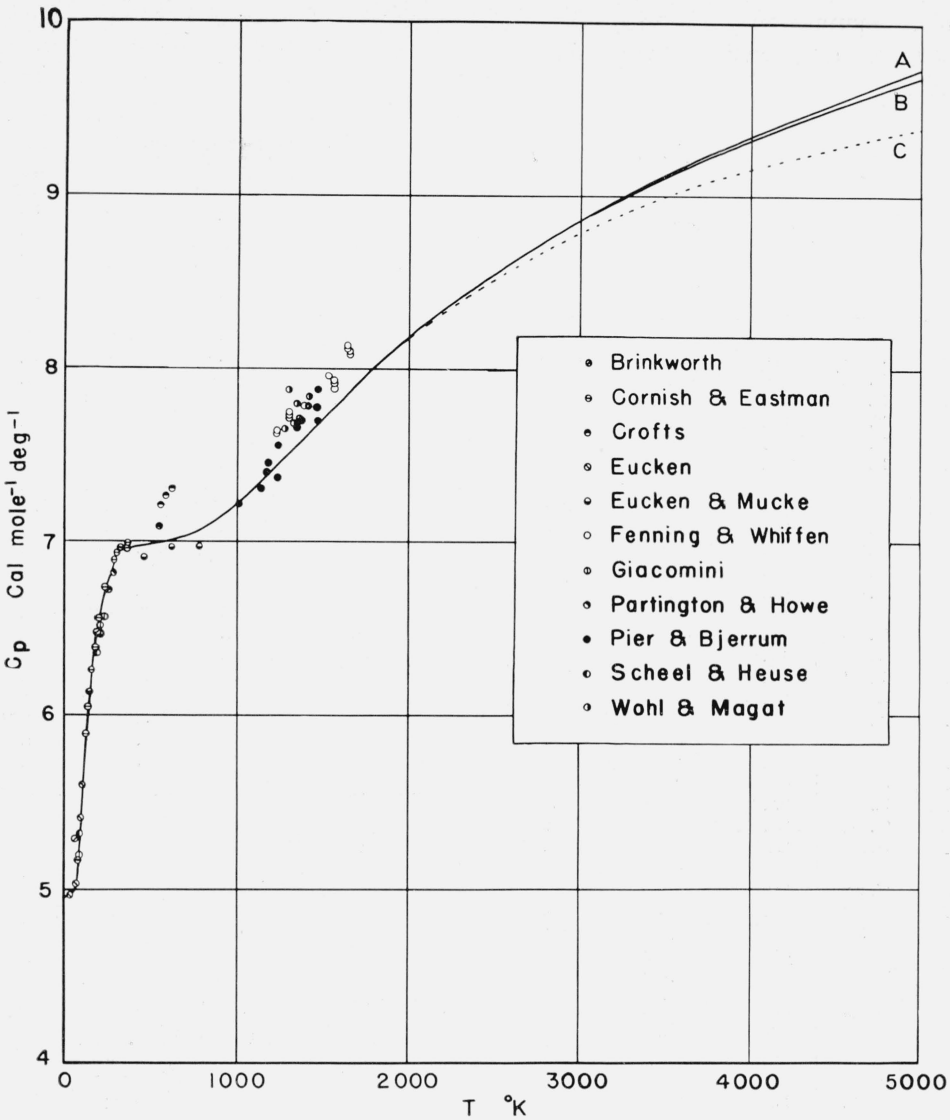

FIGURE 3. *Specific heat of normal hydrogen at constant pressure.*

TABLE 7. *Thermodynamic functions for* H_2 *in ideal gaseous state*

[Based only on levels below minimum dissociation energy]

T	Entropy	Enthalpy	$-\frac{F^\circ-E_0^\circ}{T}$	Specific heat
° *K*	*cal mole*$^{-1}$ *deg*$^{-1}$	*cal mole*$^{-1}$	*cal mole*$^{-1}$ *deg*$^{-1}$	*cal mole*$^{-1}$ *deg*$^{-1}$
3,000	51.221	23,230.8	43.478	8.859
4,000	53.838	32,341	45.753	9.341
5,000	55.960	41,854	47.589	9.675

molecular heat capacity if the quantized rotational-vibrational levels above the minimum dissociation energy are included as molecular levels, and curve B represents the molecular heat capacity if the molecular levels are regarded as extending only up to the minimum dissociation energy. In table 7 are tabulated the values of the thermodynamic functions for n-H_2 based on calculations involving only energy levels below the minimum dissociation energy.

For convenience in the calculation of the thermodynamic functions of the real gas n-H_2, values for n-H_2 in the ideal gas state at all temperatures for which there are entries in the tables of PVT data were obtained from table 4 by interpolation and are tabulated in table 8. The interpolated values of S°, $-(F^\circ-E_0^\circ)/T$, and C_p° agree to within ± 0.001 with values that would have been ob-

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tained by direct summation. In the case of $H^\circ - E_0^\circ$, the agreement is within three in the last digit carried.

TABLE 8. *Thermodynamic functions for normal* H_2 *in the ideal gaseous state*

Values for S° and $-(F^\circ - E_0^\circ)/T$ include nuclear spin

T	S°	$H^\circ - E_0^\circ$	$-\frac{F^\circ - E_0^\circ}{T}$	C_p°
° K	*cal mole* $^{-1}$ *deg* $^{-1}$	*cal mole* $^{-1}$	*cal mole* $^{-1}$ *deg* $^{-1}$	*cal mole* $^{-1}$ *deg* $^{-1}$
16	17.942	333.473	−2.900	4.968
18	18.527	343.408	−0.551	4.968
20	19.050	353.344	1.382	4.968
22	19.524	363.280	3.011	4.968
24	19.956	373.215	4.405	4.968
26	20.353	383.151	5.616	4.968
28	20.722	393.087	6.683	4.968
30	21.064	403.022	7.630	4.968
32	21.385	412.959	8.480	4.968
34	21.686	422.896	9.248	4.968
36	21.970	432.832	9.947	4.968
38	22.239	442.767	10.587	4.968
40	22.494	452.705	11.176	4.969
42	22.737	462.643	11.722	4.970
44	22.968	472.583	12.227	4.971
46	23.189	482.527	12.699	4.973
48	23.400	492.474	13.140	4.975
50	23.603	502.426	13.554	4.978
52	23.798	512.384	13.944	4.982
54	23.986	522.351	14.313	4.986
56	24.168	532.327	14.662	4.991
58	24.343	542.315	14.993	4.998
60	24.513	552.318	15.307	5.005
65	24.915	577.399	16.032	5.029
70	25.288	602.622	16.679	5.061
75	25.639	628.022	17.265	5.101
80	25.969	653.638	17.799	5.148
85	26.283	679.507	18.289	5.202
90	26.581	705.660	18.741	5.261
95	26.868	732.122	19.161	5.325
100	27.142	758.916	19.554	5.393
105	27.408	786.056	19.922	5.463
110	27.664	813.549	20.268	5.534
115	27.911	841.400	20.595	5.606
120	28.151	869.609	20.904	5.678
125	28.384	898.175	21.198	5.748
130	28.610	927.086	21.479	5.816
135	28.831	956.335	21.747	5.883
140	29.047	985.91	22.005	5.947
145	29.257	1,015.80	22.251	6.008
150	29.461	1,045.99	22.488	6.067
155	29.661	1,076.47	22.716	6.123
160	29.856	1,107.22	22.936	6.177
165	30.047	1,138.23	23.149	6.228
170	30.234	1,169.49	23.355	6.276
180	30.595	1,232.71	23.747	6.366
190	30.942	1,296.78	24.116	6.446
200	31.275	1,361.61	24.466	6.518
210	31.594	1,427.10	24.798	6.581
220	31.901	1,493.20	25.114	6.638

TABLE 8. *Thermodynamic functions for normal* H_2 *in the ideal gaseous state*—Continued

T	S°	$H^\circ - E_0^\circ$	$-\frac{F^\circ - E_0^\circ}{T}$	C_p°
° K	*cal mole* $^{-1}$ *deg* $^{-1}$	*cal mole* $^{-1}$	*cal mole* $^{-1}$ *deg* $^{-1}$	*cal mole* $^{-1}$ *deg* $^{-1}$
230	32.197	1,559.85	25.415	6.688
240	32.483	1,626.96	25.704	6.731
250	32.758	1,694.47	25.981	6.770
260	33.024	1,762.33	26.246	6.803
270	33.282	1,830.49	26.502	6.831
280	33.531	1,898.92	26.749	6.856
300	34.005	2,036.44	27.217	6.894
320	34.452	2,174.63	27.656	6.922
340	34.872	2,313.28	28.068	6.943
360	35.269	2,452.29	28.457	6.957
380	35.646	2,591.53	28.826	6.968
400	36.003	2,730.95	29.175	6.975
420	36.344	2,870.51	29.509	6.980
440	36.668	3,010.14	29.826	6.984
460	36.979	3,149.85	30.131	6.987
480	37.276	3,289.62	30.422	6.990
500	37.561	3,429.46	30.702	6.993
520	37.837	3,569.34	30.973	6.996
540	38.100	3,709.28	31.231	6.999
560	38.355	3,849.30	31.481	7.002
580	38.600	3,989.36	31.722	7.005
600	38.838	4,129.51	31.955	7.009
650	39.399	4,480.19	32.506	7.021

The contributions to the entropy and to the related free energy functions arising from (1) the nuclear spins, (2) the triple degeneracy of the lowest rotational state of o-H_2 and p-D_2, and (3) the mixing of the ortho and para varieties in n-H_2 and n-D_2 have been included through eq 2.3, 2.4, 2.15, and 2.16 in all the tables. A comparison of the entropies and free energies of hydrogen and deuterium calculated from calorimetric data with values in the tables must take into account the degeneracies existing in the solid state at the lowest temperature of the calorimetric measurements. There must accordingly be added to the calorimetric values of entropy calculated from data extending from 10° K to higher temperatures, the entropies of table 9. In calculations concerning chemical reactions above room temperature nuclear spin entropies are customarily omitted for all components of the reactions.

To obtain entropies of n-H_2, HD, and n-D_2 suitable for such use above room temperature, there should be subtracted from table values of the entropies $R\ ln\ (2i_1+1)\ (2i_2+2)$ where i_1 and i_2 are the two nuclear spins within the molecule [14]. For n-H_2 this is equal to $R\ ln\ 4 = 2.755$

TABLE 9. *Low-temperature (10° K) entropy contributions arising from rotational and nuclear-spin degeneracies*

	H_2		HD	D_2	
Variety	Para	Ortho	Only 1	Ortho	Para
Values of J	Even	Odd	Both odd and even	Even	Odd
Weight of lowest rotational level $(2J+1)$.	1	3	1	1	3
Nuclear spin weight, see eq 2.3 and 2.4.	1	3	6	6	3
Total added entropy	0	R ln 9=4.366 cal mole $^{-1}$deg^{-1}.	R ln 6=3.560 cal mole $^{-1}$deg $^{-1}$.	R ln 6=3.560 cal mole $^{-1}$deg^{-1}.	R ln 9=4.366 cal mole $^{-1}$deg^{-1}.

	n-H_2	n-D_2
$-R(x_o \ln x_o + x_p \ln x_p)$	$R(\ln 4 - \frac{3}{4} \ln 3) = 1.117$ cal mole^{-1} deg^{-1}	$R(\ln 3 - \frac{2}{3} \ln 2) = 1.265$ cal mole^{-1} deg^{-1}
$x_o s_o + x_p s_p$	$\frac{3}{4} R \ln 9 = 3.275$ cal mole^{-1} deg^{-1}	$R(\frac{1}{3} \ln 3 + \frac{2}{3} \ln 2) = 3.829$ cal mole $^{-1}$ deg^{-1}
Total added entropy $(x_j s_j - R x_j \ln x_j)$	$R(\ln 4 + \frac{3}{4} \ln 3) = 4.392$ cal mole^{-1}deg $^{-1}$	$\frac{7}{3} R \ln 3 = 5.094$ cal mole^{-1}deg^{-1}

cal mole^{-1} deg^{-1}; for HD, $R\ ln\ 6 = 3.560$ cal mole^{-1} deg^{-1}, and for n-D_2, $R\ ln\ 9 = 4.366$ cal mole^{-1} deg^{-1}.

The reliability to be expected in thermodynamic functions for the ideal gas state calculated from spectroscopic data has been considered by earlier writers on the basis of the reliability of spectroscopic constants and the gas constant R. The former estimate of one or two hundredths of a calorie mole^{-1} deg^{-1} for the probable error in the free energy function, specific heat and entropy, appears reasonable. Over much of the temperature range it is probably a more liberal estimate than necessary, as more recent and presumably better spectroscopic data and values for the physical constants have been used. A larger allowance may be necessary for the higher temperatures, however, possibly twice as much at 5,000° K.

The results of the present calculations below 2,000° K are in fairly close agreement with those of Giauque [4], Johnston and Long [18], Davis and Johnston [17], and Wagman, et al. [28]. Above 2,000° K the effect of the new calculations of the high rotational levels of H_2 is apparent.

This can be seen in figure 3 in which the results of Davis and Johnston (curve C) for the specific heat of hydrogen, the most sensitive property calculated, are compared with table values of this paper (curves A and B). Curve A, corresponding to table 4, is based on the inclusion of the quantized rotational-vibrational levels above the minimum dissociation energy as molecular levels, and curve B, corresponding to table 7, is based only on levels below the minimum dissociation energy.

In figure 3 are plotted also a large number of scattered points representing the experimental observations of many investigators. [33 to 37, 40 to 46, 50, 51, 56]. In cases where mean specific heats were reported, they have been plotted for the mean temperatures of the experimental intervals. At room temperatures and below, the theoretical and experimental specific heats are in good agreement, as has been the case since the correct treatment of the ortho and para forms by Dennison [1] in 1927. Above 1,200° K the observations obtained by the explosion method lie above the theoretical curve. The difficulties of the explosion method are great and the accuracy not high [53], consequently the authors feel that the calculated curve and table are more reliable.

At atmospheric pressure and a temperature of 2,000° K, there is a small but perceptible dissociation of H_2, HD, and D_2. As the heat of dissociation of hydrogen is large there are significant differences between the calculated properties of molecular H_2, HD, and D_2, tables 4 to 6, and the properties of the dissociating gases. At 2,000° K the table value of C_p for molecular H_2 is 8.195 cal mole^{-1} deg^{-1}, whereas for an ideal gas mixture of molecular and atomic hydrogen in equilibrium at atmospheric pressure the value is 8.797, a difference of 0.60 cal mole^{-1} deg $^{-1}$. For HD and D_2 the differences between the two specific heats are 0.41 and 0.57 cal mole^{-1} deg^{-1}, respectively. The effect of pressure upon the specific heat of dissociating hydrogen is illustrated in figure 4 and discussed in section III. At temperatures where there is appreciable dissociation of HD, equilibrium mixtures of H_2, HD, and D_2, are established.

III. Equilibrium Constants for Dissociation, Isotopic Exchange, and Ortho-Para Conversion

The equilibrium constant K of a gaseous reaction

$$\alpha_1 A_1+\alpha_2 A_2+\alpha_3 A_3\ldots=\beta_1 B_1+\beta_2 B_2+\beta_3 B_3\ldots, \quad (3.1)$$

in which each of the participating gases $A_1, A_2, \ldots, B_1, B_2, \ldots$ has the equation of state $PV=RT$, is related to the partial pressures of the gases and to their free energies, F^*, at unit pressure by the equation

$$RT\ln\frac{P_{B_1}^{\beta_1}P_{B_2}^{\beta_2}P_{B_3}^{\beta_3}\ldots}{P_{A_1}^{\alpha_1}P_{A_2}^{\alpha_2}P_{A_3}^{\alpha_3}\ldots}=RT\ln K= -(\Sigma\beta_j F_{B_j}^{*}-\Sigma\alpha_j F_{A_j}^{*})=-\Delta F^*. \quad (3.2)$$

Equilibrium constants for dissociation, isotopic exchange,[6] and ortho-para conversion of hydrogen may be calculated by using the $-(F^\circ-E_0^\circ)/T$ values of tables 4, 5, and 6. E_0° is the internal energy per mole of molecules without translational motion in the lowest energy level $J=0$, $v=0$ and in the ideal gas state, and F° is for the ideal gas state and a pressure of 1 atm: Using $-(F^\circ-E_0^\circ)/T$ instead of F^*,

$$R\ln K=\Delta\frac{-(F^\circ-E_0^\circ)}{T}-\frac{\Delta E_0^\circ}{T}. \quad (3.3)$$

The values of ΔE_0° for the reactions considered in this section are given by the spectroscopic data used in the previous section. Using free energy values as given in the tables of this paper, the atmosphere is the unit of pressure for K and P in the mass action law,

$$\frac{P_{B_1}^{\beta_1}P_{B_2}^{\beta_2}P_{B_3}^{\beta_3}\ldots}{P_{A_1}^{\alpha_1}P_{A_2}^{\alpha_2}P_{A_3}^{\alpha_3}\ldots}=K. \quad (3.4)$$

Deviations from the laws of ideal gases can be taken into account by use of fugacities or activities in place of partial pressures and the forms of eq 3.2, 3.3, and 3.4 for K are retained. When fugacities or activities are substituted for partial pressures, F^* becomes the free energy at unit fugacity or activity. For a fuller discussion of the use of fugacities and activities the reader is referred to references [29 to 32].

The entropies of monatomic H and D (see p. 383) must include the nuclear and electron spin entropies besides the entropy of translation, eq

[6] Equilibrium H_2 and D_2.

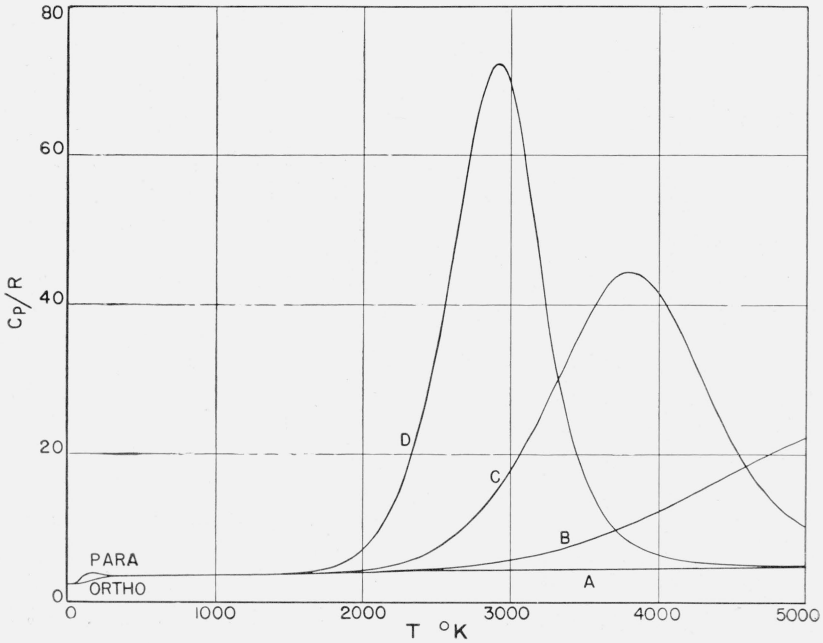

FIGURE 4. *Curves showing effect of dissociation on specific heat of* H_2.

2.12, when used with table values of the entropy and free energy of molecular H_2, HD, and D_2, in the calculation of equilibrium constants for dissociation. Accordingly for H,

$$-\frac{F^\circ-E_0^\circ}{RT}=\frac{5}{2}\ln T-2.2663 \text{ and } \frac{S^\circ}{R}=\frac{5}{2}\ln T+0.2337, \tag{3.5}$$

and for D,

$$-\frac{F^\circ-E_0^\circ}{RT}=\frac{5}{2}\ln T-0.8223 \text{ and } \frac{S^\circ}{R}=\frac{5}{2}\ln T+1.6777 \tag{3.6}$$

in the ideal gas state at a pressure of 1 atm for the range of temperatures covered by the tables.

1. Dissociation of H_2, D_2, and HD

The chemical equations for dissociation and the corresponding mass action equations are

$$\text{(a) } H_2 \leftrightarrows 2H; \quad \frac{P_H^2}{P_{H_2}}=K_{H_2}. \tag{3.7}$$

$$\text{(b) } D_2 \leftrightarrows 2D; \quad \frac{P_D^2}{P_{D_2}}=K_{D_2}. \tag{3.8}$$

$$\text{(c) } HD \leftrightarrows H+D; \quad \frac{P_H P_D}{P_{HD}}=K_{HD}. \tag{3.9}$$

For these reactions, ΔE_0° of eq 3.3 is the difference between the internal energy of 2 moles of dissociated atoms and 1 mole of molecules in the rotational-vibrational state $J=0$, $v=0$. Beutler's value [21], $36{,}116\pm6$ cm^{-1}, was accepted for the dissociation of H_2 from its ground state. Assuming that the total depth of the potential energy curve is the same for H_2, HD, and D_2, the dissociation energies of HD and D_2 were obtained from the zero-point vibrational energies. These zero point energies were calculated by adding to G_0 (see eq 2.17), the term which Dunham [10] included in the energy of the ground state relative to the bottom of the potential energy curve and designated Y_{00} in his system. The values thus obtained for the zero point energies of H_2, HD, and D_2 were respectively 2,179.6, 1,891.0, 1,546.6 cm^{-1}, and the corresponding energies of dissociation for HD and D_2 from the ground state $36{,}404._6$ and $36{,}749._0$ cm^{-1}, respectively.

The heats of dissociation of H_2, HD, and D_2 in the ideal gas state at temperature T are equal to $\Delta E_0^\circ+5RT-(H^\circ-E_0^\circ)$, where $(H^\circ-E_0^\circ)$ is the table value of the enthalpy at temperature T. The heats of dissociation at 0° and 298.16° K are given in table 11. The theoretical value for the heat of dissociation of n-H_2 at 298° K agrees well with the calorimetric value $105{,}000\pm3{,}500$ cal mole^{-1} obtained by Bichowsky and Copeland [47].

On the assumption that the atomic and molecular forms of hydrogen and deuterium are individually ideal gases, the fraction of the originally totally nondissociated hydrogen which has dissociated is $\sqrt{K/(K+4P)}$, where K is the dissociation constant and P is the total pressure in atmospheres.

The dissociation constants K and fractions of originally undissociated diatomic molecules, dissociated at 1-atmosphere pressure, are given in table 10 for H_2, HD, and D_2.

The experimental values of the equilibrium dissociation constants of H_2 as determined by Langmuir and Mackay [32], and by Langmuir [39], are in agreement with the theoretical values of table 10. Langmuir's x-values are 0.17 percent at

TABLE 10. *Dissociation constants, K, and fraction dissociated, x, at 1-atm pressure*

T, °K	K	x
For $H_2 \rightleftarrows 2H$		
	atm	
300	18.39×10^{-72}	21.44×10^{-37}
500	4.939×10^{-41}	3.514×10^{-21}
1,000	5.174×10^{-18}	1.137×10^{-9}
1,500	3.100×10^{-10}	8.675×10^{-6}
2,000	2.641×10^{-6}	8.125×10^{-4}
3,000	2.480×10^{-2}	0.07850
4,000	2.5236	.6220
5,000	41.038	.9546
For $HD \rightleftarrows H+D$		
300	2.732×10^{-72}	8.264×10^{-37}
500	1.265×10^{-41}	1.779×10^{-21}
1,000	1.987×10^{-18}	7.048×10^{-10}
1,500	1.350×10^{-10}	5.810×10^{-6}
2,000	1.215×10^{-6}	5.512×10^{-4}
For $D_2 \rightleftarrows 2D$		
300	1.319×10^{-72}	5.742×10^{-37}
500	1.171×10^{-41}	1.711×10^{-21}
1,000	2.972×10^{-18}	8.620×10^{-11}
1,500	2.330×10^{-10}	7.632×10^{-6}
2,000	2.227×10^{-6}	7.462×10^{-4}

2,000° K, 1.6 percent at 2,500° K, 7.2 percent at 3,000° K, and 21 percent at 3,500° K.

TABLE 11. *Heats of dissociation of* H_2, HD, *and* D_2 *in cal mole*$^{-1}$

T	p-H_2	o-H_2	n-H_2	HD	o-D_2	p-D_2	n-D_2
°K							
0	103, 239	102, 900	102, 985	104, 064	105, 048	104, 877	104, 991
298. 16	104, 191	104, 173	104, 177	104, 992	105, 962	105, 962	105, 962

An equation of state for 1 mole of molecular H_2, HD, or D_2 capable of forming 2 moles of atoms when completely dissociated, assuming as before that atoms and molecules individually behave as ideal gases, is

$$\frac{PV}{RT}=1+\sqrt{\frac{K}{K+4P}} \tag{3.10}$$

or

$$\frac{PV}{RT}=1-\frac{KV}{8RT}\left(1-\sqrt{1+16\frac{RT}{KV}}\right), \tag{3.11}$$

where K is a function of T determined by eq 3.3 and V is the volume per $2N_0$ atoms uncombined or combined as molecules.

The thermodynamic properties of an equilibrium mixture of atomic and molecular hydrogen in the ideal gas state can in principle be calculated from the properties of atomic hydrogen at low pressures and the equation of state (eq 3.10) or (eq. 3.11). It is simpler, however, to determine the properties of the mixture from the properties of the atomic and molecular varieties and the fraction dissociated.

The equation given by Epstein [30] for the heat capacity of a reacting gas mixture, when applied to the heat capacity of an equilibrium mixture of atomic and molecular hydrogen, is

$$\frac{(C_p^\circ)_{\text{mixture}}}{R}=2x\frac{(C_p^\circ)_{\text{atomic}}}{R}+(1-x)\frac{(C_p^\circ)_{\text{molecular}}}{R}+\frac{(1-x^2)x}{2}\left[2\frac{(H^\circ)_{\text{atomic}}}{RT}-\frac{(H^\circ)_{\text{molecular}}}{RT}\right]^2, \tag{3.12}$$

where x is the fraction of the originally totally nondissociated hydrogen that has dissociated, $(C_p^\circ)_{\text{atomic}}$ and $(C_p^\circ)_{\text{molecular}}$ are heat capacities per mole of atoms and molecules respectively in the ideal gas state, and $(C_p^\circ)_{\text{mixture}}$ is for a mixture containing $2N_0$ of atoms combined or uncombined, the components being in the ideal gas state. $(C_p^\circ)_{\text{mixture}}$ is a function of P as well as T since x is a function of P. In figure 4, curves D, C, and B show the variation of $(C_p^\circ/R)_{\text{mixture}}$ for H_2 with temperature for pressures of 0.01, 1, and 100 atmospheres, respectively. Curve A drawn for comparison is the heat capacity of 1 mole of undissociated H_2, that is, $(C_p^\circ/R)_{\text{molecular}}$. It appears from these curves that when dissociation has its greatest importance, thermal effects originating in other ways are likely to be dwarfed by comparison. Wildt [19] has calculated the ratio of specific heats of hydrogen at high temperatures using principles similar to those employed here. The results obtained have application to stellar atmospheres.

2. Ortho-Para Equilibrium

$$o\text{-}H_2 \leftrightarrows p\text{-}H_2,\ \frac{P_{p\text{-}H_2}}{P_{o\text{-}H_2}}=\left(\frac{p\text{-}H_2}{o\text{-}H_2}\right)=K. \tag{3.13}$$

$$p\text{-}D_2 \leftrightarrows o\text{-}D_2,\ \frac{P_{o\text{-}D_2}}{P_{p\text{-}D_2}}=\left(\frac{o\text{-}D_2}{p\text{-}D_2}\right)=K. \tag{3.14}$$

The equilibrium constants of the ortho-para conversion of H_2 and D_2 in the ideal gas state are independent of P. Accordingly, pressure does not appreciably change the ortho-para ratio under equilibrium conditions. Although the lowest rotational levels of the ortho and para varieties differ, ΔE_0° for the two reactions (eq 3.13 and eq 3.14) is zero, because in the calculations for both the ortho and para varieties the ground state of the molecule, $J=0$ and $v=0$, was arbitrarily selected as the origin of energies.

In table 12 are given values of the percentage para composition in the ideal gas state of equilibrium mixtures of ortho-para varieties calculated from the state-sums, $\Sigma g_j e^{-\epsilon^j/kT}$, see eq 2.2 and eq 2.14. These values are in close agreement with earlier values obtained by Harkness and Deming [11] and are in agreement with the variations in the relative intensities of the ortho-para spectral lines and with estimates of the ortho-para compositions based on measurements of thermal conduction from heated wires. The success in explaining the heat capacity of gaseous hydrogen at moderate and low temperatures is also corroborating evidence for table 12 [48].

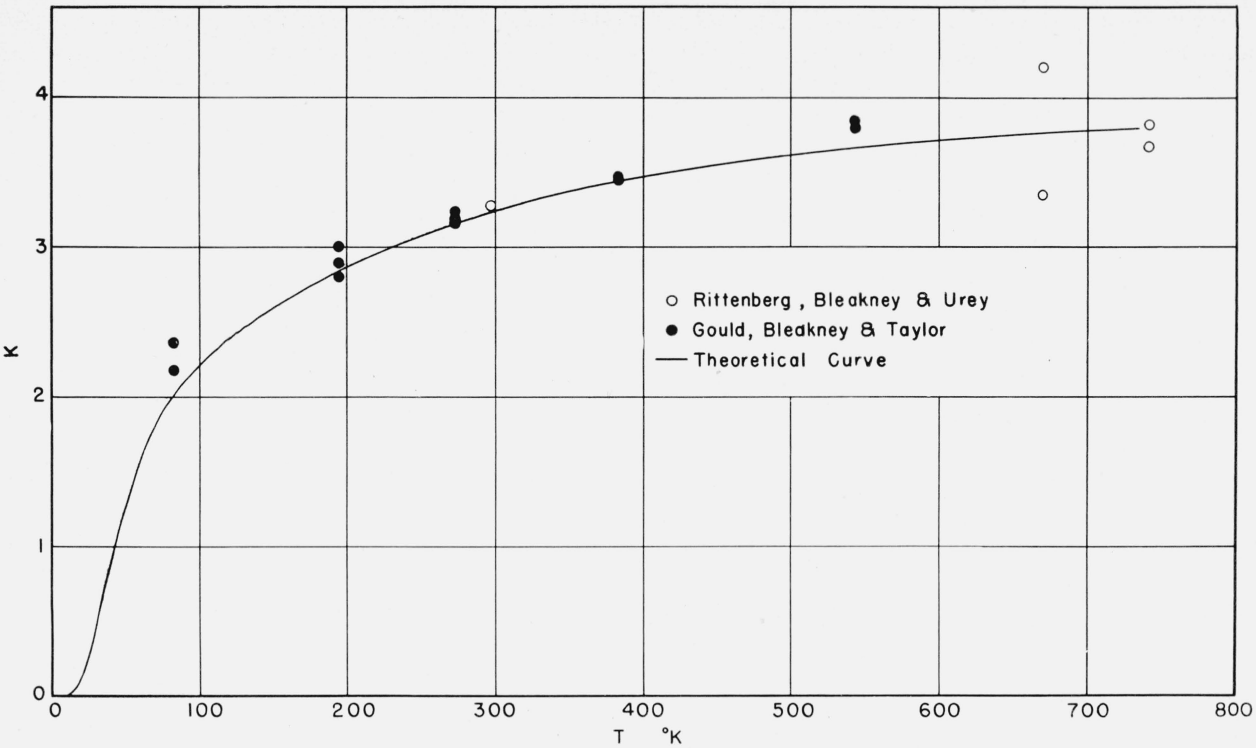

FIGURE 5. *The equilibrium constant for* $H_2+D_2 \rightleftarrows 2HD$.

TABLE 12. *Ortho-para composition at equilibrium*

T	Percentage in para form for H_2	Percentage in para form for D_2
°K		
10	99.9999	0.0277
20	99.821	1.998
20.39	99.789	----------
23.57	----------	3.761
30	97.021	7.864
33.19	95.034	----------
40	88.727	14.784
50	77.054	20.718
60	65.569	25.131
70	55.991	28.162
80	48.537	30.141
90	42.882	31.395
100	38.620	32.164
120	32.959	32.916
150	28.603	33.246
200	25.974	33.327
250	25.264	----------
298.16	25.075	33.333
300	25.072	33.333
350	25.019	----------
400	25.005	----------
500	25.000	----------

3. Isotopic Exchange

The chemical and mass action equations for isotopic exchange are

$$H_2+D_2 \rightleftarrows 2HD; \frac{P^2_{HD}}{P_{H_2}P_{D_2}}=\frac{(HD)^2}{(H_2)(D_2)}=K_{ex}. \qquad (3.15)$$

The equilibrium constant K_{ex} of the isotopic exchange reaction (eq 3.15) is related to the dissociation constants K of eq 3.7, 3.8, and 3.9 by the equation

$$K_{ex}=\frac{K_{H_2}K_{D_2}}{K^2_{HD}}. \qquad (3.16)$$

The equilibrium constant K_{ex} for isotopic exchange in the ideal gas state is independent of P, and accordingly the relative equilibrium concentrations of H_2, HD, and D_2 are also independent of pressure in the ideal gas state. For this reaction the ΔE_0° of eq 3.3, the difference between twice the energy of the ground state of HD minus the sum of the energies of the ground states of H_2 and D_2, is equal to twice the zero-point vibrational energy of HD minus the sum of the zero-point vibrational energies of H_2 and D_2. Using the values given in section III, 1 for the zero point energies, ΔE_0° is 159.5 cal for the formation of 2 moles of HD.

In figure 5 are plotted experimental values of K_{ex}, whereas the curve was derived from spectroscopic data as has been indicated. The data of Rittenberg, Bleakney, and Urey [54] were obtained from measurements on hydrogen-deuterium mixtures prepared by the decomposition of mix-

tures of HI and DI, and those of Gould, Bleakney, and Taylor [55] were obtained with mixtures of hydrogen and deuterium that had been adsorbed on various catalysts or had been diffused through palladium. Some of the observations of Gould, Bleakney, and Taylor plotted in figure 5 were not plotted by them in their published article.

Although the theoretical curve of figure 5 is thought to be more reliable than the experimental data, it is to be pointed out that the uncertainties in the zero-point energies of H_2, HD, and D_2 can give rise to perceptible shifts in the curve. Thus a change in ΔE_0° of 3 cal mole^{-1}, which is equivalent to about 1 cm^{-1} in $2(G_0)_{HD}-(G_0)_{H2}-(G_0)_{D2}$, changes K_{ex} by about 1.5 percent at 100° K. It seems doubtful that ΔE_0° is known better than to a very few calories per mole, for while it is plausible, it is apparently not certain that D_e, the dissociation energy above the minimum of the potential energy curve, is so nearly the same for H_2, HD, and D_2 [25]. The theoretical values of Urey and Rittenberg [13] are, therefore, practically as reliable as the newly calculated ones.

IV. PVT Data and Relations for Hydrogen and Deuterium

In order to calculate the thermodynamic properties of gaseous hydrogen at high densities (in principle at any densities other than very low) from values of the properties for the hypothetical ideal gaseous state, it is necessary to have information concerning the relations between pressure, volume, and temperature for each temperature in question extending from very low to high densities.

1. Hydrogen

The available PVT data for hydrogen fall between 14° and 700° K. They consist, in general, of measurements of volume of known amounts of gas at several different pressures along selected isotherms. The quantities usually reported are values of PV or PV/P_0V_0 at the measured pressures or densities. In this report this information is presented in the form of tables in which integral values of the variables of state are spaced closely enough to allow accurate interpolation.

The dependent variable Z appearing in the tables is PV/RT. Through the definition of R, this quantity has the value 1 at extremely low densities, and it is of the same order of magnitude over a very extended range of densities. The independent variables chosen are T, the Kelvin temperature, and ρ, the Amagat density, which is defined as the ratio of the observed density to the density at standard conditions (0°C and 1 atmosphere). Density was chosen as an independent variable of state in preference to pressure because this resulted in simpler representation of the PV/RT isotherms. The Amagat density is also the ratio of the volume V_0 of the gas at standard conditions to its observed volume.

$$=\frac{\text{observed density}}{\text{density at standard conditions}}=\frac{V_0}{V}. \quad (4.1)$$

The best value for V_0, the molar volume of hydrogen at standard conditions, is 22.4279 liters or 22428.5 cm^3, according to the values of RT_0 obtained by Cragoe [90] and the value of PV/RT for hydrogen at standard conditions as given by Cragoe and the present correlation. The density of hydrogen at standard conditions is 0.089888 gram liter^{-1}.

Values of PV/RT, or Z for n-H_2 are given in table 13 for different values of T and ρ. Corresponding values of P and of the derivatives $(dZ/dT)_\rho$, $(d^2Z/dT^2)_\rho$ and $(dZ/d\rho)_T$ needed for the calculation of some of the more important thermal properties of the real gas from ideal gas values (see section V) are given as functions of the same variables of state ρ and T in tables 14, 15, 16, and 17, respectively. The temperature intervals used are of graduated size, being as small as 2 degrees at low temperatures and as much as 20 deg above 0° C. The density intervals, except for entries at $\rho=1$, 2, 3, 6, and 10, are uniformly equal to 20 Amagats from $\rho=0$ to $\rho=500$.

TABLE 13. *Values of $Z=PV/RT$ for hydrogen at integral values of T, the absolute temperature, and ρ, the density in Amagat units*

Temperature	$\rho=1$	2	3	6	10	20	40	60	80	100	120	140	160	180	200
°K															
16	0.990904	0.981826	0.972765												
18	.992299	.984612	.976940	0.95401											
20	.993373	.986758	.980157	.96043	0.93430										
22	.994225	.988460	.982708	.96552	.94274										
24	.994917	.989846	.984783	.96965	.94962	0.90021									
26	.995492	.990994	.986505	.97309	.95532	.91150	.8265								
28	.995977	.991962	.987955	.97598	.96012	.92100	.8452	0.7724							
30	.996389	.992784	.989187	.97844	.96420	.92910	.8610	.7958	0.7334	0.6739					
32	.996742	.993490	.990245	.98055	.96771	.93606	.8747	.8159	.7598	.7062	0.6551	0.6067	0.5609	0.5176	
34	.997048	.994102	.991162	.98238	.97075	.94209	.8866	.8334	.7826	.7342	.6882	.6446	.6033	.5644	0.5279
36	.997315	.994636	.991962	.98397	.97340	.94735	.8969	.8487	.8025	.7587	.7171	.6777	.6404	.6054	.5726
38	.997550	.995104	.992664	.98537	.97573	.95197	.90598	.8620	.8201	.7803	.7426	.7069	.6732	.6415	.6119
40	.997758	.995520	.993287	.98662	.97779	.95606	.91403	.8739	.8357	.7995	.7652	.7328	.7023	.6737	.6470
42	.997943	.995892	.993844	.98773	.97964	.95972	.92125	.8846	.8497	.8166	.7854	.7560	.7284	.7026	.6786
	$\rho=220$	240	260	280	300	320	340	360	380	400	420	440	460	480	500
34	0.4937	0.4619	.04327	0.4062	0.3825	0.3613	0.3425	0.3259	0.3115	0.2992	0.2890	0.2808	0.2748	0.2717	0.2724
36	.5419	.5135	.4875	.4639	.4428	.4239	.4071	.3924	.3800	.3700	.3624	.3573	.3547	.3550	.3590
38	.5844	.5591	.5360	.5151	.4965	.4799	.4652	.4525	.4421	.4343	.4292	.4268	.4272	.4305	.4374
40	.6224	.5998	.5794	.5610	.5446	.5302	.5178	.5073	.4990	.4933	.4905	.4904	.4933	.4992	.5085
42	.6565	.6364	.6183	.6021	.5880	.5758	.5657	.5574	.5512	.5476	.5468	.5488	.5537	.5617	.5730
	$\rho=520$	540	560	580	600	620	640	660	680	700					
34	0.2775	0.2878	0.3038	0.3258	0.3544	0.3913	0.4385	0.4971	0.5678	0.6512					
36	.3675	.3809	.3995	.4242	.4557	.4944	.5406	.5947							
38	.4489	.4657	.4882	.5167	.5520										
40	.5225	.5421	.5682												
42	.5890	.6110													

TABLE 13. *Values of $Z=PV/RT$ for hydrogen at integral values of T, the absolute temperature, and ρ, the density in Amagat units*—Continued

Temperature	$\rho=1$	2	3	6	10	20	40	60	80	100	120	140	160	180	200
°K															
42	0.997943	0.995892	0.993844	0.98773	0.97964	0.95972	0.92125	0.8846	0.8497	0.8166	0.7854	0.7560	0.7284	0.7026	0.6786
44	.998110	.996226	.994344	.98873	.98130	.96302	.92775	.8942	.8623	.8321	.8037	.7770	.7520	.7287	.7071
46	.998261	.996528	.994798	.98963	.98280	.96601	.93364	.90288	.8737	.8462	.8204	.7961	.7734	.7524	.7330
48	.998399	.996802	.995209	.990453	.98417	.96872	.93898	.91079	.8841	.8590	.8355	.8135	.7929	.7740	.7567
50	.998524	.997052	.995583	.991199	.98541	.97118	.94384	.91798	.8936	.8707	.8493	.8293	.8108	.7938	.7783
52	.998638	.997280	.995925	.991881	.98654	.97342	.94827	.92455	.90224	.8814	.8619	.8438	.8272	.8120	.7982
54	.998743	.997488	.996238	.992507	.98758	.97549	.95235	.93060	.91018	.8911	.8735	.8572	.8422	.8287	.8165
56	.998839	.997682	.996528	.993086	.98854	.97742	.95615	.93620	.91755	.90020	.8842	.8695	.8560	.8440	.8334
58	.998930	.997863	.996800	.993628	.98944	.97920	.95966	.94138	.92436	.90859	.8941	.8808	.8688	.8582	.8490
60	.999013	.998030	.997049	.994125	.99027	.98084	.96289	.94615	.93062	.91631	.90323	.8914	.8808	.8715	.8636
65	.999196	.998394	.997595	.995214	.99208	.98443	.96998	.95669	.94454	.93351	.92363	.91492	.90736	.90102	.8960
70	.999348	.998699	.998053	.996129	.99360	.98746	.97597	.96555	.95619	.94793	.94077	.93473	.92983	.92613	.9237
75	.999479	.998960	.998444	.996910	.99490	.99004	.98106	.97308	.96611	.96020	.95537	.95163	.94904	.94764	.9475
80	.999590	.999182	.998776	.997573	.99600	.99224	.98543	.97958	.97470	.97082	.96798	.96623	.96561	.96617	.9680
85	.999686	.999374	.999065	.998151	.99696	.99415	.98923	.98523	.98217	.98007	.97899	.97895	.98002	.98225	.9857
90	.999770	.999542	.999318	.998656	.99780	.99583	.99255	.99017	.98871	.98819	.98865	.99011	.99266	.99635	1.0012
95	.999844	.999690	.999539	.999098	.99854	.99730	.99548	.99454	.99449	.99536	.99719	.99999	1.00386	1.00884	1.0150
100	.999909	.999821	.999735	.999489	.99919	.99860	.99807	.99841	.99962	1.00173	1.00477	1.00878	1.01385	1.02004	1.0274
105	.999968	.999940	.999911	.999841	.99978	.99977	1.00038	1.00186	1.00420	1.00741	1.01154	1.01665	1.02280	1.03006	1.0385
110	1.000021	1.000046	1.000070	1.000158	1.00031	1.00082	1.00246	1.00495	1.00830	1.01250	1.01762	1.02371	1.03084	1.03905	1.0484
115	1.000068	1.000141	1.000212	1.000442	1.00078	1.00176	1.00434	1.00775	1.01200	1.01710	1.02311	1.03009	1.03808	1.04713	1.0573
120	1.000112	1.000228	1.000343	1.000703	1.00121	1.00262	1.00604	1.01028	1.01535	1.02127	1.02809	1.03586	1.04464	1.05445	1.0653
125	1.000152	1.000307	1.000463	1.000943	1.00161	1.00341	1.00760	1.01260	1.01842	1.02509	1.03265	1.04114	1.05062	1.06113	1.0727
130	1.000188	1.000379	1.000572	1.001160	1.00197	1.00413	1.00903	1.01473	1.02124	1.02860	1.03684	1.04599	1.05610	1.06725	1.0794
135	1.000221	1.000444	1.000672	1.001356	1.00230	1.00479	1.01035	1.01668	1.02383	1.03183	1.04069	1.05044	1.06113	1.07285	1.0856
140	1.000252	1.000505	1.000763	1.001542	1.00261	1.00540	1.01155	1.01847	1.02621	1.03479	1.04422	1.05453	1.06578	1.07797	1.0912
145	1.000280	1.000562	1.000847	1.001710	1.00289	1.00596	1.01267	1.02014	1.02842	1.03753	1.04748	1.05830	1.07002	1.08269	1.0964
150	1.000307	1.000615	1.000926	1.001868	1.00315	1.00648	1.01370	1.02168	1.03047	1.04007	1.05050	1.06179	1.07396	1.08707	1.1012
155	1.000332	1.000665	1.001000	1.002016	1.00340	1.00697	1.01467	1.02312	1.03237	1.04242	1.05330	1.06502	1.07762	1.09114	1.1057
160	1.000355	1.000711	1.001069	1.002154	1.00363	1.00743	1.01558	1.02447	1.03413	1.04460	1.05590	1.06803	1.08102	1.09492	1.1098
165	1.000376	1.000754	1.001133	1.002282	1.00384	1.00785	1.01641	1.02571	1.03577	1.04663	1.05831	1.07082	1.08417	1.09841	1.1136
170	1.000396	1.000793	1.001192	1.002398	1.00403	1.00823	1.01716	1.02684	1.03728	1.04850	1.06052	1.07338	1.08710	1.1016	1.1172
180	1.000430	1.000862	1.001296	1.002607	1.00438	1.00893	1.01856	1.02891	1.04001	1.05186	1.06451	1.07797	1.09226	1.1074	1.1235
190	1.000462	1.000925	1.001390	1.002795	1.00469	1.00955	1.01978	1.03072	1.04238	1.05478	1.06796	1.08193	1.09671	1.1124	1.1289
200	1.000490	1.000981	1.001474	1.002962	1.00497	1.01010	1.02085	1.03231	1.04447	1.05735	1.07100	1.08541	1.1006	1.1167	1.1336
210	1.000515	1.001031	1.001548	1.003108	1.00521	1.01058	1.02181	1.03372	1.04632	1.05964	1.07370	1.08850	1.1041	1.1205	1.1378
220	1.000537	1.001075	1.001614	1.003240	1.00543	1.01102	1.02267	1.03499	1.04798	1.06167	1.07610	1.09125	1.1072	1.1239	1.1415
230	1.000556	1.001113	1.001673	1.003358	1.00563	1.01141	1.02344	1.03611	1.04945	1.06348	1.07823	1.09370	1.1099	1.1270	1.1448
240	1.000573	1.001147	1.001725	1.003463	1.00580	1.01175	1.02411	1.03710	1.05076	1.06508	1.08011	1.09587	1.1124	1.1297	1.1477
250	1.000589	1.001178	1.001771	1.003555	1.00596	1.01205	1.02470	1.03798	1.05191	1.06649	1.08177	1.09777	1.11451	1.1320	1.1502

260	1.000602	1.001206	1.001812	1.003637	1.00609	1.01232	1.02523	1.03877	1.05293	1.06775	1.08325	1.09945	1.11638	1.1341	1.1525
270	1.000614	1.001231	1.001848	1.003709	1.006211	1.01257	1.02572	1.03948	1.05386	1.06889	1.08459	1.10098	1.11809	1.13594	1.15455
0° C	1.000618	1.001238	1.001859	1.003731	1.006247	1.01264	1.02586	1.03969	1.05414	1.06923	1.08499	1.10143	1.11859	1.13648	1.15514
280	1.000626	1.001254	1.001882	1.003777	1.006324	1.01279	1.02616	1.04012	1.05471	1.06992	1.08580	1.10235	1.11961	1.13760	1.15635
25° C	1.000644	1.001290	1.001936	1.003886	1.006508	1.01315	1.02685	1.04114	1.05603	1.07154	1.08768	1.10449	1.12199	1.14019	1.15913
300	1.000646	1.001293	1.001942	1.003896	1.006520	1.01318	1.02692	1.04124	1.05615	1.07169	1.08786	1.10469	1.12220	1.14043	1.15938
320	1.000662	1.001326	1.001991	1.003994	1.006683	1.01350	1.02755	1.04215	1.05734	1.07313	1.08953	1.10658	1.12429	1.14269	1.16179
340	1.000676	1.001354	1.002032	1.004076	1.006819	1.01377	1.02807	1.04291	1.05832	1.07431	1.09091	1.10812	1.12598	1.14451	1.16373
360	1.000688	1.001377	1.002067	1.004145	1.006934	1.01400	1.02851	1.04355	1.05914	1.07529	1.09204	1.10938	1.12736	1.14598	1.16527
100° C	1.000694	1.001390	1.002086	1.004183	1.006999	1.01412	1.02875	1.04390	1.05960	1.07584	1.09267	1.11009	1.12812	1.14679	1.16611
380	1.000697	1.001396	1.002096	1.004203	1.007030	1.01418	1.02887	1.04407	1.05981	1.07610	1.09297	1.11042	1.12848	1.14716	1.16650
400	1.000706	1.001413	1.002121	1.004253	1.007112	1.01434	1.02918	1.04452	1.06038	1.07678	1.09373	1.11126	1.12938	1.14812	1.16748
420	1.000713	1.001427	1.002142	1.004294	1.007181	1.01448	1.02944	1.04489	1.06085	1.07734	1.09436	1.11195	1.13012	1.14888	1.16826
440	1.000719	1.001439	1.002160	1.004330	1.007240	1.01459	1.02966	1.04520	1.06124	1.07780	1.09488	1.11251	1.13071	1.14948	1.16886
460	1.000724	1.001449	1.002175	1.004360	1.007290	1.01469	1.02984	1.04546	1.06157	1.07818	1.09531	1.11297	1.13118	1.14996	1.16932
480	1.000728	1.001458	1.002188	1.004385	1.007332	1.01477	1.03000	1.04568	1.06184	1.07849	1.09565	1.11333	1.13155	1.15032	1.16966
500	1.000732	1.001465	1.002199	1.004408	1.007367	1.01484	1.03013	1.04586	1.06206	1.07875	1.09593	1.11361	1.13183	1.15059	1.16991
520	1.000735	1.001471	1.002208	1.004426	1.007397	1.01490	1.03023	1.04601	1.06225	1.07895	1.09614	1.11383	1.13204	1.15078	1.17006
540	1.000737	1.001476	1.002216	1.004441	1.007423	1.01495	1.03032	1.04613	1.06239	1.07911	1.09631	1.11399	1.13219	1.15090	1.17015
560	1.000740	1.001481	1.002222	1.004454	1.007444	1.01499	1.03040	1.04623	1.06251	1.07924	1.09643	1.11411	1.13228	1.15096	1.17017
580	1.000741	1.001484	1.002228	1.004465	1.007462	1.01502	1.03046	1.04631	1.06260	1.07933	1.09652	1.11418	1.13233	1.15098	1.17014
600	1.000743	1.001487	1.002232	1.004474	1.007476	1.01505	1.03050	1.04637	1.06266	1.07939	1.09657	1.11421	1.13233	1.15095	1.17006

TABLE 13. *Values of $Z=PV/RT$ for hydrogen at integral values of T, the absolute temperature, and ρ, the density in Amagat units*—Continued

Temperature	ρ-220	240	260	280	300	320	340	360	380	400	420	440	460	480	500
°K															
42	0.6565	0.6364	0.6183	0.6021	0.5880	0.5758	0.5657	0.5574	0.5512	0.5476	0.5468	0.5488	0.5537	0.5617	0.5730
44	.6874	.6695	.6535	.6394	.6274	.6174	.6094	.6033	.5992	.5976	.5987	.6025	.6091	.6187	.6315
46	.7154	.6996	.6856	.6734	.6633	.6553	.6494	.6454	.6433	.6435	.6464	.6518	.6599	.6707	.6846
48	.7410	.7270	.7149	.7046	.6962	.6901	.6861	.6840	.6837	.6857	.6902	.6971	.7064	.7183	.7331
50	.7644	.7522	.7417	.7332	.7265	.7220	.7198	.7194	.7208	.7244	.7304	.7386	.7490	.7620	.7777
52	.7860	.7754	.7665	.7594	.7544	.7515	.7507	.7518	.7547	.7598	.7672	.7766	.7882	.8022	.8188
54	.8059	.7968	.7894	.7838	.7802	.7787	.7791	.7815	.7858	.7922	.8008	.8114	.8242	.8392	.8568
56	.8242	.8166	.8106	.8064	.8041	.8037	.8053	.8088	.8143	.8219	.8316	.8433	.8572	.8733	.8919
58	.8412	.8350	.8303	.8273	.8262	.8269	.8296	.8342	.8408	.8494	.8601	.8729	.8878	.9049	.9245
60	.8572	.8522	.8488	.8470	.8470	.8488	.8525	.8582	.8658	.8754	.8871	.9008	.9167	.9348	.9552
65	.8925	.8906	.8902	.8912	.8938	.8982	.9043	.9123	.9223	.9342	.9482	.9643	.9826	1.0032	1.0262
70	.9228	.9234	.9254	.9289	.9339	.9406	.9489	.9591	.9712	.9852	1.0012	1.0194	1.0397	1.0623	1.0874
75	.9488	.9515	.9556	.9611	.9681	.9768	.9872	.9994	1.0133	1.0291	1.0469	1.0668	1.0889	1.1132	1.1400
80	.9711	.9756	.9815	.9888	.9976	1.0080	1.0201	1.0339	1.0495	1.0669	1.0861	1.1075	1.1311	1.1568	1.1850
85	.9904	.9965	1.0040	1.0128	1.0232	1.0350	1.0485	1.0636	1.0806	1.0994	1.1199	1.1425	1.1672	1.1941	1.2234
90	1.0074	1.0148	1.0236	1.0339	1.0456	1.0587	1.0733	1.0896	1.1077	1.1275	1.1493	1.1730	1.1986	1.2265	1.2568
95	1.0224	1.0311	1.0411	1.0525	1.0653	1.0795	1.0953	1.1127	1.1317	1.1525	1.1752	1.1999	1.2264	1.2551	1.2863
100	1.0359	1.0457	1.0567	1.0691	1.0829	1.0981	1.1148	1.1332	1.1531	1.1748	1.1983	1.2238	1.2511	1.2806	1.3125
105	1.0481	1.0588	1.0707	1.0840	1.0987	1.1148	1.1323	1.1514	1.1722	1.1947	1.2189	1.2450	1.2732	1.3034	1.3358
110	1.0589	1.0705	1.0833	1.0974	1.1128	1.1297	1.1480	1.1678	1.1893	1.2124	1.2373	1.2640	1.2929	1.3236	1.3565
115	1.0686	1.0810	1.0946	1.1094	1.1256	1.1431	1.1620	1.1825	1.2046	1.2283	1.2538	1.2811	1.3104	1.3416	1.3750
120	1.0773	1.0905	1.1048	1.1203	1.1371	1.1552	1.1747	1.1957	1.2184	1.2427	1.2687	1.2965	1.3262	1.3579	1.3916
125	1.0854	1.0991	1.1140	1.1302	1.1475	1.1662	1.1862	1.2077	1.2309	1.2557	1.2821	1.3103	1.3404	1.3725	1.4065
130	1.0927	1.1070	1.1224	1.1391	1.1570	1.1762	1.1967	1.2187	1.2423	1.2675	1.2943	1.3228	1.3533	1.3856	1.4199
135	1.0994	1.1142	1.1301	1.1473	1.1656	1.1853	1.2063	1.2287	1.2527	1.2782	1.3053	1.3341	1.3648	1.3974	1.4319
140	1.1055	1.1208	1.1372	1.1548	1.1736	1.1936	1.2150	1.2378	1.2621	1.2879	1.3153	1.3444	1.3753	1.4081	1.4428
145	1.1111	1.1269	1.1438	1.1618	1.1810	1.2014	1.2231	1.2462	1.2707	1.2968	1.3245	1.3539	1.3850	1.4179	1.4527
150	1.1163	1.1325	1.1498	1.1681	1.1877	1.2085	1.2305	1.2539	1.2787	1.3051	1.3330	1.3626	1.3939	1.4269	1.4618
155	1.1212	1.1377	1.1553	1.1740	1.1939	1.2150	1.2373	1.2610	1.2861	1.3127	1.3408	1.3705	1.4019	1.4351	1.4701
160	1.1257	1.1426	1.1605	1.1795	1.1997	1.2211	1.2436	1.2675	1.2928	1.3195	1.3478	1.3776	1.4091	1.4424	1.4776
165	1.1299	1.1471	1.1653	1.1846	1.2050	1.2267	1.2495	1.2737	1.2992	1.3260	1.3542	1.3841	1.4157	1.4490	1.4841
170	1.1337	1.1512	1.1697	1.1892	1.2098	1.2316	1.2547	1.2790	1.3046	1.3316	1.3601	1.3901	1.4216	1.4548	1.4899
180	1.1405	1.1585	1.1774	1.1974	1.2184	1.2406	1.2640	1.2886	1.3145	1.3418	1.3705	1.4007	1.4323	1.4655	1.5005
190	1.1463	1.1647	1.1840	1.2044	1.2258	1.2483	1.2720	1.2969	1.3230	1.3505	1.3794	1.4097	1.4414	1.4747	1.5097
200	1.1514	1.1701	1.1898	1.2105	1.2322	1.2550	1.2790	1.3041	1.3305	1.3581	1.3871	1.4175	1.4493	1.4827	1.5177
210	1.1559	1.1749	1.1949	1.2159	1.2379	1.2610	1.2852	1.3105	1.3370	1.3648	1.3939	1.4244	1.4563	1.4897	1.5247
220	1.1599	1.1793	1.1995	1.2207	1.2430	1.2663	1.2906	1.3161	1.3428	1.3707	1.3999	1.4304	1.4624	1.4958	1.5307
230	1.1635	1.1831	1.2036	1.2250	1.2474	1.2709	1.2954	1.3210	1.3478	1.3758	1.4051	1.4357	1.4676	1.5010	1.5359
240	1.1666	1.1864	1.2071	1.2287	1.2512	1.2749	1.2996	1.3253	1.3522	1.3802	1.4096	1.4402	1.4721	1.5055	1.5403
250	1.1693	1.1893	1.2102	1.2319	1.2546	1.2784	1.3031	1.3290	1.3559	1.3840	1.4134	1.4440	1.4759	1.5092	1.5440
260	1.1718	1.1919	1.2129	1.2348	1.2576	1.2814	1.3062	1.3321	1.3591	1.3872	1.4166	1.4472	1.4790	1.5122	1.5469
270	1.17397	1.19420	1.21530	1.23728	1.26020	1.28407	1.30894	1.33486	1.36185	1.38998	1.41927	1.44980	1.48160	1.51473	1.54925
0°C	1.17460	1.19487	1.21600	1.23801	1.26094	1.28483	1.30971	1.33563	1.36263	1.39074	1.42003	1.45053	1.48230	1.51539	1.54986
280	1.17588	1.19623	1.21741	1.23948	1.26245	1.28637	1.31127	1.33719	1.36418	1.39227	1.42152	1.45196	1.48366	1.51666	1.55103

25° C	1.17883	1.19932	1.22063	1.24279	1.26583	1.28979	1.31470	1.34060	1.36752	1.39552	1.42463	1.45490	1.48638	1.51911	1.55316
300	1.17910	1.19960	1.22092	1.24308	1.26613	1.29009	1.31500	1.34089	1.36781	1.39579	1.42489	1.45514	1.48659	1.51930	1.55331
320	1.18164	1.20224	1.22364	1.24586	1.26892	1.29287	1.31774	1.34356	1.37036	1.39820	1.42710	1.45711	1.48828	1.52065	1.55428
340	1.18365	1.20432	1.22576	1.24798	1.27104	1.29494	1.31973	1.34544	1.37211	1.39976	1.42844	1.45820	1.48906	1.52109	1.55431
360	1.18525	1.20595	1.22740	1.24961	1.27262	1.29645	1.32114	1.34672	1.37323	1.40069	1.42914	1.45862	1.48917	1.52084	1.55366
100° C	1.18612	1.20682	1.22826	1.25045	1.27342	1.29720	1.32182	1.34731	1.37370	1.40102	1.42932	1.45862	1.48897	1.52040	1.55296
380	1.18651	1.20722	1.22865	1.25083	1.27378	1.29753	1.32210	1.34754	1.37387	1.40112	1.42934	1.45854	1.48878	1.52009	1.55252
400	1.18751	1.20820	1.22960	1.25173	1.27460	1.29825	1.32270	1.34799	1.37414	1.40118	1.42915	1.45809	1.48801	1.51898	1.55101
420	1.18827	1.20895	1.23031	1.25236	1.27515	1.29869	1.32302	1.34815	1.37411	1.40095	1.42868	1.45734	1.48696	1.51758	1.54923
440	1.18886	1.20950	1.23080	1.25279	1.27549	1.29892	1.32310	1.34807	1.37386	1.40048	1.42797	1.45636	1.48568	1.51598	1.54727
460	1.18930	1.20989	1.23113	1.25304	1.27564	1.29896	1.32301	1.34782	1.37342	1.39983	1.42709	1.45522	1.48426	1.51422	1.54516
480	1.18960	1.21015	1.23132	1.25315	1.27565	1.29884	1.32276	1.34741	1.37283	1.39904	1.42607	1.45394	1.48270	1.51236	1.54296
500	1.18980	1.21029	1.23140	1.25314	1.27554	1.29861	1.32238	1.34688	1.37212	1.39813	1.42494	1.45257	1.48105	1.51041	1.54068
520	1.18991	1.21034	1.23138	1.25303	1.27533	1.29828	1.32191	1.34625	1.37132	1.39714	1.42373	1.45112	1.47934	1.50841	1.53837
540	1.18995	1.21032	1.23127	1.25284	1.27503	1.29786	1.32136	1.34555	1.37044	1.39607	1.42245	1.44961	1.47758	1.50638	1.53603
560	1.18992	1.21022	1.23110	1.25258	1.27466	1.29738	1.32074	1.34478	1.36951	1.39495	1.42113	1.44807	1.47579	1.50432	1.53369
580	1.18983	1.21007	1.23088	1.25226	1.27424	1.29684	1.32008	1.34397	1.36853	1.39379	1.41977	1.44650	1.47398	1.50226	1.53135
600	1.18970	1.20987	1.23060	1.25189	1.27377	1.29626	1.31936	1.34311	1.36751	1.39260	1.41839	1.44490	1.47216	1.50019	1.52902

TABLE 14. *Pressure (in atmospheres) at integral values of T, the absolute temperature, and ρ, the density in Amagat units*

Temperature	ρ=1	2	3	6	10	20	40	60	80	100	120	140	160	180	200
°K															
16	0.05800	0.11495	0.17083												
18	.06535	.13171	.19301	0.37696											
20	.07269	.14441	.21516	.42166	0.68364										
22	.08002	.15912	.23729	.46628	.75880										
24	.08736	.17383	.25941	.51085	.83382	1.58080									
26	.09469	.18853	.28152	.55538	.90873	1.73410	3.1448								
28	.10203	.20323	.30362	.59988	.98355	1.88695	3.4633	4.7475							
30	.10936	.21793	.32571	.64435	1.05828	2.03952	3.7805	5.2407	6.4397	7.3966					
32	.11669	.23262	.35800	.68879	1.13295	2.19178	4.0967	5.7313	7.1163	8.2678	9.2035	9.9441	10.507	10.908	
34	.12402	.24732	.36988	.73320	1.20754	2.34377	4.4114	6.2201	7.7879	9.1329	10.273	11.226	12.007	12.637	13.133
36	.13136	.28821	.39195	.77759	1.28206	2.4955	4.7252	6.7069	8.4557	9.9928	11.334	12.496	13.495	14.353	15.083
38	.13869	.27669	.41402	.82195	1.35652	2.6470	5.0382	7.1904	9.1212	10.848	12.389	13.759	14.975	16.053	17.014
40	.14602	.29138	.43608	.86632	1.43093	2.7983	5.3505	7.6734	9.7839	11.700	13.438	15.014	16.444	17.746	18.937
42	.15334	.30606	.45814	.91065	1.50532	2.9494	5.6624	8.1557	10.445	12.548	14.482	16.263	17.908	19.433	20.855
	ρ=220	240	260	280	300	320	340	360	380	400	420	440	460	480	500
34	13.511	13.790	13.994	14.148	14.274	14.382	14.485	14.594	14.724	14.887	15.099	15.369	15.724	16.223	16.942
36	15.702	16.232	16.694	17.108	17.496	17.866	18.230	18.606	19.019	19.493	20.047	20.706	21.490	22.443	23.642
38	17.874	18.655	19.375	20.051	20.708	21.350	21.990	22.647	23.356	24.152	25.061	26.108	27.320	28.728	30.405
40	20.039	21.066	22.046	22.988	23.910	24.829	25.764	26.726	27.750	28.876	30.148	31.577	33.208	35.066	37.208
42	22.193	23.470	24.702	25.905	27.106	28.313	29.555	30.834	32.185	33.658	35.289	37.105	39.138	41.429	44.024
	ρ=520	540	560	580	600	620	640	660	680	700					
34	17.950	19.332	21.162	23.506	26.451	30.179	34.909	40.811	48.028	56.703					
36	25.170	27.091	29.466	32.405	36.012	40.372	45.569	51.696							
38	32.453	34.962	38.009	41.664	46.046										
40	39.762	42.840	46.565												
42	47.063	50.699													
	ρ=1	2	3	6	10	20	40	60	80	100	120	140	160	180	200
42	0.15334	0.30606	0.45814	0.91065	1.50532	2.9494	5.6624	8.1557	10.445	12.548	14.482	16.263	17.908	19.433	20.855
44	.16067	.32074	.48020	.95498	1.57968	3.1005	5.9739	8.6368	11.105	13.395	15.525	17.511	19.369	21.115	22.766
46	.16800	.33542	.50226	.99930	1.65400	3.2515	6.2851	9.1170	11.763	14.241	16.568	18.757	20.826	22.792	24.672
48	.17533	.35010	.52431	1.04361	1.72832	3.4024	6.5959	9.5964	12.421	15.085	17.607	20.000	22.279	24.466	26.577
50	.18266	.36478	.54636	1.08792	1.80261	3.5531	6.9062	10.076	13.077	15.928	18.643	21.238	23.731	26.138	28.475
52	.18999	.37946	.56841	1.13221	1.87686	3.7038	7.2162	10.554	13.732	16.768	19.677	22.527	25.180	27.806	30.371
54	.19732	.39414	.59046	1.17650	1.95110	3.8544	7.5260	11.031	14.385	17.605	20.709	23.709	26.622	29.470	32.262
56	.20464	.40881	.61251	1.22079	2.02533	4.0051	7.8359	11.509	15.039	18.443	21.739	24.940	28.060	31.126	34.150
58	.21197	.42349	.63456	1.26508	2.09957	4.1557	8.1455	11.986	15.692	19.280	22.767	26.167	29.497	32.780	36.031
60	.21930	.43817	.65660	1.30935	2.17380	4.3062	8.4548	12.462	16.343	20.114	23.793	27.395	30.936	34.435	37.915
65	.23762	.47485	.71171	1.42002	2.35925	4.6821	9.2268	13.651	17.970	22.200	26.358	30.461	34.524	38.569	42.615
70	.25593	.51154	.76681	1.53066	2.54462	5.0578	9.9979	14.837	19.590	24.277	28.912	33.514	38.101	42.693	47.312

75	.27425	.54822	.82190	1.64128	2.72995	5.4332	10.768	16.020	21.208	26.347	31.458	36.557	41.666	46.805	51.998
80	.29257	.58490	.87699	1.75186	2.91516	5.8083	11.537	17.203	22.823	28.415	33.998	39.592	45.220	50.901	56.664
85	.31088	.62157	.93207	1.86243	3.10035	6.1832	12.305	18.383	24.435	30.478	36.534	42.621	48.763	54.983	61.307
90	.32920	.65824	.98715	1.97298	3.28549	6.5580	13.073	19.562	26.044	32.538	39.064	45.642	52.297	59.053	65.934
95	.34751	.69492	1.04222	2.08352	3.47059	6.9326	13.840	20.740	27.652	34.595	41.591	48.659	55.825	63.115	70.556
100	.36583	.73159	1.09729	2.19403	3.65563	7.3069	14.606	21.917	29.258	36.649	44.112	51.670	59.348	67.174	75.177
105	.38414	.76826	1.15235	2.30454	3.84067	7.6813	15.372	23.092	30.861	38.700	46.630	54.677	62.866	71.226	79.788
110	.40245	.80493	1.20742	2.41505	4.05570	8.0555	16.137	24.266	32.463	40.748	49.144	57.678	66.377	75.269	84.385
115	.42077	.84159	1.26248	2.52554	4.21066	8.4296	16.903	25.440	34.063	42.793	51.655	60.676	69.882	79.302	88.969
120	.43908	.87826	1.31754	2.63604	4.39562	8.8036	17.667	26.613	35.662	44.837	54.164	63.668	73.381	83.328	93.540
125	.45739	.91493	1.37261	2.74653	4.5806	9.1777	18.432	27.785	37.260	46.880	56.671	66.659	76.876	87.350	98.114
130	.47571	.95159	1.42767	2.85701	4.7655	9.5516	19.196	28.957	38.858	48.922	59.177	69.649	80.368	91.368	102.676
135	.49402	.98826	1.48272	2.96748	4.9505	9.9255	19.961	30.129	40.454	50.963	61.681	72.635	83.856	95.380	107.238
140	.51233	1.02492	1.53778	3.07795	5.1354	10.2993	20.725	31.300	42.050	53.002	64.182	75.619	87.343	99.385	111.783
145	.53064	1.06159	1.59284	3.18842	5.3203	10.6731	21.489	32.471	43.646	55.040	66.682	78.599	90.823	103.385	116.327
150	.54896	1.09825	1.64789	3.29888	5.5052	11.0469	22.252	33.641	45.241	57.078	69.180	81.501	94.300	107.383	120.865
155	.56727	1.13492	1.70295	3.40935	5.6901	11.4207	23.016	34.812	46.835	59.114	71.677	84.553	97.776	111.378	125.404
160	.58558	1.17158	1.75800	3.51981	5.8750	11.7945	23.780	35.982	48.428	61.148	74.172	87.528	101.248	115.369	129.930
165	.60389	1.20824	1.81305	3.63027	6.0599	12.1681	24.543	37.151	50.021	63.182	76.664	90.499	104.716	119.353	134.449
170	.62221	1.24491	1.86810	3.74071	6.2447	12.5416	25.305	38.319	51.612	65.212	79.152	93.464	108.181	123.327	138.971
180	.65883	1.31823	1.97820	3.96158	6.6143	13.2885	26.831	40.655	54.792	69.270	84.123	99.385	115.089	131.27	147.98
190	.69545	1.39155	2.08830	4.18245	6.9839	14.0354	28.355	42.989	57.967	73.321	89.085	105.292	121.977	139.19	156.95
200	.73208	1.46487	2.19839	4.40331	7.3535	14.7822	29.879	45.322	61.141	77.368	94.041	111.190	128.85	147.08	165.90
210	.76870	1.53819	2.30848	4.62415	7.7231	15.5286	31.402	47.653	64.311	81.413	98.991	117.082	135.72	154.96	174.84
220	.80532	1.61151	2.41857	4.84499	8.0926	16.2752	32.9255	49.983	67.481	85.453	103.937	122.967	142.59	162.83	183.76
230	.841944	1.68482	2.52865	5.06581	8.46213	17.0215	34.4480	52.312	70.647	89.489	108.876	128.845	149.43	170.70	192.66
240	.878565	1.75814	2.63873	5.28661	8.83154	17.7676	35.9693	54.638	73.811	93.521	113.808	134.714	156.28	178.55	201.55
250	.915186	1.83145	2.74880	5.50739	9.20099	18.5134	37.4896	56.963	76.970	97.546	118.733	140.570	163.101	186.37	210.41
260	.951806	1.90476	2.85887	5.72816	9.57026	19.2591	39.0093	59.287	80.127	101.568	123.651	146.417	169.910	194.18	219.26
270	.988428	1.97807	2.96894	5.94891	9.93956	20.0048	40.5291	61.6092	83.2820	105.5872	128.5657	152.260	176.716	201.979	228.098
0° C	1.000000	2.00124	3.00372	6.01867	10.05625	20.2403	41.0090	62.3428	84.2791	106.857	130.118	154.105	178.864	204.440	230.885
280	1.02505	2.05138	3.07901	6.16966	10.3089	20.7502	42.0482	63.9304	86.4362	109.603	133.476	158.096	183.510	209.766	236.915
25° C	1.09155	2.18451	3.27888	6.57052	10.9795	22.1038	44.8054	68.1434	92.1574	116.889	142.379	168.676	195.827	223.879	252.887
300	1.09829	2.19800	3.29913	6.61113	11.0474	22.2409	45.0850	68.5706	92.7366	117.626	143.281	169.748	197.072	225.308	254.502
320	1.17153	2.34461	3.51924	7.05258	11.7858	23.7311	48.1202	73.2059	99.0306	125.637	153.068	181.374	210.602	240.805	272.033
340	1.24476	2.49121	3.73935	7.49396	12.5240	25.2210	51.1536	77.8380	105.318	133.636	162.841	192.978	224.101	256.263	289.518
360	1.31800	2.63782	3.95945	7.93532	13.2623	26.7107	54.1858	82.4672	111.599	141.626	172.598	204.562	237.574	271.686	306.954
100° C	1.36619	2.73428	4.10427	8.22572	13.7480	27.6904	56.1797	85.5106	115.729	146.878	179.011	212.176	246.425	281.816	318.404
380	1.39124	2.78441	4.17954	8.37665	14.0004	28.1996	57.2161	87.0921	117.873	149.607	182.342	216.129	251.022	287.074	324.349
400	1.46447	2.93101	4.39963	8.81797	14.7385	29.6885	60.2456	91.7154	124.144	157.580	192.073	227.676	264.444	302.436	341.707
420	1.53771	3.07761	4.61970	9.25925	15.4764	31.1772	63.2739	96.3353	130.409	165.545	201.793	239.209	277.849	317.768	359.032
440	1.61094	3.22420	4.83978	9.70051	16.2144	32.6654	66.3011	100.952	136.669	173.502	211.502	250.726	291.232	333.074	376.322
460	1.68417	3.37079	5.05984	10.14175	16.9522	34.1535	69.3270	105.568	142.926	181.453	221.203	262.231	304.596	348.359	393.582
480	1.75740	3.51737	5.27990	10.5830	17.6900	35.6413	72.3524	110.181	149.178	189.396	230.892	273.721	317.943	363.619	410.814
500	1.83064	3.66396	5.49996	11.0242	18.4277	37.1289	75.3766	114.791	155.426	197.336	240.574	285.197	331.273	378.859	428.023
520	1.90387	3.81054	5.72001	11.4653	19.1654	38.6163	78.3993	119.400	161.672	205.267	250.245	296.664	344.588	394.078	445.201
540	1.97710	3.95712	5.94006	11.9065	19.9031	40.1036	81.4217	124.007	167.912	213.194	259.910	308.118	357.888	409.278	462.359
560	2.05033	4.10370	6.16010	12.3476	20.6407	41.5905	84.4439	128.612	174.151	221.116	269.566	319.565	371.173	424.459	479.492
580	2.12356	4.25027	6.38014	12.7888	21.3782	43.0772	87.4649	133.215	180.386	229.032	279.216	330.998	384.446	439.625	496.604
600	2.19679	4.39684	6.60017	13.2299	22.1157	44.5639	90.4844	137.817	186.617	236.943	288.857	342.421	397.703	454.773	513.693

TABLE 14. *Pressure (in atmospheres) at integral values of T, the absolute temperature, and ρ, the density in Amagat units*—Continued

Temperature	ρ=220	240	260	280	300	320	340	360	380	400	420	440	460	480	500
42	22.193	23.470	24.702	25.905	27.106	28.313	29.555	30.834	32.185	33.658	35.289	37.105	39.138	41.429	44.024
44	24.344	25.866	27.352	28.820	30.299	31.804	33.354	34.962	36.654	38.480	40.479	42.675	45.104	47.806	50.829
46	26.488	28.257	30.000	31.732	33.489	35.291	37.159	39.102	41.140	43.319	45.690	48.266	51.087	54.180	57.607
48	28.628	30.641	32.642	34.646	36.678	38.781	40.966	43.243	45.625	48.167	50.907	53.864	57.064	60.548	64.371
50	30.763	33.024	35.276	37.555	39.869	42.264	44.769	47.376	50.105	53.006	56.117	59.449	63.027	66.908	71.132
52	32.897	35.404	37.914	40.452	43.057	45.751	48.558	51.490	54.560	57.820	61.302	65.008	68.978	73.256	77.887
54	35.028	37.780	40.549	43.358	46.242	49.230	52.333	55.583	58.993	62.604	66.448	70.534	74.903	79.582	84.636
56	37.150	40.154	43.180	46.260	49.423	52.692	56.097	59.655	63.397	67.357	71.559	76.022	80.787	85.883	91.367
58	39.270	42.524	45.809	49.154	52.595	56.149	59.854	63.726	67.798	72.096	76.655	81.500	86.659	92.169	98.089
60	41.397	44.897	48.444	52.060	55.779	59.624	63.626	67.820	72.222	76.866	81.787	87.005	92.566	98.497	104.84
65	46.694	50.830	55.041	59.342	63.766	68.352	73.117	78.103	83.346	88.864	94.706	100.90	107.49	114.51	122.02
70	51.993	56.756	61.619	66.610	71.752	77.084	82.625	88.425	94.516	100.92	107.69	114.87	122.48	130.59	139.24
75	57.276	62.661	68.175	73.842	79.692	85.769	92.100	98.723	105.66	112.95	120.65	128.80	137.44	146.62	156.40
80	62.530	68.531	74.691	81.035	87.596	94.409	101.51	108.94	116.73	124.91	133.51	142.63	152.29	162.52	173.42
85	67.759	74.374	81.178	88.189	95.458	103.00	110.86	119.07	127.70	136.76	146.27	156.33	166.97	178.24	190.23
90	72.976	80.195	87.631	95.322	103.29	111.55	120.16	129.16	138.60	148.50	158.94	169.94	181.55	193.85	206.92
95	78.177	86.010	94.081	102.43	111.08	120.06	129.43	139.22	149.47	160.23	171.55	183.50	196.08	209.39	223.54
100	83.378	91.819	100.52	109.52	118.86	128.56	138.67	149.25	160.31	171.92	184.13	197.00	210.55	224.89	240.10
105	88.579	97.618	106.94	116.60	126.62	137.04	147.89	159.23	171.12	183.58	196.66	210.44	224.99	240.34	256.58
110	93.753	103.40	113.35	123.66	134.35	145.48	157.08	169.19	181.88	195.17	209.14	223.82	239.35	255.68	272.95
115	98.912	109.16	119.74	130.70	142.08	153.90	166.22	179.11	192.59	206.72	221.56	237.16	253.61	270.94	289.26
120	104.05	114.90	126.11	137.72	149.77	162.29	175.35	188.98	203.27	218.23	233.94	250.45	267.83	286.16	305.48
125	109.20	120.64	132.46	144.72	157.43	170.67	184.44	198.83	213.91	229.70	246.26	263.66	281.98	301.28	321.61
130	114.34	126.36	138.80	151.70	165.09	179.01	193.52	208.67	224.53	241.14	258.55	276.82	296.08	316.33	337.66
135	119.46	132.08	145.12	158.67	172.71	187.34	202.57	218.47	235.11	252.53	270.77	289.93	310.08	331.29	353.62
140	124.57	137.78	151.44	165.62	180.34	195.64	211.59	228.24	245.65	263.87	282.95	302.99	324.04	346.19	369.50
145	129.68	143.48	157.76	172.57	187.95	203.95	220.61	238.00	256.16	275.18	295.11	316.02	337.98	361.05	385.32
150	134.78	149.16	164.06	179.49	195.54	212.23	229.60	247.72	266.66	286.49	307.24	329.02	351.88	375.87	401.11
155	139.88	154.84	170.34	186.41	203.11	220.48	238.56	257.43	277.14	297.76	319.34	341.96	265.70	390.63	416.83
160	144.97	160.52	176.62	193.33	210.68	228.74	247.51	267.11	287.57	308.96	331.37	354.82	379.43	405.29	432.47
165	150.06	166.19	182.90	200.23	218.23	236.97	256.46	276.80	298.03	320.19	343.34	367.64	393.12	419.86	447.80
170	155.13	171.84	189.15	207.10	225.73	245.12	265.33	286.38	308.34	331.28	355.29	380.42	406.72	434.32	463.33
180	165.24	183.10	201.60	220.79	240.71	261.44	283.02	305.50	328.95	353.45	379.07	405.87	433.89	463.25	494.07
190	175.30	194.31	213.99	234.42	255.63	277.68	300.63	324.55	349.47	375.51	402.72	431.17	460.90	492.05	524.72
200	185.35	205.48	226.36	248.01	270.49	293.86	318.20	343.52	369.95	397.50	426.29	456.37	487.82	520.76	555.26
210	195.38	216.64	238.69	261.57	285.32	310.02	335.72	362.47	390.34	419.43	449.79	481.52	514.68	549.38	585.72
220	205.39	227.81	251.02	275.11	300.14	326.15	353.19	381.36	410.71	441.30	473.24	506.58	541.45	577.90	616.02
230	215.39	238.93	263.33	288.63	314.90	342.22	370.62	400.17	430.97	463.08	496.59	531.57	568.08	606.27	646.21
240	225.36	250.02	275.58	302.08	329.59	358.22	387.98	418.93	451.18	484.76	519.84	556.42	594.59	634.52	676.24
250	235.29	261.07	287.80	315.49	344.26	374.17	405.24	437.60	471.26	506.35	542.96	581.13	620.97	662.58	706.11
260	245.22	272.11	299.98	328.88	358.88	390.05	422.45	456.17	491.27	527.82	565.96	605.72	647.16	690.46	735.73
270	255.128	283.117	312.130	342.219	373.456	405.898	439.629	474.697	511.200	549.220	588.834	630.143	673.236	718.215	765.191
0° C	258.252	286.592	315.965	346.429	378.048	410.892	445.026	480.530	517.479	555.952	596.044	637.839	681.437	726.937	774.451
280	265.008	294.102	324.252	355.525	387.979	421.685	456.713	493.138	531.041	570.500	611.610	651.455	699.141	745.765	794.443

25° C	282.903	313.986	346.195	379.594	414.248	450.228	487.607	526.460	566.867	608.920	652.702	698.312	745.850	795.416	847.130
300	284.714	315.997	348.415	382.026	416.903	453.112	490.727	529.824	570.486	612.796	656.850	702.738	750.559	800.425	852.440
320	304.349	337.806	372.470	408.406	445.677	484.361	524.533	566.271	609.653	654.778	701.727	750.602	801.506	854.545	909.838
340	323.921	359.539	396.435	434.669	474.323	515.458	558.159	602.505	648.584	696.478	746.285	798.111	852.047	908.217	966.721
360	343.439	381.204	420.317	460.839	502.848	546.415	591.623	638.553	687.296	737.937	790.571	845.302	902.234	961.484	1,023.16
100° C	356.255	395.424	435.987	478.007	521.558	566.717	613.565	662.185	712.665	765.092	819.575	876.202	935.090	996.343	1,060.083
380	362.904	402.806	444.119	486.916	531.268	577.252	624.944	674.438	725.817	779.172	834.608	892.214	952.108	1,014.40	1,079.21
400	382.326	424.350	467.855	512.912	559.589	607.971	658.134	710.172	764.168	820.216	878.418	938.883	1,001.70	1,067.01	1,134.90
420	401.700	445.844	491.532	538.829	587.822	638.586	691.208	745.769	802.359	861.086	922.036	985.320	1,051.04	1,119.33	1,190.28
440	421.037	467.287	515.143	564.681	615.978	669.113	724.167	781.236	840.414	901.787	965.462	1,031.55	1,100.15	1,171.39	1,245.38
460	440.338	488.685	538.703	590.467	644.053	699.549	757.032	816.595	878.333	942.340	1,008.72	1,077.59	1,149.05	1,223.21	1,300.22
480	459.599	510.042	562.212	616.188	672.061	729.897	789.797	851.840	916.128	982.756	1,051.83	1,123.45	1,197.75	1,274.83	1,354.82
500	478.830	531.355	585.675	641.862	700.003	760.174	822.469	886.984	953.806	1,023.04	1,094.79	1,169.16	1,246.27	1,326.24	1,409.18
520	498.029	552.633	609.093	667.479	727.883	790.387	855.064	922.032	991.380	1,063.21	1,137.61	1,214.71	1,294.62	1,377.46	1,463.35
540	517.201	573.878	632.463	693.046	755.701	820.514	887.582	956.997	1,028.85	1,103.25	1,180.31	1,260.12	1,342.82	1,428.51	1,517.32
560	536.344	595.084	655.797	718.565	783.462	850.589	920.023	991.873	1,066.23	1,143.20	1,222.88	1,305.40	1,390.86	1,479.40	1.571.12
580	555.457	616.260	679.097	744.038	811.176	880.600	952.405	1,026.68	1,103.52	1,183.04	1,265.35	1,350.56	1,438.77	1,530.13	1,624.75
600	574.547	637.405	702.354	769.467	838.838	910.559	984.709	1,061.40	1,140.72	1,222.79	1,307.71	1,395.59	1,486.55	1,580.71	1,678.22

TABLE 15. *Values of $(dZ/dT)_\rho$ at integral values of T, the*

Temperature	$\rho=1\frac{1}{4}$	2	3	6	10	20
° K	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
16	8.04×10^{-4}	16.1×10^{-4}	24.1×10^{-4}			
18	6.07	12.1	18.2	36.2×10^{-4}		
20	4.76	9.50	14.2	28.4	47.1×10^{-4}	
22	3.82	7.64	11.4	22.8	37.9	
24	3.14	6.28	9.41	18.8	31.2	59.8×10^{-4}
26	2.62	5.24	7.86	15.7	26.0	51.1
28	2.21	4.43	6.65	13.3	22.0	43.7
30	1.90	3.80	5.69	11.3	18.8	37.5
32	1.64	3.28	4.91	9.79	16.3	32.3
34	1.43	2.85	4.27	8.51	14.2	28.1
36	1.25	2.50	3.74	7.46	12.4	24.6
38	1.10	2.20	3.30	6.59	10.9	21.7
40	0.982	1.96	2.94	5.87	9.73	19.4
42	.881	1.76	2.64	5.26	8.74	17.4
	220	240	260	280	300	320
34	256×10^{-4}	274×10^{-4}	291×10^{-4}	306×10^{-4}	320×10^{-4}	331×10^{-4}
36	226	242	257	271	284	296
38	200	215	229	242	254	266
40	180	193	205	217	228	240
42	162	174	185	196	207	218
	1	2	3	6	10	20
42	0.881×10^{-4}	1.76×10^{-4}	2.64×10^{-4}	5.26×10^{-4}	8.74×10^{-4}	17.4×10^{-4}
44	.794	1.59	2.38	4.75	7.89	15.7
46	.719	1.44	2.16	4.30	7.15	14.2
48	.653	1.30	1.96	3.91	6.49	12.9
50	.596	1.19	1.78	3.56	5.92	11.8
52	.546	1.09	1.63	3.26	5.43	10.8
54	.502	1.00	1.51	3.01	5.00	9.99
56	.466	0.931	1.40	2.79	4.64	9.24
58	.434	.867	1.30	2.59	4.30	8.53
60	.403	.803	1.20	2.39	3.97	7.84
65	.335	.669	1.00	2.00	3.32	6.59
70	.281	.561	0.841	1.68	2.79	5.56
75	.238	.473	.713	1.42	2.39	4.73
80	.205	.411	.616	1.23	2.07	4.09
85	.180	.360	.540	1.08	1.80	3 57
90	159	.317	.475	0.949	1.58	3.14
95	.140	.279	.418	.836	1.39	2.77
100	.124	.247	.371	.742	1.24	2.46
105	.110	.220	.331	.662	1.10	2.20
110	.099	.198	.297	.593	0.991	1.98
115	.091	.182	.272	.544	.904	1.80
120	.083	.166	.248	.495	.824	1.64
125	.075	.151	.226	.452	.754	1.50
130	.069	.139	.208	.416	.692	1.38
135	.064	.128	.191	.383	.638	1.27
140	.059	.118	.177	.354	.588	1.17
145	.054	.108	.163	.328	.543	1.08
150	.051	.102	.153	.305	.508	1.01
155	.047	.095	.142	.284	.473	0.94
160	.044	.088	.133	.265	.442	.88

absolute temperature, and ρ, the density in Amagat units

40	60	80	100	120	140	160	180	200
°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
100.5×10^{-4}								
85.9	124.8×10^{-4}							
73.6	108.0	141.5×10^{-4}	173.3×10^{-4}					
63.4	93.5	122.4	150.1	176.8×10^{-4}	202.3×10^{-4}	226.3×10^{-4}	249.0×10^{-4}	
55.1	81.3	106.5	130.8	154.2	176.6	197.7	217.8	237.1×10^{-4}
48.3	71.2	93.4	114.8	135.4	155.1	173.9	191.7	208.8
42.7	63.0	82.7	101.6	119.7	137.2	154.0	170.1	185.5
38.1	56.2	73.7	90.5	106.6	122.4	137.5	152.1	166.1
34.2	50.4	66.1	81.3	95.9	110.2	123.8	137.1	149.8
340	360	380	400	420	440	460	480	500
340×10^{-4}	349×10^{-4}	358×10^{-4}	370×10^{-4}	384×10^{-4}	401×10^{-4}	419×10^{-4}	437×10^{-4}	455×10^{-4}
306	315	325	336	349	364	380	396	412
276	287	297	308	320	332	346	360	373
251	262	272	283	294	304	316	328	338
229	240	250	260	270	280	289	298	307
40	60	80	100	120	140	160	180	200
34.2×10^{-4}	50.4×10^{-4}	66.1×10^{-4}	81.3×10^{-4}	95.9×10^{-4}	110.2×10^{-4}	123.8×10^{-4}	137.1×10^{-4}	149.8×10^{-4}
30.9	45.5	59.8	76.6	87.0	99.9	112.2	124.2	135.7
28.0	41.3	54.4	67.0	79.2	90.9	102.1	113.0	123.5
25.4	37.6	49.6	61.1	72.2	82.9	93.2	103.2	113.0
23.2	34.4	45.3	55.9	66.0	75.8	85.4	94.5	103.7
21.3	31.6	41.5	51.2	60.5	69.5	78.3	86.8	95.3
19.7	29.1	38.2	47.1	55.7	63.9	72.0	79.8	87.7
18.2	26.9	35.3	43.5	51.4	59.0	66.5	73.8	81.1
16.8	24.9	32.7	40.3	47.7	54.8	61.8	68.7	75.6
15.5	23.0	30.4	37.5	44.5	51.3	57.9	64.4	70.8
13.0	19.3	25.4	31.3	37.2	43.0	48.7	54.3	59.9
11.0	16.3	21.5	26.5	31.5	36.5	41.5	46.4	51.2
9.40	13.9	18.4	22.8	27.1	31.4	35.6	39.8	44.0
8.13	12.1	16.0	19.8	23.5	27.2	30.8	34.4	38.0
7.09	10.6	14.0	17.3	20.6	23.8	26.9	30.0	33.1
6.23	9.30	12.3	15.3	18.2	21.0	23.7	26.5	29.2
5.50	8.20	10.9	13.5	16.1	18.6	21.1	23.6	26.1
4.89	7.30	9.69	12.0	14.3	16.6	18.9	21.2	23.4
4.38	6.53	8.66	10.7	12.8	14.9	17.0	19.0	21.0
3.95	5.88	7.78	9.63	11.5	13.4	15.3	17.1	18.9
3.57	5.32	7.04	8.73	10.4	12.1	13.8	15.4	17.0
3.25	4.84	6.42	7.97	9.50	11.0	12.5	14.0	15.4
2.98	4.44	5.89	7.32	8.71	10.1	11.5	12.8	14.1
2.74	4.08	5.41	6.73	8.00	9.24	10.4	11.7	12.9
2.52	3.75	4.98	6.19	7.36	8.51	9.58	10.7	11.8
2.32	3.46	4.60	5.71	6.79	7.85	8.84	9.84	10.8
2.15	3.21	4.26	5.28	6.28	7.25	8.18	9.10	9.99
2.00	2.98	3.95	4.89	5.81	6.71	7.57	8.43	9.26
1.86	2.77	3.66	4.53	5.38	6.21	7.02	7.82	8.59
1.74	2.58	3.40	4.20	4.99	5.76	6.51	7.25	7.96

TABLE 15. *Values of $(dZ/dT)_p$ at integral values of T, the absolute*

Temperature	1	2	3	6	10	20
° K	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
165	4.1×10^{-6}	8.3×10^{-6}	12.4×10^{-6}	24.8×10^{-6}	41.2×10^{-6}	82×10^{-6}
170	3.8	7.6	11.5	22.9	38.2	76
180	3.3	6.6	9.9	19.9	33.1	66
190	2.9	5.8	8.8	17.6	29.3	58
200	2.6	5.2	7.7	15.8	26.0	51
210	2.3	4.6	6.9	13.9	23.1	46
220	2.1	4.1	6.2	12.4	20.4	41
230	1.8	3.6	5.4	10.7	18.0	36
240	1.6	3.2	4.8	9.5	16.0	32
250	1.4	2.9	4.3	8.6	14.4	29
260	1.3	2.6	4.0	7.9	13.1	26
270	1.200	2.398	3.594	7.167	11.90	23.57
0° C	1.164	2.325	3.484	6.947	11.53	22.84
280	1.089	2.175	3.259	6.499	10.79	21.35
25° C	0.9169	1.832	2.744	5.470	9.075	17.94
300	.9014	1.801	2.698	5.377	8.921	17.64
320	.7517	1.502	2.249	4.482	7.431	14.67
340	.6306	1.259	1.886	3.757	6.226	12.27
360	.5315	1.061	1.590	3.164	5.241	10.32
100° C	.4759	0.9503	1.423	2.832	4.689	9.219
380	.4496	.8977	1.344	2.675	4.427	8.700
400	.3814	.7614	1.140	2.267	3.750	7.355
420	.3241	.6468	0.9683	1.925	3.181	6.227
440	.2756	.5500	.8231	1.635	2.700	5.274
460	.2344	.4676	.6996	1.389	2.291	4.464
480	.1990	3970	5939	1.178	1.941	3.771
500	.1687	.3363	.5029	0.9965	1.640	3.176
520	.1424	.2838	.4243	.8399	1.380	2.662
540	.1196	.2383	.3561	.7039	1.155	2.216
560	.0998	.1986	.2967	.5855	0.9583	1.828
580	.0824	.1639	.2447	.4819	.7867	1.489
600	.0675	.1335	.1991	.3911	.6361	1.193
	220	240	260	280	300	320
42	162×10^{-4}	174×10^{-4}	185×10^{-4}	196×10^{-4}	207×10^{-4}	218×10^{-4}
44	147	158	168	178	188	198
46	134	144	153	162	172	182
48	122	131	140	149	158	167
50	112	121	129	137	145	153
52	103	111	119	126	133	140
54	95.3	103	110	116	123	129
56	88.3	95.4	102	108	114	120
58	82.4	89.0	95.4	101	107	113
60	77.2	83.6	89.9	95.9	102	107
65	65.4	70.9	76.3	81.5	86.6	91.4
70	56.0	60.6	65.1	69.5	73.9	78.3
75	48.1	52.0	55.8	59.6	63.4	67.1
80	41.5	44.9	48.2	51.5	54.7	57.9
85	36.1	39.0	41.9	44.8	47.7	50.4
90	31.8	34.4	37.0	39.6	42.0	44.4
95	28.5	30.8	33.0	35.2	37.3	39.4
100	25.5	27.6	29.6	31.5	33.3	35.1
105	23.0	24.8	26.5	28.2	29.8	31.4
110	20.7	22.3	23.8	25.3	26.8	28.2
115	18.6	20.1	21.6	22.8	24.2	25.4
120	16.8	18.2	19.5	20.7	21.9	23.0

temperature, and ρ, the density in Amagat units—Continued

40	60	80	100	120	140	160	180	200
°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
162×10^{-6}	240×10^{-6}	316×10^{-6}	390×10^{-6}	463×10^{-6}	534×10^{-6}	604×10^{-6}	672×10^{-6}	737×10^{-6}
151	223	293	361	429	495	559	622	682
131	194	254	312	370	427	483	536	587
114	169	222	273	323	372	419	464	507
101	150	197	242	285	327	367	405	442
91	134	175	215	253	290	325	358	391
81	119	156	192	226	258	289	319	348
71	105	138	170	200	229	257	283	308
63	93	122	151	178	203	228	251	274
56	83	109	134	158	180	202	222	242
51	75	98	120	141	161	180	198	215
46.21	67.90	88.63	108.4	127.0	144.7	161.2	176.6	190.7
44.76	65.74	85.76	104.8	122.8	139.7	155.6	170.3	183.7
41.81	61.34	79.92	97.53	114.1	129.7	144.1	157.5	169.6
35.04	51.26	66.59	80.99	94.42	106.9	118.2	128.5	137.7
34.43	50.36	65.40	79.51	92.66	104.8	115.9	125.9	134.8
28.56	41.63	53.87	65.24	75.70	85.22	93.74	101.2	107.6
23.82	34.61	44.61	53.80	62.13	69.58	76.09	81.62	86.13
19.95	28.88	37.08	44.52	51.15	56.95	61.87	65.87	68.90
17.79	25.69	32.88	39.34	45.04	49.94	53.99	57.16	59.40
16.77	24.18	30.90	36.91	42.16	46.64	50.29	53.08	54.96
14.12	20.27	25.78	30.62	34.75	38.15	40.78	42.59	43.56
11.90	17.00	21.50	25.37	28.58	31.10	32.90	33.93	34.17
10.03	14.25	17.90	20.97	23.41	25.21	26.33	26.73	26.38
8.443	11.92	14.86	17.25	19.06	20.25	20.81	20.70	19.88
7.086	9.926	12.27	14.09	15.36	16.06	16.15	15.62	14.42
5.922	8.221	10.05	11.39	12.21	12.49	12.20	11.32	9.81
4.919	6.753	8.144	9.070	9.510	9.439	8.833	7.665	5.906
4.050	5.484	6.499	7.076	7.192	6.825	5.953	4.549	2.588
3.295	4.383	5.074	5.350	5.190	4.574	3.478	1.880	−0.246
2.636	3.423	3.834	3.852	3.456	2.627	1.345	−0.414	−2.673
2.059	2.585	2.754	2.549	1.951	0.943	−0.496	−2.387	−4.751

340	360	380	400	420	440	460	480	500
229×10^{-4}	240×10^{-4}	250×10^{-4}	260×10^{-4}	270×10^{-4}	280×10^{-4}	289×10^{-4}	298×10^{-4}	307×10^{-4}
209	220	230	240	249	257	265	272	279
192	201	211	220	229	236	243	249	254
175	184	193	202	210	216	223	228	233
161	169	177	185	192	198	204	209	214
148	155	162	169	176	182	188	193	198
136	143	149	156	162	167	173	179	183
126	132	138	144	149	155	160	166	171
118	124	129	134	140	145	150	156	161
112	117	122	126	131	137	142	148	153
96.1	101	105	109	114	118	123	127	132
82.7	86.6	90.6	94.3	98.1	102	106	110	113
70.8	74.5	78.0	81.4	84.7	87.9	91.0	94.1	97.2
61.0	64.1	67.2	70.3	73.2	75.8	78.5	81.0	83.5
53.0	55.6	58.2	60.8	63.2	65.4	67.6	69.8	72.1
46.6	48.8	51.0	53.1	55.2	57.2	59.1	61.0	62.9
41.4	43.3	45.2	47.1	48.9	50.6	52.3	53.9	55.5
36.9	38.7	40.4	42.0	43.6	45.1	46.6	48.0	49.3
33.0	34.5	36.0	37.5	38.9	40.3	41.6	42.8	43.9
29.6	30.9	32.2	33.5	34.8	36.0	37.2	38.2	39.2
26.6	27.8	29.0	30.2	31.3	32.3	33.3	34.2	35.0
24.1	25.1	26.2	27.3	28.3	29.1	29.9	30.6	31.3

TABLE 15. *Values of $(dZ/dT)_p$ at integral values of T, the absolute*

Temperature	220	240	260	280	300	320
100° C	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
125	15.3×10^{-4}	16.5×10^{-4}	17.7×10^{-4}	18.8×10^{-4}	19.9×10^{-4}	20.9×10^{-4}
130	14.0	15.1	16.2	17.2	18.2	19.2
135	12.8	13.8	14.8	15.8	16.7	17.6
140	11.7	12.7	13.6	14.5	15.3	16.1
145	10.8	11.7	12.5	13.3	14.1	14.8
150	10.1	10.9	11.6	12.3	13.0	13.7
155	9.35	10.1	10.8	11.4	12.0	12.6
160	8.65	9.32	9.96	10.5	11.1	11.7
165	8.00	8.60	9.16	9.67	10.3	10.7
170	739×10^{-6}	792×10^{-6}	841×10^{-6}	887×10^{-6}	933×10^{-6}	980×10^{-6}
180	634	678	719	758	796	831
190	547	585	621	655	687	718
200	478	512	544	575	604	631
210	423	453	482	509	535	559
220	375	401	426	450	473	493
230	332	354	375	396	415	432
240	294	312	330	347	362	376
250	260	275	290	304	316	326
260	230	243	255	266	276	284
270	203.6	215.2	225.4	234.1	241.3	246.8
0° C	196.0	206.9	216.4	224.5	231.0	235.9
280	180.5	190.1	198.3	205.1	210.3	213.9
25° C	145.6	152.3	157.6	161.5	164.0	164.8
300	142.5	148.9	154.0	157.7	159.9	160.5
320	112.9	117.0	119.8	121.2	121.3	119.8
340	89.56	91.86	92.95	92.78	91.28	88.36
360	70.92	71.87	71.70	70.33	67.70	63.75
100° C	60.67	60.92	60.07	58.09	54.90	50.44
380	55.88	55.80	54.66	52.40	48.97	44.28
400	43.62	42.75	40.88	37.96	33.94	28.75
420	33.56	32.07	29.65	26.24	21.80	16.26
440	25.24	23.27	20.42	16.66	11.92	6.157
460	18.32	15.97	12.81	8.776	3.834	−2.069
480	12.52	9.885	6.479	2.260	−2.815	−8.792
500	7.644	4.786	1.201	−3.148	−8.303	−14.30
520	3.527	0.496	−3.220	−7.657	−12.85	−18.84
540	0.041	−3.122	−6.930	−11.42	−16.62	−22.58
560	−2.925	−6.186	−10.06	−14.57	−19.76	−25.66
580	−5.455	−8.789	−12.70	−17.22	−22.37	−28.20
600	−7.613	−11.00	−14.93	−19.43	−24.54	−30.28

temperature, and ρ, the density in Amagat units—Continued

340	360	380	400	420	440	460	480	500
°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}	°K^{-1}
21.9×10^{-4}	22.9×10^{-4}	23.9×10^{-4}	24.8×10^{-4}	25.6×10^{-4}	26.3×10^{-4}	27.0×10^{-4}	27.6×10^{-4}	28.1×10^{-4}
20.1	21.0	21.8	22.5	23.2	23.8	24.4	24.9	25.3
18.4	19.2	19.9	20.5	21.1	21.7	22.1	22.5	22.9
16.9	17.6	18.2	18.8	19.3	19.8	20.2	20.5	20.8
15.5	16.1	16.7	17.2	17.7	18.1	18.5	18.8	19.0
14.3	14.8	15.3	15.8	16.2	16.6	16.9	17.1	17.3
13.2	13.7	14.1	14.5	14.8	15.1	15.3	15.5	15.6
12.2	12.7	13.0	13.3	13.5	13.7	13.9	14.0	14.0
11.2	11.6	11.9	12.1	12.3	12.5	12.6	12.6	12.6
$102_0\times10^{-6}$	$105_0\times10^{-6}$	$108_0\times10^{-6}$	$111_0\times10^{-6}$	$113_0\times10^{-6}$	$114_0\times10^{-6}$	$114_0\times10^{-6}$	$114_0\times10^{-6}$	$114_0\times10^{-6}$
863	892	918	940	958	971	980	986	988
746	771	792	810	825	837	846	852	854
656	678	696	711	722	730	736	741	744
580	598	613	625	634	640	644	646	647
511	527	539	548	554	558	560	561	560
447	460	470	476	480	482	482	481	479
389	399	406	410	412	412	410	407	402
336	344	348	350	350	348	343	337	329
290	295	297	297	294	290	283	273	262
250.6	252.6	252.6	250.5	246.1	239.5	230.2	218.3	203.5
239.0	240.3	239.7	237.0	232.0	224.7	214.9	202.4	187.0
215.7	215.8	213.9	210.0	203.8	195.3	184.3	170.7	154.2
164.0	161.4	157.0	150.5	142.0	131.1	117.9	102.1	83.59
159.5	156.7	152.0	145.4	136.6	125.6	112.2	96.25	77.58
116.8	112.1	105.6	97.22	86.85	74.34	59.57	42.39	22.64
83.95	77.96	70.30	60.85	49.52	36.19	20.73	3.011	−17.11
58.40	51.55	43.14	33.06	21.21	7.491	−8.216	−26.03	−46.08
44.64	37.40	28.67	18.34	6.314	−7.497	−23.21	−40.93	−60.78
38.29	30.90	22.03	11.61	−0.457	−14.28	−29.95	−47.58	−67.30
22.33	14.60	5.500	−5.058	−17.16	−30.88	−46.34	−63.61	−82.82
9.574	1.666	−7.529	−18.08	−30.08	−43.59	−58.70	−75.52	−94.14
−0.687	−8.670	−17.86	−28.31	−40.11	−53.33	−68.04	−84.33	−102.3
−8.984	−16.97	−26.08	−36.37	−47.92	−60.79	−75.06	−90.81	−108.1
−15.72	−23.64	−32.63	−42.72	−53.99	−66.49	−80.30	−95.48	−112.1
−21.20	−29.03	−37.85	−47.72	−58.68	−70.80	−84.14	−98.76	−114.7
−25.67	−33.38	−42.03	−51.65	−62.30	−74.03	−86.91	−101.0	−116.3
−29.32	−36.89	−45.34	−54.71	−65.04	−76.39	−88.82	−102.4	−117.1
−32.30	−39.72	−47.96	−57.08	−67.10	−75.08	−90.06	−103.1	−117.3
−34.72	−41.99	−50.03	−58.89	−68.60	−79.22	−90.78	−103.3	−116.9
−36.69	−43.79	−51.63	−60.24	−69.65	−79.92	−91.08	−103.2	−116.2

TABLE 16. *Values of* $(-d^2Z/dT^2)_\rho$ *at integral values of* T,

Temperature	$\rho=1$	2	3	6	10	20
°K	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
16	11.4×10^{-5}	22.6×10^{-5}	33.7×10^{-5}			
18	7.9	15.7	23.5	47.0×10^{-5}		
20	5.5	11.0	16.5	33.0	54.0×10^{-5}	
22	4.0	7.9	11.7	23.5	38.6	
24	3.0	5.9	8.8	17.4	29.2	48.5×10^{-5}
26	2.3	4.6	6.8	13.5	22.7	41.0
28	1.8	3.6	5.4	10.7	17.8	34.3
30	1.4	2.9	4.3	8.6	14.3	28.4
32	1.2	2.4	3.5	7.0	11.7	23.3
34	0.96	2.0	2.9	5.8	9.7	19.0
36	.79	1.7	2.4	4.8	8.0	15.5
38	.66	1.4	2.0	4.0	6.6	12.8
40	.55	1.1	1.7	3.3	5.5	10.7
42	.47	0.92	1.4	2.8	4.6	9.2
	220	240	260	280	300	320
34	167×10^{-5}	178×10^{-5}	186×10^{-5}	190×10^{-5}	190×10^{-5}	188×10^{-5}
36	138	146	154	160	162	161
38	114	121	128	135	138	138
40	96	102	108	114	118	119
42	82	87	92	97	101	103
	$\rho=1$	2	3	6	10	20
	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
42	0.47×10^{-5}	0.92×10^{-5}	1.4×10^{-5}	2.8×10^{-5}	4.6×10^{-5}	9.2×10^{-5}
44	.40	.79	1.2	2.4	4.0	8.0
46	.35	.69	1.0	2.1	3.5	6.9
48	.31	.61	0.91	1.9	3.1	6.0
50	.27	.53	.80	1.6	2.7	5.2
52	.23	.46	.69	1.4	2.3	4.5
54	.20	.40	.60	1.2	2.0	4.0
56	.18	.35	.53	1.1	1.8	3.6
58	.16	.32	.48	0.96	1.7	3.3
60	.15	.30	.45	.90	1.5	3.0
65	.12	.24	.37	.74	1.2	2.4
70	.10	.19	.30	.60	0.96	1.9
75	.078	.15	.23	.48	.76	1.5
80	.063	.12	.18	.38	.61	1.2
85	.051	.10	.15	.31	.49	0.97
90	.042	.084	.13	.25	.41	.80
95	.036	.070	.11	.21	.35	.67
100	.030	.059	.091	.18	.29	.57
105	.025	.049	.075	.15	.24	.48
110	.020	.041	.062	.12	.20	.40
115	.017	.035	.052	.10	.17	.34
120	.015	.030	.045	.089	.15	.30
125	.013	.026	.039	.080	.13	.26
130	.012	.023	.035	.071	.12	.23
135	.011	.021	.032	.062	.11	.21
140	.0095	.019	.028	.055	.093	.19
145	.0082	.016	.024	.048	.081	.16
150	.0071	.014	.021	.043	.070	.14
155	.0063	.013	.019	.039	.062	.13
160	.0058	.012	.018	.036	.057	.12
165	.0054	.012	.017	.033	.054	.12
170	.0050	.011	.016	.031	.050	.11

the absolute temperature, and ρ, the density in Amagat units

40	60	80	100	120	140	160	180	200
°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
79.8×10⁻⁵								
67.1	99.0×10⁻⁵							
55.8	81.9	106.2×10⁻⁵	128.0×10⁻⁵					
45.9	67.2	87.2	105.7	123.0×10⁻⁵	139.6×10⁻⁵	155.6 × 10⁻⁵	171.0 × 10⁻⁵	
37.5	55.1	71.9	87.8	102.8	116.9	130.1	142.9	155.2 × 10⁻⁵
30.7	45.4	59.6	72.9	85.6	97.5	108.5	118.9	128.0
25.4	37.6	49.4	60.6	71.1	81.1	90.4	98.8	106.6
21.2	31.3	41.0	50.3	59.1	67.5	75.3	82.4	89.3
18.0	26.4	34.3	42.0	49.4	56.5	63.1	69.6	75.9

340	360	380	400	420	440	460	480	500
183×10⁻⁵	178×10⁻⁵	177×10⁻⁵	181×10⁻⁵	189×10⁻⁵	199×10⁻⁵	210×10⁻⁵	220×10⁻⁵	229×10⁻⁵
158	154	152	154	160	170	182	193	204
137	134	132	133	138	147	159	171	183
119	118	117	118	122	130	141	153	165
104	105	106	108	112	118	127	137	148

40	60	80	100	120	140	160	180	200
°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
18.0×10⁻⁵	26.4×10⁻⁵	34.3×10⁻⁵	42.0×10⁻⁵	49.4×10⁻⁵	56.5×10⁻⁵	63.1×10⁻⁵	69.6×10⁻⁵	75.9×10⁻⁵
15.5	22.7	29.3	35.6	41.8	47.9	53.8	59.8	65.6
13.5	19.7	25.4	30.8	36.2	41.5	46.9	52.1	56.9
11.8	17.2	22.4	27.3	32.0	36.6	41.2	45.7	49.7
10.3	15.2	19.9	24.3	28.5	32.5	36.4	40.2	43.7
9.0	13.4	17.6	21.6	25.4	29.0	32.4	35.6	38.7
8.0	11.9	15.6	19.2	22.7	25.9	28.8	31.6	34.4
7.2	10.6	13.9	17.1	20.3	23.1	25.6	28.0	30.5
6.5	9.5	12.4	15.3	18.2	20.7	22.8	24.8	26.9
5.8	8.6	11.3	13.8	16.3	18.5	20.4	22.0	23.8
4.6	6.7	8.8	10.8	12.7	14.5	16.1	17.5	19.0
3.6	5.3	6.9	8.5	10.0	11.5	13.0	14.4	15.7
2.9	4.2	5.5	6.7	8.0	9.3	10.6	11.8	13.0
2.3	3.4	4.5	5.4	6.5	7.6	8.6	9.7	10.7
1.9	2.8	3.7	4.5	5.3	6.1	7.0	7.9	8.8
1.6	2.4	3.1	3.8	4.5	5.2	5.8	6.4	7.2
1.3	2.0	2.6	3.3	3.9	4.4	4.8	5.3	5.9
1.1	1.7	2.2	2.8	3.3	3.7	4.1	4.6	5.0
0.94	1.4	1.9	2.4	2.8	3.2	3.6	4.1	4.4
.80	1.2	1.6	2.0	2.4	2.8	3.2	3.6	3.9
.68	1.0	1.3	1.6	2.0	2.4	2.8	3.1	3.4
.58	0.87	1.1	1.4	1.7	2.0	2.4	2.6	2.9
.51	.77	1.0	1.2	1.5	1.7	2.1	2.3	2.5
.46	.69	0.90	1.1	1.3	1.5	1.8	2.0	2.2
.41	.61	.80	1.0	1.2	1.3	1.5	1.8	2.0
.37	.54	.72	0.91	1.1	1.2	1.4	1.6	1.8
.33	.48	.65	.82	0.97	1.1	1.3	1.4	1.6
.29	.44	.60	.75	.89	1.0	1.2	1.3	1.4
.26	.40	.55	.69	.82	0.93	1.1	1.2	1.3
.25	.37	.51	.63	.75	.87	1.0	1.1	1.2
.24	.35	.47	.58	.70	.81	0.91	1.0	1.1
.22	.32	.43	.53	.64	.74	.84	0.93	1.0

TABLE 16. *Values of* $(-d^2Z/dT^2)_\rho$ *at integral values of* T, *the*

Temperature	$\rho=1$	2	3	6	10	20
°K	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
170	0.50×10^{-7}	1.1×10^{-7}	1.6×10^{-7}	3.1×10^{-7}	5.0×10^{-7}	11×10^{-7}
180	.44	0.88	1.3	2.6	4.3	9.3
190	.38	.76	1.1	2.2	3.7	7.5
200	.33	.66	1.0	2.0	3.2	6.2
210	.29	.58	0.87	1.8	2.7	5.4
220	.26	.51	.78	1.6	2.4	4.7
230	.23	.45	.69	1.4	2.2	4.2
240	.20	.40	.60	1.2	2.0	3.7
250	.17	.34	.52	1.0	1.7	3.2
260	.14	.28	.43	0.86	1.4	2.8
270	.1185	.2370	.3554	.7101	1.182	2.356
0° C	.1140	.2280	.3419	.6830	1.137	2.271
280	.10501	.2100	.3148	.6289	1.047	2.086
25° C	.08510	.1701	.2551	.5094	0.8476	1.691
300	.08336	.1666	.2498	.4990	.8302	1.653
320	.06706	.1341	.2010	.4013	.6674	1.328
340	.05459	.1091	.1636	.3266	.5430	1.079
360	.04490	.08970	.1345	.2685	.4463	0.8866
100° C	.03969	.07932	.1189	.2373	.3945	.7837
380	.03727	.07448	.1116	.2228	.3702	.7350
400	.03119	.06233	.09342	.1864	.3097	.6143
420	.02629	.05254	.07875	.1571	.2609	.5173
440	.02231	.04458	.06682	.1333	.2213	.4385
460	.01905	.03806	.05703	.1137	.1888	.3739
480	.01635	.03266	.04894	.09758	.1620	.3205
500	.01410	.02817	.04221	.08414	.1396	.2761
520	.01221	.02440	.03660	.07286	.1209	.2389
540	.01062	.02122	.03180	.06336	.1051	.2076
560	.06928	.01853	.02776	.05530	.09169	.1810
580	.00812	.01623	.02431	.04842	.08027	.1583
600	.00714	.01426	.02136	.04254	.07049	.1390

	$\rho=220$	240	260	280	300	320
42	82×10^{-5}	87×10^{-5}	92×10^{-5}	97×10^{-5}	101×10^{-5}	103×10^{-5}
44	71	75	79	84	87	90
46	61	65	69	73	76	80
48	53	57	61	65	68	72
50	47	50	54	58	61	64
52	42	44	47	51	54	57
54	37	39	41	44	46	49
56	33	35	36	38	40	42
58	29	31	32	34	36	37
60	26	28	30	31	32	34
65	21	23	25	26	27	28
70	17	19	21	22	23	24
75	14	16	17	18	19	20
80	12	13	14	15	16	16
85	9.7	10	11	12	13	13
90	7.8	8.3	8.9	9.5	10	11
95	6.4	6.9	7.5	8.1	8.6	9.1
100	5.5	6.0	6.5	7.0	7.5	8.0
105	4.8	5.3	5.7	6.1	6.5	6.9
110	4.3	4.6	5.0	5.3	5.6	6.0
115	3.7	4.0	4.3	4.6	4.9	5.2
120	3.2	3.5	3.8	4.0	4.3	4.5
125	2.8	3.1	3.3	3.5	3.7	3.8
130	2.5	2.7	2.9	3.1	3.2	3.3
135	2.2	2.4	2.6	2.7	2.9	3.0
140	1.9	2.1	2.3	2.4	2.6	2.7

absolute temperature, and ρ, the density in Amagat units—Continued

40	60	80	100	120	140	160	180	200
°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
22×10^{-7}	32×10^{-7}	43×10^{-7}	53×10^{-7}	64×10^{-7}	74×10^{-7}	84×10^{-7}	93×10^{-7}	100×10^{-7}
19	27	35	44	53	61	70	79	87
15	22	29	36	43	50	58	65	72
12	18	24	29	35	41	47	53	59
10	15	20	25	29	34	39	44	48
9.6	14	18	22	26	29	33	37	41
8.5	13	17	20	23	26	29	32	36
7.5	11	15	18	20	23	26	29	32
6.5	9.1	13	16	18	20	23	26	29
5.5	8.0	10	13	16	18	20	23	26
4.684	6.986	9.264	11.52	13.76	15.82	18.19	20.38	22.56
4.523	6.756	8.970	11.17	13.35	15.51	17.66	19.79	21.91
4.142	6.171	8.175	10.15	12.11	14.05	15.96	17.86	19.74
3.358	5.001	6.620	8.216	9.786	11.33	12.85	14.35	15.81
3.276	4.872	6.440	7.981	9.496	10.98	12.45	13.89	15.30
2.628	3.900	5.145	6.362	7.553	8.716	9.851	10.96	12.03
2.132	3.160	4.160	5.135	6.082	7.002	7.893	8.756	9.588
1.749	2.587	3.400	4.189	4.951	5.687	6.395	7.075	7.725
1.546	2.286	3.004	3.697	4.366	5.008	5.624	6.211	6.768
1.448	2.138	2.806	3.450	4.069	4.664	5.232	5.773	6.285
1.208	1.706	2.202	2.865	3.373	3.857	4.317	4.751	5.158
1.016	1.496	1.957	2.397	2.816	3.214	3.586	3.939	4.265
0.8602	1.265	1.651	2.019	2.368	2.696	3.004	3.289	3.550
.7325	1.075	1.402	1.711	2.003	2.276	2.529	2.762	2.973
.6271	0.9193	1.196	1.458	1.703	1.931	2.141	2.332	2.503
.5395	.7897	1.026	1.248	1.455	1.646	1.821	1.978	2.116
.4662	.6814	0.8839	1.073	1.249	1.410	1.555	1.685	1.797
.4045	.5903	.7645	0.9265	1.076	1.212	1.333	1.440	1.531
.3522	.5132	.6635	.8026	0.9299	1.045	1.147	1.235	1.309
.3077	.4476	.5777	.6975	.8063	0.9038	0.9892	1.062	1.121
.2696	.3916	.5045	.6078	.7011	.7838	.8554	0.9152	0.9626

340	360	380	400	420	440	460	480	500
104×10^{-5}	105×10^{-5}	106×10^{-5}	108×10^{-5}	112×10^{-5}	118×10^{-5}	127×10^{-5}	137×10^{-5}	148×10^{-5}
93	95	98	101	104	109	115	123	132
84	87	91	95	98	102	106	111	116
76	80	84	88	92	95	97	99	101
68	73	77	81	85	87	87	87	88
61	65	69	73	76	77	77	77	76
53	57	61	64	66	67	67	67	65
45	48	51	54	56	56	57	57	56
39	40	42	45	47	47	48	49	49
36	36	37	39	41	42	44	45	46
29	30	31	32	33	34	36	38	39
25	26	27	28	29	30	31	33	34
21	22	23	24	25	26	27	29	30
17	18	19	20	22	23	23	24	25
14	15	16	17	18	19	19	20	20
11	12	13	14	14	15	15	16	16
9.6	10	10	11	11	12	12	13	13
8.4	8.8	9.1	9.5	9.8	10	11	11	11
7.3	7.7	8.0	8.4	8.7	9.1	9.4	10	10
6.4	6.7	7.0	7.3	7.6	8.0	8.3	8.6	8.9
5.5	5.8	6.0	6.3	6.6	6.9	7.3	7.6	7.9
4.7	4.9	5.2	5.5	5.8	6.0	6.3	6.6	6.9
4.0	4.2	4.4	4.8	5.1	5.3	5.5	5.8	6.0
3.5	3.7	4.0	4.2	4.4	4.6	4.8	5.0	5.2
3.2	3.4	3.6	3.7	3.9	4.0	4.2	4.4	4.5
2.9	3.1	3.2	3.3	3.4	3.6	3.7	3.8	3.9

TABLE 16. *Values of* $(-d^2Z/dT^2)_\rho$ *at integral values of* T, *the*

Temperature	$\rho=220$	240	260	280	300	320
°*K*	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}	°K^{-2}
145	1.7×10^{-5}	1.8×10^{-5}	2.0×10^{-5}	2.1×10^{-5}	2.3×10^{-5}	2.4×10^{-5}
150	1.5	1.6	1.8	1.9	2.1	2.2
155	1.4	1.5	1.6	1.8	1.9	2.0
160	1.3	1.4	1.5	1.7	1.8	1.9
165	1.3	1.4	1.5	1.6	1.6	1.8
170	110×10^{-7}	120×10^{-7}	130×10^{-7}	140×10^{-7}	150×10^{-7}	160×10^{-7}
180	96	100	110	120	120	130
190	78	83	87	91	96	99
200	63	67	70	73	78	81
210	52	56	59	63	66	69
220	45	49	53	56	59	62
230	40	44	48	51	53	56
240	36	40	43	46	48	51
250	32	35	38	40	43	46
260	29	31	33	35	37	40
270	24.73	26.89	29.03	31.17	33.30	35.42
0° *C*	24.01	26.09	28.15	30.20	32.23	34.24
280	21.60	23.44	25.26	27.07	28.85	30.62
25° *C*	17.25	18.66	20.04	21.38	22.69	23.96
300	16.68	18.04	19.37	20.67	21.94	23.17
320	15.08	14.09	15.08	16.02	16.93	17.80
340	10.39	11.16	11.89	12.58	13.24	13.91
360	8.343	8.929	9.480	9.994	10.47	10.90
100° *C*	7.293	7.785	8.242	8.662	9.043	9.383
380	6.767	7.218	7.635	8.017	8.360	8.664
400	5.536	5.885	6.202	6.485	6.733	6.942
420	4.564	4.834	5.076	5.285	5.461	5.601
440	3.787	3.998	4.181	4.335	4.458	4.547
460	3.161	3.325	3.464	3.575	3.658	3.709
480	2.653	2.780	2.884	2.962	3.014	3.038
500	2.236	2.334	2.411	2.464	2.493	2.496
520	1.892	1.967	2.022	2.056	2.067	2.055
540	1.606	1.603	1.701	1.720	1.718	1.693
560	1.367	1.409	1.434	1.441	1.429	1.396
580	1.166	1.196	1.211	1.208	1.188	1.149
600	0.997	1.018	1.023	1.014	0.988	0.944

TABLE 17. *Values of* $(dZ/d\rho)_T$ *at integral values of* T, *the*

Temperature	$\rho=0$	1	2	3	6	10	20
°*K*							
16	$-9,105\times10^{-6}$	$-9,087\times10^{-6}$	$-9,070\times10^{-6}$	$-9,052\times10^{-6}$			
18	−7,709	−7,694	−7,679	−7,664	$-7,620\times10^{-6}$		
20	−6,633	−6,621	−6,608	−6,595	−6,557	$-6,506\times10^{-6}$	
22	−5,781	−5,770	−5,759	−5,748	−5,714	−5,670	
24	−5,087	−5,077	−5,067	−5,058	−5,029	−4,990	$-4,892\times10^{-6}$
26	−4,512	−4,503	−4,494	−4,485	−4,460	−4,425	−4,338
28	−4,027	−4,019	−4,011	−4,003	−3,980	−3,949	−3,871
30	−3,615	−3,608	−3,601	−3,594	−3,572	−3,544	−3,474
32	−3,262	−3,255	−3,249	−3,242	−3,223	−3,197	−3,132
34	−2,955	−2,949	−2,943	−2,937	−2,919	−2,895	−2,836
36	−2,688	−2,682	−2,676	−2,671	−2,654	−2,632	−2,577
38	−2,453	−2,448	−2,443	−2,438	−2,422	−2,402	−2,350
40	−2,245	−2,240	−2,235	−2,230	−2,216	−2,197	−2,149
42	−2,059	−2,054	−2,050	−2,045	−2,032	−2,014	−1,968

absolute temperature, and ρ, the density in Amagat units—Continued

340	360	380	400	420	440	460	480	500
$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$	$°K^{-2}$
2.6×10^{-5}	2.8×10^{-5}	2.9×10^{-5}	3.0×10^{-5}	3.1×10^{-5}	3.3×10^{-5}	3.4×10^{-5}	3.4×10^{-5}	3.5×10^{-5}
2.3	2.5	2.6	2.7	2.9	3.0	3.2	3.2	3.3
2.1	2.2	2.3	2.5	2.7	2.8	3.0	3.1	3.2
2.0	2.1	2.2	2.4	2.5	2.6	2.7	2.9	3.0
2.0	2.1	2.2	2.3	2.4	2.5	2.5	2.6	2.7
170×10^{-7}	180×10^{-7}	180×10^{-7}	190×10^{-7}	190×10^{-7}	200×10^{-7}	200×10^{-7}	200×10^{-7}	210×10^{-7}
140	140	140	150	150	150	150	150	160
100	100	110	110	120	120	120	120	120
83	85	88	92	96	98	99	100	100
72	75	78	81	83	85	87	88	89
65	68	71	73	75	77	80	81	81
60	63	65	67	69	71	74	75	75
55	58	60	62	64	66	68	69	70
49	52	54	56	58	60	62	64	65
43	46	48	50	52	54	56	58	60
37.53	39.63	41.71	43.78	45.83	47.86	49.87	51.85	53.80
36.23	38.19	40.13	42.05	43.93	45.78	47.60	49.38	51.12
32.36	34.08	35.77	37.44	39.07	40.66	42.22	43.73	45.19
25.20	26.39	27.54	28.63	29.68	30.67	31.60	32.47	33.27
24.37	25.53	26.64	27.71	28.74	29.70	30.61	31.45	32.22
18.63	19.41	20.14	20.82	21.44	21.99	22.48	22.90	23.23
14.42	14.94	15.41	15.83	16.18	16.47	16.69	16.83	16.89
11.29	11.63	11.92	12.16	12.33	12.44	12.49	12.46	12.34
9.678	9.926	10.12	10.27	10.36	10.39	10.36	10.25	10.08
8.925	9.139	9.305	9.417	9.473	9.468	9.397	9.256	9.039
7.110	7.236	7.314	7.344	7.319	7.238	7.094	6.885	6.605
5.704	5.765	5.784	5.756	5.678	5.547	5.359	5.110	4.795
4.601	4.618	4.594	4.527	4.415	4.253	4.039	3.769	3.438
3.728	3.713	3.660	3.567	3.433	3.253	2.038	2.746	2.411
3.032	2.993	2.976	2.812	2.664	2.475	2.242	1.961	1.630
2.471	2.416	2.331	2.212	2.057	1.864	1.631	1.354	1.032
2.016	1.951	1.857	1.732	1.574	1.382	1.153	0.884	0.573
1.646	1.573	1.474	1.346	1.189	1.000	0.776	.517	.220
1.342	1.264	1.162	1.035	0.880	0.695	.480	.231	−.052
1.090	1.010	0.908	0.782	.630	.452	.245	.007	−.262
0.883	0.801	.700	.576	.428	.257	.059	−.167	−.422

absolute temperature, and ρ, the density in Amagat units

40	60	80	100	120	140	160	180	200
$-4,165\times10^{-6}$								
−3,715	$-3,559\times10^{-6}$							
−3,332	−3,191	$-3,049\times10^{-6}$	$-2,908\times10^{-6}$					
−3,003	−2,874	−2,745	−2,615	$-2,486\times10^{-6}$	$-2,357\times10^{-6}$	$-2,228\times10^{-6}$	$-2,098\times10^{-6}$	
−2,717	−2,598	−2,479	−2,360	−2,242	−2,123	−2,004	−1,885	$-1,768\times10^{-6}$
−2,467	−2,357	−2,247	−2,137	−2,027	−1,917	−1,807	−1,697	−1,588
−2,248	−2,145	−2,043	−1,940	−1,838	−1,735	−1,633	−1,530	−1,428
−2,053	−1,957	−1,861	−1,765	−1,669	−1,573	−1,477	−1,381	−1,283
−1,878	−1,788	−1,698	−1,608	−1,517	−1,427	−1,337	−1,245	−1,151

TABLE 17. *Values of $(dZ/d\rho,)_T$ at integral values of T, the absolute*

Temperature	$\rho=220$	240	260	280	300	320	340
°K							
34	$-1,650\times10^{-6}$	$-1,526\times10^{-6}$	$-1,392\times10^{-6}$	$-1,254\times10^{-6}$	$-1,121\times10^{-6}$	-998×10^{-6}	-884×10^{-6}
36	−1, 477	−1, 360	−1, 239	−1, 117	−1, 001	−892	−788
38	−1, 322	−1, 210	−1, 100	−989	−882	−782	−684
40	−1, 181	−1, 077	−973	−870	−768	−670	−573
42	−1, 054	−956	−857	−758	−658	−558	−461
	$\rho=520$	540	560	580	600	620	640
34	387×10^{-6}	654×10^{-6}	941×10^{-6}	$1,255\times10^{-6}$	$1,627\times10^{-6}$	$2,090\times10^{-6}$	$2,638\times10^{-6}$
36	538	795	1, 077	1, 400	1, 750	2, 120	2, 504
38	681	961	1, 260	1, 587			
40	812	1, 135					
42	940						
	$\rho=0$	1	2	3	6	10	20
42	$-2,059\times10^{-6}$	$-2,054\times10^{-6}$	$-2,050\times10^{-6}$	$-2,045\times10^{-6}$	$-2,032\times10^{-6}$	$-2,014\times10^{-6}$	$-1,968\times10^{-6}$
44	−1, 892	−1, 887	−1, 883	−1, 879	−1, 866	−1, 849	−1, 806
46	−1, 740	−1, 736	−1, 732	−1, 728	−1, 716	−1, 700	−1, 659
48	−1, 603	−1, 599	−1, 595	−1, 591	−1, 580	−1, 564	−1, 526
50	−1, 478	−1, 474	−1, 470	−1, 467	−1, 456	−1, 441	−1, 404
52	−1, 364	−1, 360	−1, 357	−1, 353	−1, 342	−1, 328	−1, 293
54	−1, 259	−1, 256	−1, 252	−1, 249	−1, 239	−1, 225	−1, 191
56	−1, 162	−1, 159	−1, 156	−1, 152	−1, 143	−1, 129	−1, 096
58	−1, 072	−1, 069	−1, 066	−1, 063	−1, 053	−1, 040	−1, 009
60	−988	−985	−982	−979	−970	−958	−928
65	−807	−804	−801	−799	−790	−779	−751
70	−654	−651	−649	−646	−638	−628	−601
75	−524	−522	−519	−516	−509	−499	−474
80	−412	−410	−407	−405	−398	−388	−364
85	−315	−313	−310	−308	−301	−292	−269
90	−231	−229	−227	−224	−218	−209	−186
95	−157	−155	−153	−150	−144	−135	−113
100	−90	−88	−86	−84	−77	−69	−48
105	−34	−32	−30	−28	−21	−12	+9
110	+19	+21	+23	+25	+32	+40	61
115	67	69	71	73	79	87	108
120	111	113	115	117	123	131	151
125	151	153	155	157	139	171	190
130	187	189	191	193	199	206	226
135	221	223	225	227	232	240	259
140	252	254	256	258	263	271	289
145	281	283	285	286	292	297	317
150	307	309	311	312	318	325	343
155	331	333	335	336	342	349	367
160	353	355	357	358	364	371	389
165	373	375	377	378	384	391	409
170	393	395	397	398	404	411	429
180	429	431	433	434	439	446	464
190	460	462	463	465	470	477	494
200	489	490	491	493	498	504	521
210	512	514	516	517	522	529	545
220	534	536	538	539	544	550	566
230	553	555	557	558	563	569	585
240	571	573	574	576	580	586	602
250	587	589	590	592	596	602	617
260	602	604	605	606	610	616	631
270	613. 9	615. 3	616. 8	618. 2	622. 5	628. 3	642. 8

360	380	400	420	440	460	480	500	
-774×10^{-6}	-667×10^{-6}	-562×10^{-6}	-460×10^{-6}	-357×10^{-6}	-234×10^{-6}	-68×10^{-6}	$+148\times10^{-6}$	
−680	−564	−442	−318	−194	−62	+99	302	
−577	−456	−324	−188	−51	+89	247	437	
−467	−347	−213	−73	+69	218	374	550	
−356	−241	−111	+29	173	321	475	639	
660	680							
$3,227\times10^{-6}$	$3,848\times10^{-6}$							
40	60	80	100	120	140	160	180	200
$-1,878\times10^{-6}$	$-1,788\times10^{-6}$	$-1,698\times10^{-6}$	$-1,608\times10^{-6}$	$-1,517\times10^{-6}$	$-1,427\times10^{-6}$	$-1,337\times10^{-6}$	$-1,245\times10^{-6}$	$-1,151\times10^{-6}$
−1,721	−1,636	−1,550	−1,465	−1,379	−1,294	−1,209	−1,122	−1,033
−1,578	−1,497	−1,416	−1,335	−1,254	−1,173	−1,092	−1,011	−926
−1,448	−1,371	−1,294	−1,216	−1,139	−1,062	−985	−908	−827
−1,330	−1,256	−1,182	−1,108	−1,034	−961	−887	−813	−736
−1,222	−1,151	−1,080	−1,009	−938	−868	−797	−726	−652
−1,123	−1,054	−986	−918	−849	−781	−713	−645	−573
−1,031	−965	−899	−834	−768	−702	−636	−570	−499
−946	−883	−820	−757	−693	−629	−565	−499	−428
−867	−807	−746	−685	−623	−561	−497	−431	−361
−694	−637	−580	−523	−465	−407	−346	−280	−210
−548	−495	−441	−386	−330	−273	−214	−150	−81
−424	−374	−322	−269	−215	−159	−100	−37	+30
−317	−269	−219	−168	−115	−60	−2	+59	124
−223	−177	−129	−80	−29	+25	+82	142	204
−141	−96	−50	−2	+48	100	156	215	275
−69	−25	+20	+67	115	167	222	279	339
−5	+38	82	128	176	227	281	338	397
+52	95	138	183	231	281	335	392	449
103	145	188	233	280	330	383	439	495
149	191	233	277	324	373	426	481	536
191	232	274	318	364	413	465	518	573
230	270	311	355	401	449	500	552	606
265	305	346	389	434	481	531	583	636
297	337	379	421	465	511	560	611	663
326	366	408	450	493	538	586	637	688
354	394	435	476	519	563	610	660	711
380	419	459	500	543	586	632	681	731
404	442	482	523	565	608	653	701	750
426	464	503	544	585	628	672	719	768
446	484	523	563	604	646	690	736	785
465	503	541	581	622	664	707	752	800
499	536	574	613	653	694	736	780	826
529	565	602	640	679	719	761	804	849
555	590	626	663	701	741	782	824	868
578	613	648	684	721	760	800	842	885
599	633	667	703	739	777	816	857	900
618	651	684	719	755	792	831	871	913
634	666	699	734	770	806	844	884	925
648	680	713	747	782	818	855	894	935
661	692	725	758	792	828	865	903	943
672.6	703.4	735.2	768.1	802.0	837.2	873.6	911.4	950.4

TABLE 17. *Values of $(dZ/d_\rho)_T$ at integral values of T, the*

Temperature	$\rho=0$	1	2	3	6	10	20
0° C	617.7×10^{-6}	619.1×10^{-6}	620.5×10^{-6}	621.9×10^{-6}	626.2×10^{-6}	631.9×10^{-6}	646.4×10^{-6}
280	625.4	626.8	628.2	629.6	633.8	639.5	653.8
25° C	643.5	644.9	646.3	647.6	651.8	657.3	671.2
300	645.2	646.6	647.9	649.3	653.4	658.9	672.8
320	661.7	663.0	664.4	665.7	669.7	675.0	688.5
340	675.5	676.8	678.1	679.4	683.2	688.4	701.6
360	687.1	688.4	689.6	690.9	694.6	699.7	712.5
100° C	693.7	695.0	696.2	697.4	701.1	706.1	718.7
380	696.9	698.1	699.4	700.6	704.2	709.2	721.6
400	705.2	706.4	707.6	708.8	712.4	717.2	729.3
420	712.3	713.4	714.6	715.8	719.3	724.0	735.8
440	718.3	719.4	720.5	721.7	725.1	729.7	741.3
460	723.4	724.5	725.6	726.7	730.1	734.6	745.9
480	727.7	728.8	729.9	731.0	734.3	738.7	749.8
500	731.4	732.5	733.5	734.6	737.8	742.1	753.0
520	734.5	735.6	736.6	737.6	740.8	745.0	755.8
540	737.1	738.2	739.2	740.2	743.3	747.5	758.0
560	739.3	740.3	741.4	742.4	745.4	749.5	759.8
580	741.2	742.2	743.1	744.1	747.1	751.2	761.3
600	742.7	743.6	744.6	745.6	748.6	752.5	762.5

Temperature	$\rho=220$	240	260	280	300	320
42	$-1,054\times10^{-6}$	-956×10^{-6}	-857×10^{-6}	-758×10^{-6}	-658×10^{-6}	-558×10^{-6}
44	−941	−847	−751	−653	−553	−452
46	−837	−747	−653	−555	−454	−351
48	−742	−654	−562	−464	−362	−258
50	−655	−569	−477	−380	−277	−174
52	−573	−489	−398	−301	−200	−98
54	−496	−413	−324	−229	−131	−31
56	−423	−342	−255	−163	−68	+30
58	−353	−274	−190	−102	−10	+86
60	−287	−211	−131	−46	+44	138
65	−137	−62	+15	+94	177	264
70	−9	+64	137	213	293	376
75	+99	169	241	316	393	475
80	191	260	331	403	480	560
85	270	338	408	480	555	633
90	340	406	475	546	620	696
95	402	467	534	604	676	751
100	457	520	586	655	725	798
105	507	568	632	699	768	840
110	552	611	673	739	807	878
115	592	650	711	775	841	911
120	628	685	745	807	872	941
125	660	716	775	836	900	968
130	689	744	802	862	925	992
135	716	770	827	886	948	1,014
140	740	794	850	908	970	1,034
145	762	816	871	930	990	1,053
150	783	836	891	948	1,008	1,070
155	802	854	908	965	1,024	1,085
160	819	871	924	980	1,038	1,099
165	835	886	938	993	1,051	1,111
170	849	899	951	1,005	1,062	1,121

absolute temperature, and ρ, the density in Amagat units—Continued

40	60	80	100	120	140	160	180	200
676.1×10⁻⁶	706.7×10⁻⁶	738.4×10⁻⁶	771.0×10⁻⁶	804.9×10⁻⁶	839.8×10⁻⁶	876.1×10⁻⁶	913.6×10⁻⁶	952.5×10⁻⁶
683.2	713.5	744.8	777.1	810.6	845.2	881.1	918.2	956.7
699.8	729.2	759.7	791.2	823.7	857.4	892.3	928.4	965.8
701.3	730.7	761.0	792.4	824.9	858.5	893.2	929.2	966.5
716.2	744.7	774.2	804.7	836.2	868.8	902.5	937.4	973.5
728.4	756.2	784.8	814.5	845.1	876.7	909.5	943.3	978.4
738.6	765.6	793.5	822.3	852.1	882.9	914.7	947.6	981.6
744.4	770.9	798.4	826.6	855.9	886.1	917.3	949.6	983.0
747.1	773.4	800.6	828.6	857.6	887.6	918.5	950.5	983.6
754.2	779.9	806.4	833.7	861.9	891.1	921.2	952.4	984.5
760.1	785.2	811.0	837.7	865.2	893.7	923.0	953.4	984.7
765.1	789.5	814.8	840.8	867.7	895.5	924.1	953.7	984.2
769.2	793.1	817.8	843.3	869.5	896.6	924.6	953.5	983.3
772.6	796.0	820.2	845.1	870.8	897.3	924.6	952.8	981.9
775.4	798.3	822.0	846.4	871.6	897.5	924.2	951.8	980.2
777.6	800.2	823.4	847.3	871.9	897.3	923.5	950.4	978.2
779.5	801.6	824.4	847.8	871.9	896.8	922.4	948.9	976.1
780.9	802.6	825.0	848.0	871.7	896.1	921.2	947.1	973.8
782.1	803.4	825.3	847.9	871.2	895.1	919.8	945.2	971.3
782.9	803.9	825.4	847.6	870.5	894.0	918.2	943.1	968.7

340	360	380	400	420	440	460	480	500
−461×10⁻⁶	−356×10⁻⁶	−241×10⁻⁶	−111×10⁻⁶	+29×10⁻⁶	173×10⁻⁶	321×10⁻⁶	475×10⁻⁶	639×10⁻⁶
−352	−249	−139	−15	+120	259	403	553	707
−250	−149	−42	+76	203	335	471	612	759
−157	−57	+48	162	281	404	531	664	804
−73	+27	130	240	353	468	588	715	849
+2	102	204	310	418	528	643	765	894
+68	168	270	373	478	585	697	815	939
128	228	329	431	534	640	750	864	984
183	282	382	484	587	692	800	913	1,031
234	332	431	532	635	740	848	961	1,079
355	450	547	647	752	861	973	1,089	1,210
464	556	652	751	855	963	1,075	1,191	1,312
561	651	745	842	944	1,050	1,160	1,274	1,394
644	733	824	919	1,018	1,122	1,231	1,345	1,465
715	802	892	984	1,081	1,183	1,291	1,405	1,526
776	860	948	1,039	1,134	1,234	1,340	1,454	1,576
829	911	997	1,086	1,180	1,279	1,384	1,496	1,616
875	956	1,041	1,129	1,221	1,319	1,422	1,531	1,646
916	996	1,080	1,167	1,258	1,355	1,456	1,561	1,670
953	1,032	1,115	1,201	1,291	1,387	1,486	1,587	1,693
985	1,064	1,146	1,231	1,320	1,414	1,511	1,611	1,715
1,014	1,092	1,173	1,257	1,345	1,437	1,533	1,633	1,736
1,041	1,117	1,197	1,280	1,366	1,457	1,552	1,652	1,754
1,064	1,140	1,218	1,299	1,384	1,473	1,567	1,667	1,768
1,085	1,159	1,236	1,316	1,399	1,487	1,580	1,678	1,779
1,103	1,176	1,252	1,331	1,413	1,500	1,591	1,686	1,785
1,120	1,191	1,266	1,345	1,426	1,511	1,600	1,693	1,790
1,136	1,205	1,278	1,356	1,436	1,520	1,607	1,699	1,795
1,150	1,218	1,290	1,366	1,444	1,526	1,612	1,704	1,799
1,162	1,229	1,300	1,374	1,451	1,531	1,616	1,707	1,801
1,173	1,240	1,309	1,381	1,457	1,536	1,619	1,707	1,800
1,183	1,248	1,317	1,388	1,462	1,539	1,620	1,706	1,797

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TABLE 17. *Values of $(dZ/d_\rho)_T$ at integral values of T, the absolute*

Temperature	$\rho=220$	240	260	280	300	320
180	874×10^{-6}	922×10^{-6}	972×10^{-6}	1.025×10^{-6}	$1,081\times10^{-6}$	$1,140\times10^{-6}$
190	895	943	992	1,043	1,098	1,156
200	913	961	1,009	1,060	1,113	1,169
210	929	976	1,024	1,074	1,126	1,180
220	943	989	1,037	1,086	1,137	1,190
230	956	1,001	1,048	1,096	1,146	1,198
240	967	1,011	1,057	1,104	1,154	1,205
250	976	1,020	1,065	1,111	1,160	1,211
260	984	1,027	1,072	1,117	1,165	1,215
270	991.0	1,033.1	1,076.8	1,122.1	1,169.3	1,218.3
0° C	992.9	1,034.7	1,078.2	1,123.3	1,170.2	1,219.0
280	996.6	1,038.0	1,081.0	1,125.6	1,172.0	1,220.2
25° C	1,004.5	1,044.7	1,086.4	1,129.7	1,174.7	1,221.4
300	1,005.2	1,045.3	1,086.8	1,130.0	1,174.8	1,221.4
320	1,011.0	1,049.8	1,090.1	1,131.8	1,175.1	1,220.1
340	1,014.7	1,052.3	1,091.3	1,131.7	1,173.6	1,217.1
360	1,016.9	1,053.4	1,091.2	1,130.3	1,170.9	1,212.9
100° C	1,017.6	1,053.4	1,090.4	1,128.8	1,168.5	1,209.7
380	1,017.8	1,053.2	1,089.9	1,127.9	1,167.2	1,207.9
400	1,017.8	1,052.2	1,087.8	1,124.7	1,162.9	1,202.4
420	1,017.1	1,050.6	1,085.2	1,121.0	1,158.0	1,196.4
440	1,015.8	1,048.4	1,082.1	1,116.9	1,152.9	1,190.2
460	1,014.0	1,045.8	1,078.6	1,112.6	1,147.6	1,183.8
480	1,011.9	1,042.9	1,074.9	1,108.0	1,142.1	1,177.4
500	1,009.5	1,039.8	1,071.0	1,103.3	1,136.6	1,171.0
520	1,006.9	1,036.5	1,067.0	1,098.5	1,131.0	1,164.6
540	1,004.2	1,033.1	1,062.9	1,093.7	1,125.4	1,158.2
560	1,001.2	1,029.6	1,058.7	1,088.8	1,119.9	1,151.9
580	998.2	1,026.0	1,054.6	1,084.0	1,114.4	1,145.7
600	995.1	1,022.3	1,050.3	1,079.2	1,108.9	1,139.5

temperature, and ρ, the density in Amagat units—Continued

340	360	380	400	420	440	460	480	400
$1,201\times10^{-6}$	$1,264\times10^{-6}$	$1,330\times10^{-6}$	$1,399\times10^{-6}$	$1,471\times10^{-6}$	$1,545\times10^{-6}$	$1,623\times10^{-6}$	$1,706\times10^{-6}$	$1,794\times10^{-6}$
1,215	1,276	1,341	1,408	1,478	1,550	1,626	1,707	1,792
1,227	1,287	1,350	1,416	1,484	1,550	1,629	1,708	1,790
1,237	1,296	1,358	1,422	1,489	1,559	1,632	1,708	1,788
1,246	1,304	1,365	1,428	1,493	1,561	1,633	1,708	1,787
1,253	1,310	1,370	1,432	1,496	1,562	1,633	1,708	1,786
1,259	1,315	1,373	1,434	1,497	1,563	1,633	1,706	1,783
1,264	1,319	1,376	1,436	1,498	1,563	1,631	1,702	1,778
1,267	1,321	1,378	1,436	1,497	1,561	1,628	1,697	1,771
1,269.3	1,322.4	1,377.6	1,435.2	1,495.1	1,557.6	1,622.8	1,690.8	1,761.8
1,269.7	1,322.5	1,377.4	1,434.6	1,494.2	1,556.3	1,621.1	1,688.6	1,759.1
1,270.3	1,322.4	1,376.6	1,433.1	1,491.9	1,553.2	1,617.1	1,683.7	1,753.1
1,269.9	1,320.3	1,372.8	1,427.3	1,484.1	1,543.3	1,604.8	1,669.0	1,735.8
1,269.7	1,320.0	1,372.3	1,426.6	1,483.2	1,542.2	1,603.5	1,667.4	1,734.0
1,266.8	1,315.3	1,365.7	1,418.1	1,472.5	1,529.2	1,588.1	1,649.5	1,713.4
1,262.2	1,309.0	1,357.7	1,408.2	1,460.6	1,515.1	1,571.8	1,630.8	1,692.0
1,256.6	1,301.8	1,348.8	1,397.5	1,448.0	1,500.6	1,555.1	1,611.8	1,670.7
1,252.4	1,296.7	1,342.6	1,390.2	1,439.6	1,490.9	1,544.1	1,599.4	1,656.8
1,250.2	1,293.9	1,339.3	1,386.4	1,435.2	1,485.8	1,538.4	1,593.0	1,649.7
1,243.3	1,285.6	1,329.6	1,375.1	1,422.3	1,471.2	1,521.9	1,574.6	1,629.2
1,236.1	1,277.2	1,319.7	1,363.8	1,409.4	1,456.7	1,505.8	1,556.6	1,609.3
1,228.7	1,268.6	1,309.9	1,352.6	1,396.8	1,442.6	1,490.0	1,539.2	1,590.1
1,221.3	1,260.1	1,300.1	1,341.6	1,384.5	1,428.9	1,474.8	1,522.4	1,571.6
1,213.9	1,251.6	1,290.5	1,330.8	1,372.4	1,415.5	1,460.1	1,506.2	1,553.9
1,206.5	1,243.2	1,281.1	1,320.2	1,360.7	1,402.6	1,445.8	1,490.6	1,536.9
1,199.2	1,234.9	1,271.8	1,310.0	1,349.4	1,390.1	1,432.1	1,475.6	1,520.5
1,192.0	1,226.8	1,262.8	1,300.0	1,338.4	1,378.0	1,418.9	1,461.2	1,504.8
1,184.9	1,218.9	1,254.0	1,290.3	1,327.7	1,366.3	1,406.2	1,447.3	1,489.8
1,177.9	1,211.2	1,245.5	1,280.9	1,317.4	1,355.0	1,393.9	1,434.0	1,475.4
1,171.1	1,203.6	1,237.2	1,271.7	1,307.4	1,344.1	1,382.0	1,421.2	1,461.5

Many thermodynamic equations involve derivatives in which P, V, and T are the variables of state. Applications of the tables of this paper in which the variables are Z, ρ, and T to calculations of properties involving derivatives in which the variables are P, V, and T may be facilitated by means of equations relating the P, V, T and the Z, ρ, T derivatives. The following are adequate for many ordinary uses:

$$\frac{T}{P}\left(\frac{dP}{dT}\right)_V=\frac{T}{P}\left(\frac{dP}{dT}\right)_\rho=\frac{T}{P}\left(\frac{dS}{dV}\right)_T=1+\frac{T}{Z}\left(\frac{dZ}{dT}\right)_\rho \tag{4.2}$$

$$-\frac{V}{P}\left(\frac{dP}{dV}\right)_T=\frac{\rho}{P}\left(\frac{dP}{d\rho}\right)_T=1+\frac{\rho}{Z}\left(\frac{dZ}{d\rho}\right)_T \tag{4.3}$$

$$-\frac{T}{V}\left(\frac{dV}{dT}\right)_P=\frac{T}{\rho}\left(\frac{d\rho}{dT}\right)_P=\frac{T}{V}\left(\frac{dS}{dP}\right)_T=\frac{1+\frac{T}{Z}\left(\frac{dZ}{dT}\right)_\rho}{1+\frac{\rho}{Z}\left(\frac{dZ}{d\rho}\right)_T}. \tag{4.4}$$

The Joule-Thomson coefficient μ may be utilized to illustrate the use of these formulas. Thus for purposes of calculations with the tables of this paper, the familiar equation

$$\mu=\left(\frac{dT}{dP}\right)_H=\frac{V}{C_p}\left[\frac{T}{V}\left(\frac{dV}{dT}\right)_P-1\right], \tag{4.5}$$

is put in the form

$$\mu=\left(\frac{dT}{dP}\right)_H=\frac{V_0}{\rho C_p}\left[\frac{1+\frac{T}{Z}\left(\frac{dZ}{dT}\right)_\rho}{1+\frac{\rho}{Z}\left(\frac{dZ}{d\rho}\right)_T}-1\right], \tag{4.6}$$

where V_0 is the molar volume of hydrogen at standard conditions and C_p is the molar heat capacity at the given conditions of T and P or T and ρ.

In correlating the PVT data for hydrogen the function

$$\sigma=\frac{T}{T_0}\frac{V}{V_0}\log_{10}\frac{PV}{RT} \tag{4.7}$$

was used, where T_0 is the Kelvin temperature of the ice point. Reported temperatures were reduced wherever possible to a thermodynamic scale having the ice point temperature 273.16°. All available data were considered in this work but only those appearing most reliable were used and these were weighted according to their apparent precision. The data used [59, 61, 63, 65, 66, 67, 70 to 74, 76, 79, 81, 85, 88, 91, 177] are plotted in figure 6 with the exception of a few observations at temperatures below 29° K and at densities lower than $\rho=10$, which were omitted because in these regions of low precision the scattering is so great that the points would be confusing.

A lower boundary to the σ versus ρ gas-liquid diagram in figure 6 is furnished by the vapor-liquid saturation line and the freezing curve. These are represented in figure 6 by dashed lines. The saturation line for the vapor rises steeply onto the diagram at low densities and with decreasing slope approaches tangency to the critical isotherm at the critical point which is indicated by an asterisk. The saturation line for liquid hydrogen is a nearly straight and horizontal line from a density somewhat greater than the critical to the triple point. The freezing curve, which represents the values of σ for liquid when for a given temperature the pressure is great enough to cause the liquid to freeze, rises nearly vertically from the triple point and bends towards higher densities.

The saturation curve on the vapor side was obtained with the help of the vapor pressure equation (eq 7.2) and the PVT representation given by eq 4.14 and table 19. On the liquid side it was obtained from the same vapor pressure equation and the volumes of the liquid at saturation pressure, given in table 31 and discussed in section VIII. The freezing curve was obtained from the melting point-pressure relations given in table 30 combined with extrapolations based on the higher density observations of Bartholomé for the isotherms of the liquid which are given in table 32.

The isothermal curves of figure 6 represent final table values. The curves are not necessarily the best fit for the experimental data for each individual isotherm inasmuch as the curves and table values are the result of correlating all the data and include the temperature dependence which, while it does not affect the relative position of points on one isotherm, may shift the whole isotherm somewhat. Isotherms that depended upon only a few individual observations and covered only a small range of densities were given less weight than others. For a given isotherm, data at higher densities, corresponding to larger deviations from the ideal gas law, were usually given

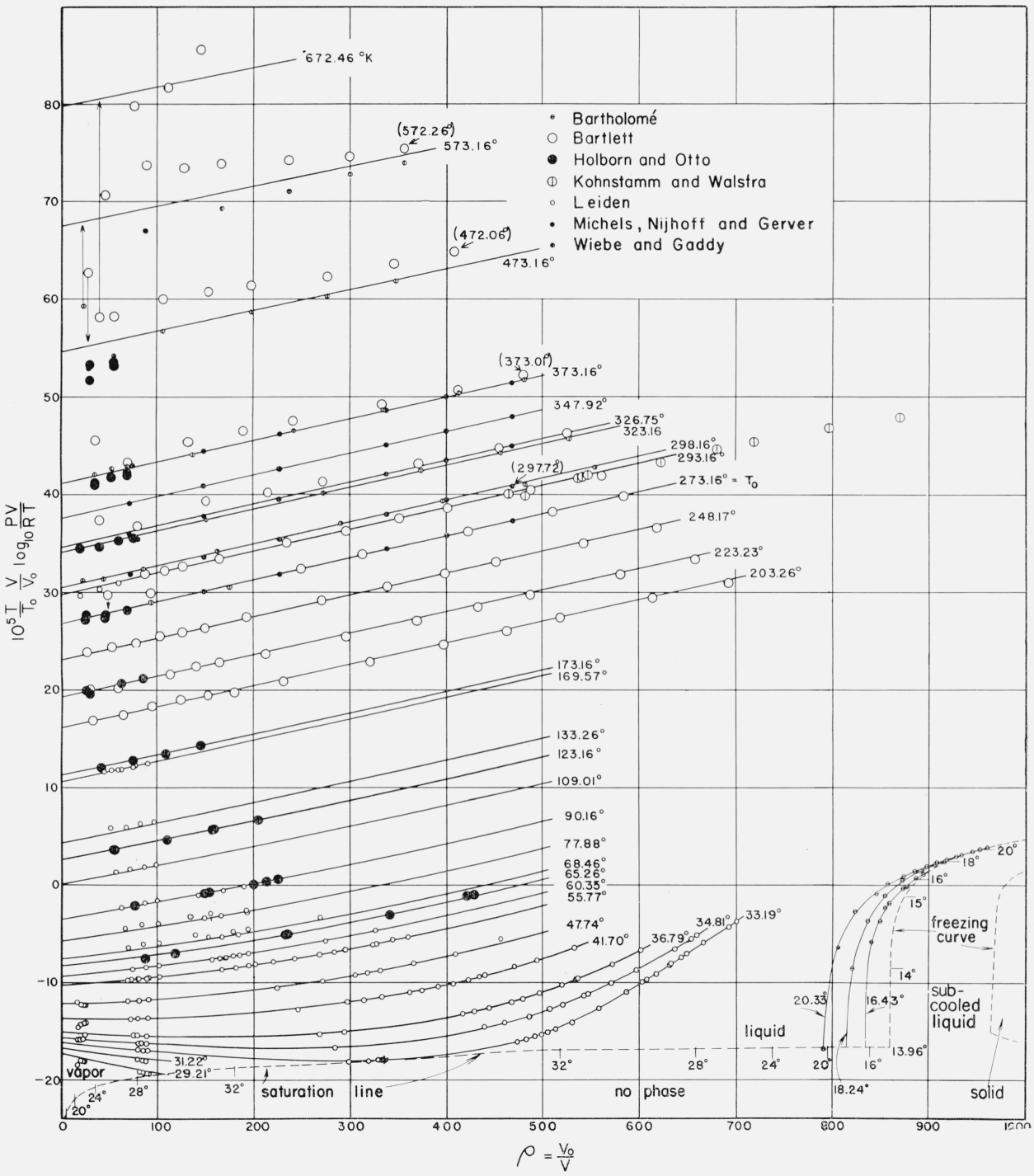

FIGURE 6. *Plot of PVT data for H_2 in the fluid states.*

greater weight than data at low densities. In fact in some instances the low density data were given zero weight. Data at the highest temperatures do not appear to be very reliable, probably because of penetration of the containers by hydrogen. At very low temperatures the deviations from the ideal gas law have not been measured very precisely because the pressure range over which

measurements can be made is limited by condensation.

Cragoe has shown that for densities up to $\rho=500$ the 0° C isotherm is fitted to within experimental accuracy by the equation $\sigma=b+c\rho$. Figure 6 shows that, although this linear relation between σ and ρ fails at low temperatures, it is valid within experimental error over a considerable range of temperatures above 200° K. This relation was made the basis for the correlation of the PVT data above 0° C. The different method used for correlating the data below 0° C is described under (b).

(a) Region Above 0° C

Above 0° C, equations of the form $\sigma=b+c\rho$ were fitted to the PVT data plotted in figure 6, and b and c, the intercept and slope of an isothermal line, were determined as functions of T. The quantity $Z=PV/RT$ thus obtained as a function of T and ρ,

$$PV/RT=\exp 2.30259\,\frac{T_0}{T}\,[b(T)\rho+c(T)\rho^2]=$$
$$\exp\,[B(T)\rho+C(T)\rho^2], \qquad (4.8)$$

was used for the calculation of the tables of Z, P, $(dZ/d\rho)_T$, $(dZ/dT)_\rho$, and $(d^2Z/dT^2)_\rho$.

Before fitting functions of T to b and c, small corrections were applied to some of the data. A constant error in T and constant factor errors along an isotherm in P, V, and the number of moles of gas, cause deviations from the true isotherm that are very nearly proportional to $1/\rho$. Such hyperbolic deviations from a straight line are most easily detected in data extending from low to high densities. A change in V by 0.2 percent is sufficient to considerably straighten the 573.16° K (300° C) isotherm of Wiebe and Gaddy, and raise the line drawn through their adjusted data so that it intersects the σ axis of figure 6 only 0.7 unit below the table line for 573.16° K and crosses the table line at $\rho=550$. Wiebe and Gaddy call attention in their paper to an estimated error of 0.05 to 0.10 percent in the volume of their high pressure steel pipette at 200° and 300° C. It would seem that some part of the 0.2-percent adjustment, which straightens the 300° C isotherm of Wiebe and Gaddy, might be attributed to small temperature and pressure errors and to some loss of hydrogen in the steel.

Hyperbolic adjustments proportional to $1/\rho$ of Bartlett's higher temperature data straighten the isotherms and improve their agreement with the lines representing the tables. A comparison of the observations of Michels, Nijhoff, and Gerver [79] at different temperatures for nearly constant values of ρ, revealed apparent small hyperbolic trends of the data for the separate isotherms superposed on one larger though small random pattern of scattering common to all their isotherms. Using their 0° C isotherm as a reference line, their other data were adjusted to remove the hyperbolic deviations. The points of figure 6 represent reported data adjusted only to the Kelvin scale having 273.16° at the ice point.

Least square determinations were made of the straight lines fitting the adjusted σ versus ρ isothermal data for the different observers separately. From these, values of intercept b and slope c were obtained for the different observers at each temperature of measurement. Holborn's data above 0° C, however, were used only for obtaining intercepts, the slopes of adjacent isotherms of other observers being used with his data.

Expanding the exponential of eq 4.8,

$$PV/RT=1+B\rho+[(1/2)B^2+C]\rho^2+[(1/6)B^3+BC]\rho^3$$
$$+[(1/24)B^4+(1/2)C^2+(1/2)B^2C]\rho^4+\ldots \qquad (4.9)$$

shows that $B\ (T)$ is the second virial coefficient and that a correlation of intercepts b of σ-isotherms is essentially a correlation of values of the second virial coefficients of hydrogen. Formulas expressing the dependence of the second virial coefficient on temperature have been derived theoretically on the assumption of simple laws of intermolecular forces. One of the most satisfactory formulas is based on a law of intermolecular force of the form $\lambda_n r^{-n}-\lambda_m r^{-m}$ and is due to Lennard-Jones. For $n=13$ and $m=7$, the Lennard-Jones formula for B is

$$B=B_1T^{-1/4}+B_2T^{-3/4}+B_3T^{-5/4}+\ldots, \qquad (4.10)$$

where all the coefficients B_i of this infinite series are determined by λ_n and λ_m. Following essentially a procedure used successfully by F. G. Keyes [89], we used only the first three terms of this series and selected values for B_1, B_2, and B_3 which resulted in the best fit of a three constant equation with the intercepts of the σ-isotherms. Our formula,

$$B=0.0055478T^{-1/4}-0.036877T^{-3/4}-0.22004T^{-5/4}, \qquad (4.11)$$

intended for use above 0° C, passes through the intercept of the −50° C isotherm determined by the correlation below 0° C.

The slopes of the σ-isotherms were represented by a two term empirical formula without theoretical justification, except that it involves powers of T which make C go to zero as T grows very large.

$$C=0.004788T^{-3/2}-0.04053T^{-2}. \qquad (4.12)$$

The exponents of T were chosen so as to simplify the temperature function coefficients in the power series in ρ of eq 4.9.

The tables from 270° to 600° K have been computed on the basis of these formulas, and in this temperature range the various derivatives tabulated have been calculated analytically.

It was not until considerably after the preparation of the tables on hydrogen that we were able to examine the data of Michels and Goudeket published in Physica 1941 [91]. Values of σ for these data on H_2 are shown as solid circles in figure 7 with the tables represented by the solid straight lines. The agreement for H_2 is not complete but seems fairly satisfactory at moderate densities. At low densities there are discrepancies, roughly hyperbolic, which have the appearance of the hyperbolic deviations resulting from small systematic errors discussed earlier in this section. If the hyperbolic deviation is attributed to a systematic error in the volume, the error amounts to 0.06 percent for the 100° C isotherm, and for the other isotherms it is of this approximate magnitude or smaller. At low densities the deviation for the 0° C isotherm does not appear to be systematic. On the other hand, it will be seen that there is a systematic deviation at densities greater than 500 with the experimental values for σ less than those obtained by linear extrapolation from the intermediate densities. This trend is supported by the high pressure data of Kohnstamm and Walstra [61, 81], also shown in the figure. If the representation of the σ isotherm by an equation is extended beyond $\rho=500$, it will be necessary to include a small quadratic term in the expression for σ.

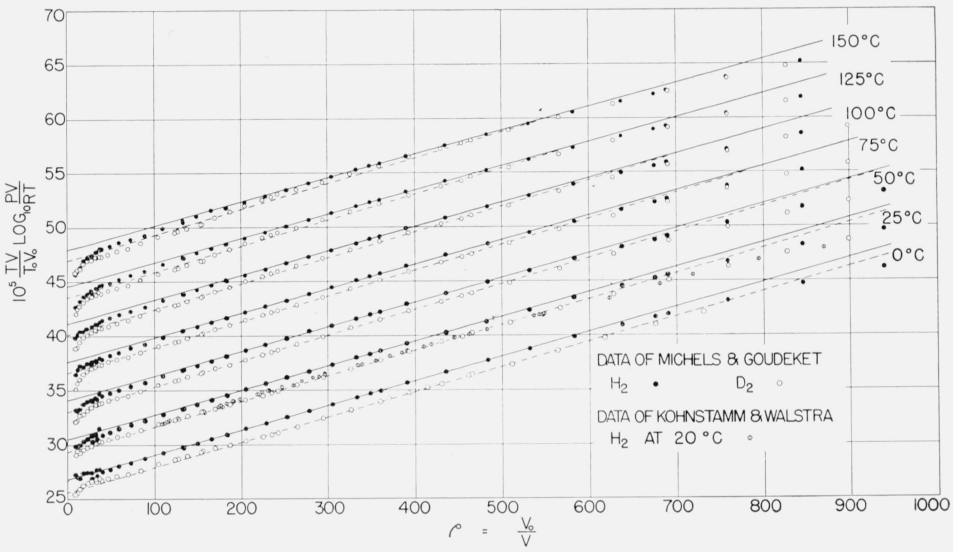

FIGURE 7. *A plot of part of the PVT data for* H_2 and D_2 *from* 0° *C to* 150° *C.*

(b) Region Below 0° C

At low temperatures the σ versus ρ isotherms are curved; making it difficult to decide how the isotherm should be drawn at low densities where the data were meager and the precision was low. Another function, $T^{3/2}V/V_0\left(1-\frac{PV}{RT}\right)$, plotted against $\rho=V_0/V$ as abscissa gave lines which appeared to be straight at low densities for temperatures below 56°K, though there is considerable curvature at high densities. In figure 8, $T^{3/2}V/V_0\left(1-\frac{PV}{RT}\right)+0.0006\rho=\psi$ is plotted against ρ, the term 0.0006ρ being added to make isotherms nearly horizontal at low densities and thus increase the scale of the plot. The sensitivity to

small changes of PV/RT at $\rho=200$ and $T=55°$ K is 18 times greater in figure 8 than in figure 6 and 14 times greater at $\rho=200$ and $T=33°$ K. The curves of figure 8 were drawn to fit the data for each particular isothern considered independently, and though the curves do not represent the tables exactly they agree closely with them. Below 31°K the data were not sufficient and precise enough to determine consistent isothermal curves when the isotherms were considered independently. The data lower than 29°K were not plotted because the double valued nature of ψ causes the data below 29° K to fall in the same region on the diagram as is covered by the data above 29° K.

At first it appeared that the critical isotherm in figure 8 could be represented by a straight line from ρ equal to zero to ρ greater than the critical density. However, the conditions that $(dP/dV)_T$ and $(d^2P/dV^2)_T$ be zero at the critical point impose upon the slope and curvature of the isotherm at the critical point the conditions

$$\left.\begin{aligned}\left(\frac{d\psi}{d\rho}\right)_{T_c}&=\frac{T_c^{3/2}}{\rho_c^2}\left(2\,\frac{P_cV_c}{RT_c}-1\right)+0.0006,\\ \left(\frac{d^2\psi}{d\rho^2}\right)_{T_c}&=\frac{2T_c^{3/2}}{\rho_c^3}\left(1-3\,\frac{P_cV_c}{RT_c}\right).\end{aligned}\right\}\qquad(4.13)$$

In addition, values for the critical temperature and pressure should satisfy the vapor-pressure equation.

Only a single determination has been made of the critical temperature and pressure of hydrogen [62]. The critical isotherm was located somewhere between the 2 measured isotherms at 32.94°[7] and 33.29° K, and was at the time (1917) considered to be 33.19° K with a certainty of about 0.1°, though in 1925 it was stated in a footnote to Leiden Communication 172a that T_c should be about 0.1° lower. The critical pressure inferred from the P versus V isotherms in 1917 was 12.80 atm. Later in 1917 [142] the vapor pressure equation of H_2 above the boiling point was determined and the value 12.75 atm deduced for P_c using $T_c=33.18°$ K (on basis of $T_0=273.09$). Two determinations [62] were made of the critical density based on the extrapolation of the rectilinear diameter. These gave $\rho_c=345$. The values reported in later Leiden Communications have not in all cases been the latest determined values. The most recently reported Leiden values [69] are

[7] Unless otherwise stated, temperatures are expressed on the Kelvin Scale with $T_0=273.16°$.

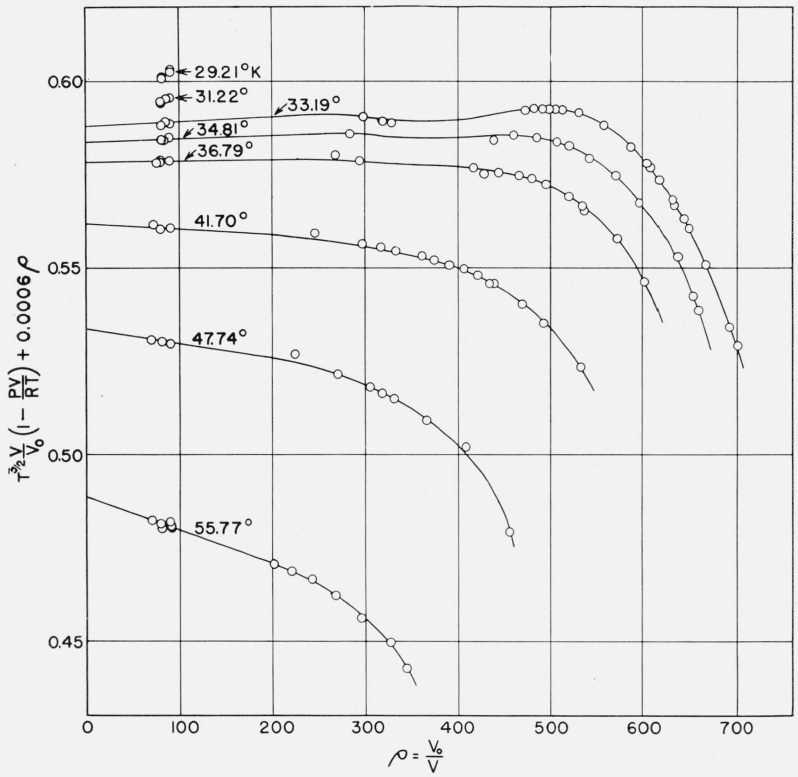

FIGURE 8. *Plot of PVT data for* H_2 *at low temperatures.*

T_c=33.19° K (on basis of T_0=273.16), P_c=12.751 atm and $1/\rho_c$=0.02909 or ρ_c=344. The lower critical temperature 33.1° K inferred from Leiden Communication 172a is supported by the agreement of the vapor pressure 12.81 atm, calculated from vapor pressure equation (eq 7.2) with the critical pressure determined in 1917 from the P versus V isotherms.

Difficulties are encountered in obtaining agreement with the experimental PVT data (fig. 8) on the basis of T_c=33.1° and P_c=12.81 atm, however, unless the critical density is inferred to be about 320, in Amagat units, instead of the reported values 345 or 344. This difference in critical density seemed too large on the basis of the probable precision of the density measurements The adjustment has instead been so made and the critical isotherm in figure 8 so drawn that T_c= 33.19°, P_c=12.98 atm, and ρ_c=335. This value of P_c is consistent with the PVT data and with vapor pressure equation (7.2). These critical constants are listed in table 18.

TABLE 18. *Critical constants of hydrogen*

T_c	P_c	$\rho_c=\frac{V_0}{V_c}$	V_c	$\frac{P_cV_c}{RT_c}$
°K	atm		cm^3mole^{-1}	
33.19	12.98	335	66.95	0.3191

It seemed reasonable to assume that the isotherms of figure 8 are straight lines up to ρ=200. This assumption was used in correlating the observed data below the critical temperature where the data were scarce and the precision low. In figure 9 the intercepts A and the slopes C' of the isotherms of figure 8 are plotted as functions of the temperature. The curve for the slope was extrapolated smoothly to lower temperatures as slopes could not be obtained from the data below 33° K.

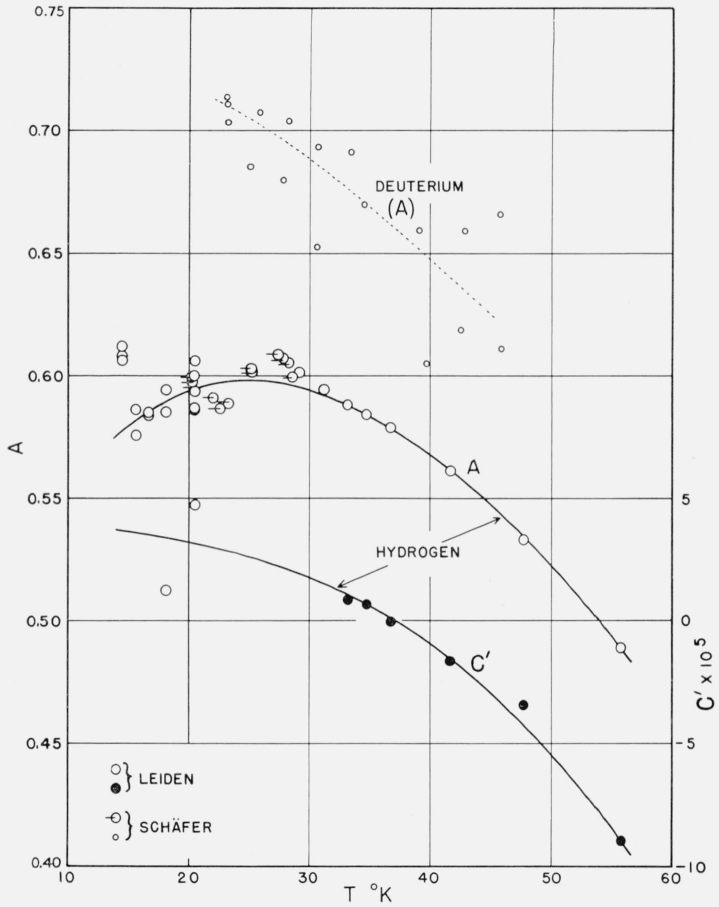

FIGURE 9. *Intercepts and slopes from figure 8.*

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Also shown in figure 9 are values for A calculated from second virial coefficients determined experimentally by Schäfer [85]. Schäfer reported the results of his PVT measurements as virial coefficients $B'(T)=d(PV/RT)/dP$ at constant temperature and at $P=0$. The values of $A=-(RT^{5/2}/V_0)B'(T)$ obtained from Schäfer's results agree well with those obtained from data of the Leiden Laboratory as shown by figure 9. Schäfer observed no consistent difference between the second virial coefficients of para hydrogen, normal hydrogen, and a one to one mixture of ortho and para varieties.

The equation for the straight part of the ψ-isotherms of figure 8 may be written

$$\frac{T^{3/2}}{\rho}\left(1-\frac{PV}{RT}\right)=A+C\rho, \qquad (4.14)$$

where $C=C'-0.0006$, C' being the slopes plotted in figure 9 of the ψ-isotherms in figure 8. Values of A and C and their derivatives are given for hydrogen in table 19. The values of PV/RT from $\rho=0$ to $\rho=200$ and from $T=14°$ to $T=56°$ K in table 13 were calculated using eq 4.14 with table 19. Table 20, giving the pressure, density, and value of PV/RT for saturated H_2 vapor, was prepared similarly using the vapor pressure equation for n-H_2 (eq 7.2). For certain uses eq 4.14 with table 19 may be more convenient than the tables of PV/RT and its derivatives.

TABLE 19. *Hydrogen values of A and C (and derivatives) in the equation for isotherms*

$$T^{3/2}\frac{V}{V_0}\left(1-\frac{PV}{RT}\right)=A+C\rho$$

[Applicable at Amagat densities less than 200]

T	A	C	dA/dT	dC/dT
° K	° $K^{3/2}$	° $K^{3/2}$	° $K^{1/2}$	° $K^{1/2}$
14	0.5754	$-5,621\times10^{-7}$	0.00388	-75×10^{-8}
16	.5827	−5,636	.00330	−82
18	.5887	−5,653	.00264	−90
20	.5933	−5,672	.00192	−100
22	.5965	−5,693	.00116	−112
24	.5981	−5,716	.00040	−127
26	.5981	−5,743	−.00032	−145
28	.5966	−5,774	−.00097	−165
30	.5940	−5,809	−.00154	−187
32	.5904	−5,848	−.00202	−213
34	.5858	−5,892	−.00243	−245
36	.5805	−5,943	−.00280	−282
38	.5746	−6,003	−.00317	−320
40	.5679	−6,071	−.00356	−358
42	.5604	−6,146	−.00397	−396
44	.5521	−6,229	−.00438	−436
46	.5429	−6,320	−.00476	−478
48	.5330	−6,420	−.00509	−522
50	.5225	−6,529	−.00540	−565
52	.5114	−5,646	−.00572	−603
54	.4996	−6,770	−.00608	−636
56	.4871	−6,900	−.00650	−664

TABLE 20. *Pressure, density, and PV/RT for saturated* H_2 *vapor*

T	P	ρ	PV/RT
° K	*atm*	*Amagats*	
14	0.0728	1.445	0.98415
16	.2018	3.562	.96768
18	.4551	7.321	.94396
20	.8891	13.311	.91283
22	1.5645	22.235	.87420
24	2.5453	35.017	.82783
26	3.8986	53.02	.77298
28	5.695	78.55	.70776
30	8.010	116.33	.62732
32	10.933	180.94	.51554
33.19	12.98	335	.3191

For temperatures below 56° K and densities greater than $\rho=200$ where ψ could not be represented by a simple function of ρ, a table was made of values of ψ for each ρ and T entry in the Z-table. The ψ-values of this table were obtained from figure 8 by graphical interpolation. Large plots of ψ-isochores, 20 Amagat units apart, on ψ versus T graphs were made of values of ψ read from figure 8. Values of ψ at 2-degree intervals were read from the isochores. A $Z(\rho,T)$ table was calculated from the $\psi(\rho,T)$ table.

From 56° to 273° K, the σ-function rather than the ψ-function was used because above 56° K the σ-isotherms approach linear functions of the density. The method of graphical interpolation used below 56° K was used above, also, to obtain a table of σ-values for the ρ and T entries of the Z-table. The accuracy of graphical interpolation was improved by using more sensitive plots than figure 6 of modified σ-functions obtained by adding to σ simple functions of T and ρ, which brought the isotherms and isochores closer together so that they could be easily plotted to a large scale. Values of σ were obtained at densities as high as $\rho=500$, although between 70° and 200° K measurements were not available at densities this high. This region was filled in by extrapolation of σ-curves to higher densities along isotherms and by interpolation along isochores between the upper

and lower temperature regions where there were data to determine the trend. From the $\sigma(\rho,T)$ table a $Z(\rho,T)$ table was obtained by calculation.

The $Z(\rho,T)$ table obtained through graphical interpolation of the ψ and σ isotherms as has just been described was smoothed along isotherms and along isochores by inspection of second differences. In general the Z-tables are smooth to one unit in the last digit.

The tables of $(dZ/dT)_\rho$ and $(dZ/d\rho)_T$ below 0° C were for the most part calculated from the smoothed Z table by the method of Rutledge [179] for the calculation of derivatives from smooth sets of tabular values of data.[8] In the region below 56° K and $\rho=200$, where the ψ versus ρ isotherms are straight lines, the following equations, obtained by differentiating eq 4.14, were used with table 19 to calculate the derivatives

$$\left(\frac{dZ}{dT}\right)_\rho=\frac{3}{2}\frac{(1-Z)}{T}-\frac{\rho}{T^{3/2}}\frac{dA}{dT}-\frac{\rho^2}{T^{3/2}}\frac{dC}{dT} \quad (4.15)$$

$$\left(\frac{dZ}{d\rho}\right)_T=-\frac{1}{T^{3/2}}[A+2(C'-0.0006)\rho]. \quad (4.16)$$

Where the derivatives could be obtained both by the method of Rutledge and by eq 4.15 and 4.16, the agreement was very satisfactory. The $(dZ/d\rho)_T$ and $(dZ/dT)_\rho$ tables were also smoothed along isotherms and isochores by inspection of second differences.

The $(d^2Z/dT^2)_\rho$ table below 0° C was obtained throughout by the method of Rutledge from the smoothed $(dZ/dT)_\rho$ table and was also smoothed. The equation for $(d^2Z/dT^2)_\rho$ corresponding to eq 4.15 for the first derivative was considered too involved for easy computation.

In general, the tables of derivatives are smooth to the last digit recorded.

(c) Reliability of Tables of PVT Data

By inspecting figures 6 to 8 it is possible to arrive at some general conclusions regarding the deviations of the observed data from the $Z(\rho,T)$ table. It may be noted that, except at low densities, the deviations of the observational values of σ from the curves representing the table are of about the same magnitude at different densities along a given isotherm up to $\rho=500$.[9] This means that deviations of $(PV/RT)-1$ along an isotherm are approximately proportional to the density. At low densities the deviations are large because the sensitivity of the σ and ψ plots approaches infinity as ρ approaches zero. It is difficult to make an estimate of the probable error in PV/RT based on the deviations because, as is seen, the greatest deviations are the systematic differences between the results of different observers and are not accidental errors as should be the case if error theory were to apply. The user of the tables can make an estimate of the mean difference between the observed and tabulated values of PV/RT, in any particular region of temperature and density by noting the deviations shown on the graph and from these calculating the corresponding deviations in PV/RT. For temperatures below 60° K it would be best to use figure 8 for this purpose as it is plotted to a larger scale than is figure 6.

In constructing the tables for the intermediate temperature regions where analytical equations of state were not used, just enough digits were retained so that changes made in smoothing would be confined to the last digit. As a considerable amount of smoothing resulted from the graphical methods used, many of the irregularities in the measured values were not apparent in the unsmoothed tables.

It is believed that throughout the table the values were carried out to at least as many significant figures as were at all justified by the data, and that the last digit recorded should be considered very uncertain. In that part of the table between 77° and 200° K which was filled in by interpolation and extrapolation the last two digits should be considered uncertain, the last recorded digit being retained to achieve continuity with the rest of the table.

The tables are thought to be most reliable for temperatures between 273° and 373° K (0° and 100° C), because at these temperatures the experimental difficulties encountered are not as great as at higher and lower temperatures. Also, as is shown by figure 6 the results of several different investigators are in agreement at these temperatures. Above 373° K the experimental data are not as self-consistent as at temperatures immediately below. As the values of PV/RT given in the tables for these higher temperatures are derived largely from an extrapolation based on the temperature region between 273° and 373° K,

[8] Assuming that differences of higher order than the fourth are negligible.

[9] For still greater densities larger deviations occur as shown by figure 7.

an estimate of reliability of the high temperature portion of the tables involves both the applicability of the correlating function, eq 4.8, and the precision of the experimental data. Considering the differences between the isothermal lines determined by different sets of experimental data of different observers and the same observer at different temperatures, it seems probable that the extrapolation is more reliable than the experimental data at temperatures above 473° K.

It is doubted that PV/RT is known to better than 0.2 percent for densities as high as 100 Amagats near 33° K, the critical temperature.

Below the critical temperature, the data are not very satisfactory. In addition to the difficulties of making measurements at low temperatures, there exists the circumstance that below the critical temperature the range of vapor densities that can be covered is limited by the density of saturated vapor. At low densities the deviations $(1-Z)$ from the ideal gas law are small and hence difficult to measure precisely.

There is another method of obtaining values of second virial coefficients which may be advantageous for the low temperature region. It involves the determination of the velocity of sound, which has been carried out for gaseous hydrogen at liquid-hydrogen temperatures and various pressures by van Itterbeek and Keesom [77], using a resonance method. The change of the velocity of sound with pressure at very low pressures is related to the value of the second virial coefficient and to its first and second derivatives. Because of this relationship, it is possible to determine the second virial coefficient from the velocity of sound if the second virial coefficient is already known in an adjacent range of temperature. Van Itterbeek and Keesom concluded that the agreement between their own measurements and the PVT data was "rather good", although for both types of data the scattering was quite appreciable.

In calculating the tables of derivatives by the method of Rutledge, the criterion for retaining significant figures in the recorded values was the same as that previously mentioned, namely, enough places were carried so that the changes resulting from the smoothing were in general confined to the last digit. As in the case of the tables of PV/RT, it is believed that the tabulated values of the derivatives are given to as many significant figures as are justified by the data.

2. Deuterium

The interesting features of the PVT data for deuterium are most evident when deuterium is compared with hydrogen. The difference between the second virial coefficients of H_2 and D_2 has been investigated theoretically [86, 87], though a complete treatment of the problem has not been made.

Assuming the same intermolecular forces for H_2 and D_2, classical mechanics and statistics lead to the same equation of state for H_2 and D_2. The quantum theory of virial coefficients leads to effective volumes of molecules and to second virial coefficients that are larger than the classical values, the differences being small at ordinary temperatures but becoming large at low temperatures.[10]

In table 21 are given ratios between quantum mechanical and classical values of second virial coefficients, for gases whose molecules are rigid nonattracting spheres. They may also be considered as ratios between apparent molecular volumes for the two treatments. These ratios are based on formulas derived by Uhlenbeck and Beth [84]. Columns 2 and 3 are for gases with molecular weights 2 and 4, respectively. The value of the ratio depends, among other things, upon the diameters of the rigid spheres. Here the size of the spheres was taken to be the same for the two

TABLE 21. *Ratio between quantum mechanical and classical second virial coefficients for nonattracting rigid spherical molecules* [a] *of molecular weight M*

T	$\frac{B \text{ quantum}}{B \text{ classical}}$ for $M=2$	$\frac{B \text{ quantum}}{B \text{ classical}}$ for $M=4$
°K		
600	1.21	1.15
300	1.30	1.21
100	1.52	1.37
25	2.7	2.0
5	4.6	2.6

[a] With diameters calculated from the van der Waals' b for hydrogen.

[10] The application of quantum mechanics instead of ordinary mechanics has as one effect for rigid spherical molecules the removal of the classical discontinuity in the calculated distribution of molecules for pair separations corresponding to contact between the spheres. As smaller separations are prevented by the impenetrability of the spheres, the continuity is established by a reduction of the molecular density for separations greater than that corresponding to contact. The effect is large for separations of sphere surfaces up to a considerable fraction of the de Broglie wavelength (for which $h/\sqrt{2mkT}$ is a representative value) and depends through this upon the temperature. This reduction of molecular density beyond the minimum separation could be represented roughly in a classical description as an increase of the volume from which 1 molecule causes the centers of other molecules to be excluded. In classical theory the second virial coefficient for nonattracting rigid spheres is proportional to the excluded volume.

gases and to be equal to the size calculated from the van der Waals b for H_2.

Although it would scarcely be expected that the results of calculations for rigid nonattracting spheres would apply to real H_2 and D_2 molecules, it would seem likely that qualitative indications would be correct, at least at higher temperatures where the excluded volume predominates over the intermolecular attractive forces in determining the magnitude of the second virial coefficient. This is borne out by experiment, the difference in second virial coefficients $(B_{H_2}-B_{D_2})$, being positive, though smaller than would be indicated by table 21 for rigid spheres by a factor of about 2.6 at 300° K. Uhlenbeck and Beth derived an approximate quantum mechanical representation for the second virial coefficient applicable at high

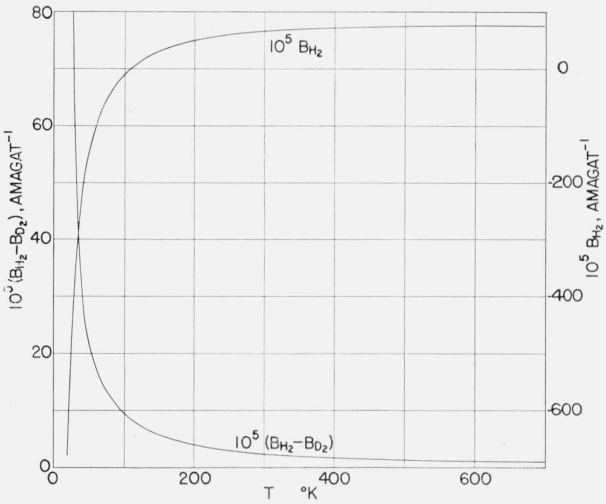

FIGURE 10. *Second virial coefficient for* H_2 *and the difference between second virial coefficients for* H_2 *and* D_2.

temperatures for molecules with radially symmetrical force fields. Their formulas were applied to hydrogen and deuterium by de Boer and Michels [87] upon the assumption that the intermolecular forces were the same for H_2 and D_2. They obtained differences between the virial coefficients for H_2 and D_2 represented by the upper temperature portion of one of the curves of figure 10. In a later paper by Michels and Goudeket [92] attention was called to the fact that the intermolecular forces of hydrogen and deuterium do differ a little because the mean internuclear separations of H_2 and D_2 molecules are different as a result of the different zero point vibrations of their nuclei.

The effect of the intermolecular attractive forces overbalances the effect of the excluded volume or the repulsive forces of the molecules in determining the magnitude of the second virial coefficient at low temperatures, and makes the coefficient negative. Nevertheless, at low temperatures, as at high temperatures, the difference in second virial coefficients $B_{H_2}-B_{D_2}$ is positive, partly for the reason already discussed in the case of high temperatures, namely the larger apparent quantum-mechanical volume of H_2 molecules, and partly for another reason. There is a closer spacing of the discrete negative energy states and smaller zero point energy for pairs of D_2 molecules than for pairs of H_2 molecules because of the mass difference, so that by reason of the Boltzmann factor, exp $[-\text{energy}/kT]$, there is a greater degree of association or clustering together of D_2 molecules than of H_2 molecules. Without a consideration of the Boltzmann factors for these negative energy levels the effect of the difference of mass would be less clear, as the quantum treatment for the continuum would require that the spacing of the levels there be smaller for D_2 than for H_2 in essentially the same ratio as in the case of the discrete negative energy levels. With these or similar ideas in mind, Schäfer [86] derived a formula for the difference in second virial coefficients for H_2 and D_2 at low temperatures, which involved a constant whose magnitude he so chose as to obtain a fit with his experimental values for the difference in the second virial coefficients.

Figure 9 shows values of A in the equation of state (eq 4.14) calculated from the second virial coefficients of deuterium for the temperature range 23° to 45° determined experimentally by Schäfer [85].

$$A=-T^{3/2}(dZ/d\rho)_{T,\rho=0}=-T^{3/2}B_1, \qquad (4.17)$$

where B_1 is the second virial coefficient in the equation of state $PV=RT\ (1+B_1\rho+B_2\rho^2+\ldots)$. The dashed line curve in figure 9 was obtained by adding to the A's for H_2 the differences between the A's calculated from the differences between the second virial coefficients of H_2 and D_2 which Schäfer determined partly theoretically and partly empirically. Schäfer's measurements were made on deuterium at low densities and hence do not give information on higher virial coefficients. Approximate values of PV for deuterium at low

temperatures may be found by using values of A from figure 9 in eq 4.14, and either neglecting the C term or preferably using the corresponding value of C for H_2.

Values of the function $\sigma=(TV/T_0V_0)\log_{10}(PV/RT)$ calculated from the data of Michels and Goudeket [92] for D_2 are shown as open circles in figure 7. The dashed straight lines for deuterium are obtainable from the equation

$$PV/RT=\exp[B(T)\rho+C(T)\rho^2], \qquad (4.18)$$

where

$$B(T)=0.0055298T^{-1/4}-0.036040T^{-3/4}-0.25878T^{-5/4}$$

and

$$C(T)=0.00580T^{-3/2}-0.0565T^{-2}.$$

The constants in the formula for B have been so chosen that the difference between D_2 and H_2 intercepts on the σ—axis is in close agreement with the theoretical result of de Boer and Michels [87] from 250° to 450° K.

In figure 10, a curve marked $10^5(B_{H_2}-B_{D_2})$ shows the trend of differences between second virial coefficients based on the theoretical calculations above 150° K and on the results of Schäfer below 50° K with an interpolation between. It may be inferred that the differences between the PVT data for H_2 and D_2 decrease rather rapidly with increase of temperature. For comparison, the curve marked $10^5\ B_{H_2}$, in figure 10, shows on a different scale the magnitude of the corresponding second virial coefficient for H_2 at the same temperatures.

If it is assumed that the σ or $(TV/T_0V_0)\log(PV/RT)$ isotherms for D_2 and H_2 are parallel, values of PV/RT for D_2 may be obtained from those tabulated for H_2 by (1) calculating the σ_{H_2} or σ for H_2, from the values of PV/RT, T and ρ, (2) subtracting the difference $(\sigma_{H_2}-\sigma_{D_2})_{\rho=0}$ to get σ_{D_2}, and then (3) calculating the corresponding value of PV/RT for D_2. A plot of the difference $10^5\ (\sigma_{H_2}-\sigma_{D_2})_{\rho=0}$ which may be used for this purpose is shown in figure 11. An alternative method based on the assumption that only the second term of the series expansion eq 4.9 for PV/RT is to be changed is as follows. $10^5\ (B_{H_2}-B_{D_2})$, obtained from figure 11 by multiplying $10^5\ (\sigma_{H_2}-\sigma_{D_2})_{\rho=0}$ by 2.302585 T_0/T or obtained directly from figure 10, is multiplied by 10^{-5} and the product subtracted from PV/RT for H_2 to give PV/RT for D_2. This alternative method is simpler than the other method and may be as reliable.

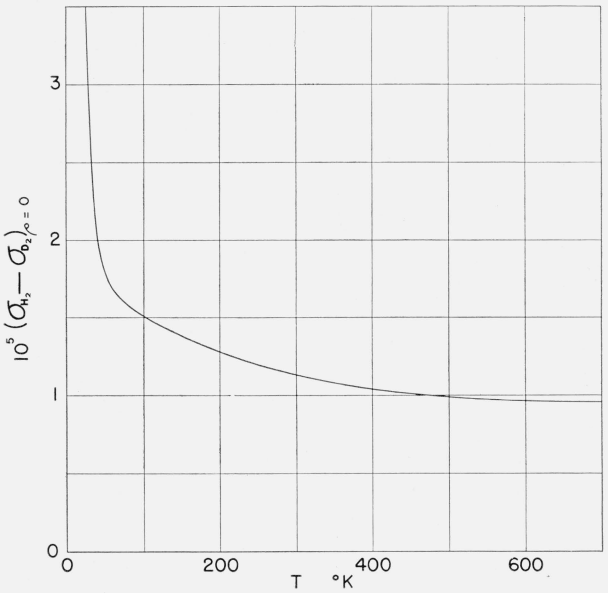

FIGURE 11. *Difference between intercepts of σ versus ρ isotherms for H_2 and D_2.*

V. Calculation of Thermal Properties of the Real Gas

The calculation of thermodynamic properties of a real gas from values of these properties for the ideal gas rests upon the principle that the difference between values of a thermodynamic function at different densities for the same temperature may be determined from data of state for the gas at the given temperature.

The entropy and free energy of a gas are dependent upon the pressure, even in the ideal state, and in tables 4 to 8 they are given for the hydrogens in the ideal gas state at a pressure of 1 standard atm. On the other hand, the internal energy, enthalpy, and specific heat in the ideal gas state are independent of density at constant temperature.

Equations 5.1 to 5.8 show how, using the data of state expressed in the form, $Z=Z(\rho,\ T)$, the thermodynamic properties of the real gas at a temperature T and an Amagat density ρ may be calculated from properties for the ideal gas state

at a pressure of 1 atm, given for the hydrogens in tables 4 to 8.

$$\frac{S_{\rho,\,T\,(\text{real gas})}}{R}=\frac{S^{\circ}_{P=1,\,T\,(\text{ideal})}}{R}+\ln\frac{P_0V_0}{RT_0}-\ln\frac{T}{T_0}-\ln\rho-\int_0^{\rho}[(Z-1)/\rho]d\rho-\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho \tag{5.1}$$

This can be expressed in a slightly different form by using the identity

$$\int_0^{\rho}[(Z-1)/\rho]d\rho+\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho=\left(d\left\{T\int_0^{\rho}[(Z-1)/\rho]d\rho\right\}/dT\right). \tag{5.2}$$

$$\frac{H_{\rho,\,T\,(\text{real gas})}}{RT}=\frac{H^{\circ}_{T\,(\text{ideal})}}{RT}-\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho+(Z-1). \tag{5.3}$$

$$\frac{F_{\rho,\,T\,(\text{real gas})}}{RT}=\frac{F^{\circ}_{P=1,\,T\,(\text{ideal})}}{RT}-\ln\frac{P_0V_0}{RT_0}+\ln\frac{T}{T_0}+\ln\rho+\int_0^{\rho}[(Z-1)/\rho]d\rho+(Z-1). \tag{5.4}$$

$$\ln\,[f\,(\text{fugacity of real gas})/P]=\int_0^{\rho}(Z-1)/\rho]d\rho-\ln Z+(Z-1). \tag{5.5}$$

$$\frac{E_{\rho,\,T\,(\text{real gas})}}{RT}=\frac{E^{\circ}_{T\,(\text{ideal})}}{RT}-[T(dZ/dT)_{\rho}/\rho]d\rho. \tag{5.6}$$

$$\frac{(C_v)_{\rho,\,T\,(\text{real gas})}}{R}=\frac{(C^{\circ}_v)_{T\,(\text{ideal})}}{R}-2\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho-\int_0^{\rho}[T^2(d^2Z/dT^2)_{\rho}/\rho]d\rho. \tag{5.7}$$

$$\left.\begin{aligned}&\frac{(C_P)_{\rho,\,T\,(\text{real gas})}}{R}=\frac{(C^{\circ}_P)_{T\,(\text{ideal})}}{R}-\\&2\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho-\int_0^{\rho}[T^2(d^2Z/dT^2)_{\rho}/\rho]\,d\rho+\\&\{[Z+T(dZ/dT)_{\rho}]^2/[Z+\rho(dZ/d\rho)_T]\}-1.\end{aligned}\right\} \tag{5.8}$$

In order to facilitate the calculation of the thermodynamic properties of hydrogen in the real gas state, tables 22 and 23 were computed.[11] Lagrangian four point formulas [181] were used for the tabular integrations.

Table 22 is intended for use in the calculation of entropies. The values in the second column, headed $(S^{\circ}_{p=1}-S^{\circ}_{p=1})/R$, are for the difference between entropies of hydrogen in the ideal gas state at 1-atm pressure and at unit Amagat density, divided by R.

$$\frac{S^{\circ}_{p=1,\,T\,(\text{ideal})}-S^{\circ}_{p=1,\,T\,(\text{ideal})}}{R}=-\ln\frac{P_0V_0}{RT_0}+\ln\frac{T}{T_0}=-0.000618+\ln T/T_0 \tag{5.9}$$

The row at the bottom of the table, headed $(S^{\circ}_{\rho=1}-S^{\circ})/R$, is for the difference between entropies in the ideal gas states at Amagat densities one and ρ, divided by R.

$$\frac{S^{\circ}_{p=1,\,T\,(\text{ideal})}-S^{\circ}_{p,\,T\,(\text{ideal})}}{R}=\ln\rho \tag{5.10}$$

The other rows and columns of table 22 headed $(S^{\circ}-S)/R$ give the differences between the entropies in the ideal and real gas states at the same temperature and density, divided by R.

$$\frac{S^{\circ}_{\rho,\,T\,(\text{ideal})}-S_{\rho,\,T\,(\text{real})}}{R}=\int_0^{\rho}[(Z-1)/\rho]d\rho+\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho \tag{5.11}$$

In order, then, to get S/R for the real gas hydrogen at a temperature T and Amagat density ρ, one subtracts from S°/R, obtained from S° given in table 8, the sum of three numbers for the appropriate values of T and ρ to be obtained from table 22: one comes from the second column, headed $(S^{\circ}_{p=1}-S^{\circ}_{\rho=1})/R$; another from the bottom row of the table, headed $(S^{\circ}_{\rho=1}-S^{\circ})/R$; and the third from the rows and columns of the table headed $(S^{\circ}-S)/R$.

Table 23 is for the difference between the enthalpy of hydrogen in the ideal and real gas states at temperature T and Amagat density ρ, divided by RT.

$$\frac{H^{\circ}_{T\,(\text{ideal})}-H_{\rho,\,T\,(\text{real})}}{RT}=\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]\,d\rho-(Z-1). \tag{5.12}$$

Hence to obtain H/RT for hydrogen in the real gas state, one subtracts the appropriate value of $(H^{\circ}-H_{\rho})/RT$ in table 23 from the value of H°/RT obtained from H° given in table 8 for the deal gas state.

[11] For the calculation of these tables the authors are indebted to Messrs Roger E. Clapp, Kingsley Elder, Jr., and Robert Mann, who worked as student assistants at the National Bureau of Standards during the summer of 1941.

TABLE 22. *Entropy differences divided by R, for normal* H_2

$\frac{S^\circ - S}{R}$, Entropy of ideal gas minus entropy of real gas at same T and ρ, divided by R.

$\frac{S^\circ_{P(=1)} - S^\circ_{(\rho=1)}}{R}$, Entropy of ideal gas at pressure of 1 atmosphere minus entropy of ideal gas at density of 1 Amagat, divided by R.

$\frac{S^\circ_{P(=1)} - S^\circ}{R}$, Entropy of ideal gas at density of 1 Amagat minus entropy of ideal gas at density of ρ Amagats, divided by R.

Temperature	$\frac{S^\circ_{(P=1)} - S^\circ_{(\rho=1)}}{R}$	$\frac{S^\circ - S}{R}$														
		$\rho=1$ Amagat	2	3	6	10	20	40	60	80	100	120	140	160	180	200
°K																
16	−2.83809	0.00373	0.00745	0.01117												
18	−2.72030	.00323	.00645	.00968	0.01933											
20	−2.61494	.00288	.00576	.00864	.01724	0.0287										
22	−2.51963	.00264	.00529	.00792	.01583	.0263										
24	−2.43262	.00245	.00489	.00733	.01463	.0245	0.0488									
26	−2.35258	.00230	.00459	.00690	.01378	.0230	.0458	0.0915								
28	−2.27847	.00218	.00435	.00653	.01304	.0218	.0436	.0867	0.129							
30	−2.20948	.00208	.00415	.00623	.01245	.0208	.0416	.0827	.123	0.163	0.202					
32	−2.14494	.00198	.00396	.00595	.01189	.0198	.0396	.0787	.117	.155	.193	0.230	0.266	0.302	0.337	
34	−2.08432	.00190	.00379	.00569	.01137	.0190	.0379	.0753	.112	.148	.184	.220	.255	.290	.324	0.358
36	−2.02716	.00182	.00363	.00545	.01088	.0181	.0362	.0719	.107	.142	.176	.211	.245	.278	.311	.344
38	−1.97309	.00175	.00349	.00524	.01047	.0174	.0347	.0692	.103	.137	.170	.203	.236	.268	.300	.332
40	−1.92180	.00169	.00338	.00508	.01014	.0169	.0337	.0672	.100	.133	.165	.198	.229	.261	.293	.324
42	−1.87301	.00165	.00329	.00494	.00988	.0165	.0329	.0655	.098	.130	.161	.193	.225	.256	.287	.317
44	−1.82649	.00160	.00320	.00480	.00960	.0160	.0320	.0640	.096	.128	.158	.190	.221	.252	.283	.313
46	−1.78204	.00156	.00313	.00469	.00938	.0156	.0313	.0626	.094	.125	.156	.186	.217	.248	.278	.308
48	−1.73948	.00153	.00306	.00460	.00919	.0153	.0306	.0613	.092	.122	.153	.183	.213	.244	.274	.303
50	−1.69865	.00150	.00300	.00451	.00902	.0150	.0301	.0601	.090	.120	.150	.180	.210	.240	.270	.299
52	−1.65943	.00148	.00295	.00443	.00886	.0148	.0295	.0591	.089	.118	.148	.177	.207	.237	.266	.295
54	−1.62169	.00146	.00291	.00436	.00873	.0146	.0291	.0582	.088	.117	.146	.175	.204	.234	.262	.291
56	−1.58532	.00144	.00287	.00431	.00862	.0144	.0287	.0575	.087	.116	.144	.173	.202	.231	.259	.288
58	−1.55023	.00142	.00284	.00426	.00851	.0142	.0284	.0568	.086	.114	.142	.171	.200	.228	.257	.285
60	−1.51633	.00140	.00280	.00420	.00840	.0140	.0280	.0560	.084	.112	.140	.168	.197	.225	.254	.283
65	−1.43629	.00135	.00270	.00405	.00810	.01352	.0271	.0540	.0812	.109	.136	.164	.192	.219	.248	.276
70	−1.36218	.00131	.00261	.00392	.00784	.01309	.0263	.0525	.0790	.106	.132	.159	.186	.213	.241	.269
75	−1.29319	.00127	.00254	.00381	.00762	.01271	.0254	.0510	.0768	.103	.129	.155	.182	.209	.236	.263
80	−1.22865	.00124	.00248	.00371	.00743	.01240	.0248	.0499	.0752	.101	.126	.152	.179	.205	.232	.259
85	−1.16802	.00121	.00242	.00364	.00728	.01214	.0244	.0490	.0739	.099	.124	.150	.176	.202	.228	.254
90	−1.11087	.00119	.00238	.00357	.00714	.01192	.0239	.0481	.0726	.097	.122	.148	.173	.199	.225	.251
95	−1.05680	.00117	.00234	.00351	.00702	.01171	.0234	.0472	.0712	.096	.120	.145	.170	.196	.221	.247
100	−1.00551	.00115	.00229	.00344	.00689	.01149	.0230	.0464	.0700	.094	.118	.143	.168	.193	.218	.244
105	−0.95672	.00113	.00226	.00339	.00679	.01133	.0227	.0458	.0691	.093	.117	.141	.165	.190	.215	.241
110	−.91020	.00112	.00224	.00335	.00671	.01120	.0224	.0452	.0683	.092	.115	.139	.163	.188	.213	.238
115	−.86574	.00111	.00222	.00333	.00665	.01111	.0222	.0448	.0677	.091	.114	.138	.162	.186	.211	.236
120	−.82318	.00110	.00220	.00331	.00661	.01104	.0221	.0445	.0672	.090	.113	.137	.161	.185	.209	.234

125	−.78236	.00109	.00219	.00329	.00658	.01098	.0220	.0442	.0667	.090	.113	.136	.160	.184	.208	.233
130	−.74314	.00109	.00218	.00327	.00654	.01092	.0219	.0440	.0664	.089	.112	.136	.159	.183	.207	.232
135	−.70540	.00109	.00217	.00325	.00650	.01086	.0218	.0438	.0662	.089	.112	.135	.158	.182	.206	.230
140	−.66903	.00108	.00215	.00323	.00647	.01080	.0216	.0435	.0656	.088	.111	.134	.157	.181	.205	.229
145	−.63394	.00107	.00214	.00321	.00643	.01074	.0215	.0433	.0653	.088	.110	.133	.157	.180	.204	.228
150	−.60004	.00107	.00213	.00320	.00639	.01068	.0214	.0430	.0649	.087	.110	.133	.156	.179	.203	.227
155	−.56725	.00106	.00212	.00318	.00636	.01062	.0213	.0428	.0646	.087	.109	.132	.155	.178	.202	.225
160	−.53550	.00106	.00211	.00316	.00632	.01056	.0212	.0426	.0642	.087	.109	.131	.154	.177	.201	.224
165	−.50473	.00105	.00210	.00315	.00629	.01051	.0211	.0424	.0639	.086	.108	.130	.153	.176	.199	.222
170	−.47488	.00104	.00209	.00313	.00626	.01046	.0210	.0422	.0636	.085	.107	.129	.152	.174	.197	.220
180	−.41772	.00103	.00207	.00310	.00620	.01033	.0208	.0418	.0629	.0843	.1059	.127	.149	.172	.194	.217
190	−.36365	.00102	.00204	.00307	.00613	.01021	.0205	.0413	.0622	.0834	.1047	.126	.147	.169	.191	.214
200	−.31236	.00100	.00202	.00303	.00606	.01007	.0203	.0408	.0615	.0824	.1035	.125	.146	.167	.189	.211
210	−.26357	.00099	.00200	.00299	.00599	.01004	.0201	.0403	.0608	.0814	.1023	.124	.145	.166	.188	.210
220	−.21705	.00098	.00197	.00295	.00592	.00994	.0198	.0398	.0600	.0805	.1011	.122	.143	.165	.186	.208
230	−.17260	.00097	.00195	.00292	.00585	.00976	.0196	.0394	.0593	.0795	.0999	.120	.141	.162	.184	.205
240	−.13004	.00096	.00193	.00289	.00578	.00964	.0194	.0389	.0587	.0786	.0988	.119	.139	.160	.181	.203
250	−.08922	.00095	.00191	.00286	.00573	.00952	.0192	.0385	.0581	.0778	.0978	.118	.138	.158	.179	.200
260	−.04999	.00095	.00190	.00284	.00568	.00948	.0191	.0382	.0576	.0770	.0968	.117	.137	.157	.177	.198
270	−.01225	.000938	.001877	.002816	.005636	.009402	.01885	.03786	.05705	.07641	.09595	.1157	.1356	.1557	.1760	.1965
280	+.024114	.000931	.001861	.002793	.005589	.009323	.01869	.03754	.05656	.07574	.09510	.1146	.1344	.1543	.1743	.1946
300	+.093106	.000916	.001833	.002750	.005504	.009180	.01840	.03694	.05565	.07451	.09354	.1127	.1321	.1516	.1713	.1912
320	.157645	.000902	.001805	.002708	.005420	.009042	.01812	.03639	.05481	.07338	.09210	.1110	.1300	.1492	.1686	.1881
340	.218270	.000890	.001781	.002672	.005347	.008919	.01787	.03589	.05404	.07234	.09079	.1094	.1281	.1470	.1661	.1853
360	.275428	.000879	.001759	.002639	.005280	.008807	.01765	.03543	.05334	.07140	.08959	.1079	.1264	.1450	.1638	.1827
380	.329495	.000868	.001737	.002605	.005213	.008696	.01742	.03498	.05266	.07048	.08844	.1065	.1248	.1431	.1617	.1803
400	.38079	.00086	.00172	.00257	.00515	.00859	.0172	.0346	.0520	.0697	.0874	.1053	.1233	.1414	.1597	.1781
420	.42958	.00085	.00170	.00255	.00510	.00850	.0170	.0342	.0515	.0689	.0864	.1041	.1219	.1398	.1578	.1760
440	.47610	.00084	.00168	.00252	.00504	.00841	.0169	.0338	.0509	.0681	.0855	.1030	.1205	.1383	.1561	.1741
460	.52055	.00083	.00166	.00250	.00499	.00833	.0167	.0335	.0504	.0675	.0846	.1019	.1193	.1368	.1545	.1723
480	.56311	.00082	.00165	.00247	.00494	.00825	.0165	.0332	.0499	.0668	.0838	.1009	.1181	.1355	.1530	.1706
500	.60393	.00082	.00163	.00245	.00490	.00817	.0164	.0329	.0495	.0662	.0830	.1000	.1170	.1342	.1515	.1689
520	.64315	.00081	.00162	.00243	.00486	.00810	.0162	.0326	.0490	.0656	.0823	.0990	.1160	.1330	.1501	.1674
540	.68089	.00080	.00160	.00241	.00482	.00803	.0161	.0323	.0486	.0650	.0815	.0982	.1149	.1318	.1488	.1659
560	.71726	.00080	.00159	.00239	.00478	.00797	.0160	.0320	.0482	.0645	.0809	.0974	.1140	.1307	.1476	.1645
580	.75235	.00079	.00158	.00237	.00474	.00790	.0158	.0318	.0478	.0640	.0802	.0966	.1131	.1297	.1464	.1632
600	.78625	.00078	.00157	.00235	.00470	.00784	.0157	.0315	.0474	.0635	.0796	.0958	.1122	.1286	.1452	.1619
$\frac{S^\circ_{(p=1)}-S^\circ}{R}$	----------	0	.69315	1.09861	1.79176	2.30259	2.9957	3.6889	4.0943	4.3820	4.6052	4.7875	4.9416	5.0752	5.1930	5.2983

TABLE 22. *Entropy differences divided by R, for normal* H_2—Continued

Temperature	$\frac{S^\circ_{(P=1)}-S^\circ_{(\rho=1)}}{R}$	$\frac{S^\circ-S}{R}$														
		$\rho=220$	240	260	280	300	320	340	360	380	400	420	440	460	480	500
16																
18																
20																
22																
24																
26																
28																
30																
32																
34	−2.0843	0.391	0.424	0.457	0.489	0.520	0.551	0.581	0.610	0.638	0.666	0.694	0.723	0.753	0.784	0.816
36	−2.0272	.376	.408	.441	.473	.504	.535	.565	.594	.623	.652	.682	.712	.742	.774	.807
38	−1.9731	.364	.395	.427	.458	.489	.519	.550	.580	.610	.640	.671	.701	.733	.766	.800
40	−1.9218	.355	.386	.417	.448	.478	.509	.539	.570	.601	.632	.664	.696	.728	.762	.796
42	−1.8730	.348	.379	.409	.439	.470	.500	.531	.563	.594	.626	.658	.691	.724	.758	.792
44	−1.8265	.343	.374	.404	.434	.465	.495	.526	.557	.589	.622	.655	.688	.721	.755	.789
46	−1.7820	.338	.368	.399	.428	.459	.489	.520	.551	.583	.616	.649	.682	.716	.750	.784
48	−1.7395	.333	.363	.393	.422	.453	.483	.514	.545	.577	.609	.642	.676	.710	.743	.777
50	−1.6987	.328	.358	.388	.417	.447	.478	.508	.539	.571	.603	.636	.669	.702	.736	.769
52	−1.6594	.325	.354	.383	.413	.443	.472	.503	.534	.565	.596	.629	.661	.694	.728	.762
54	−1.6217	.320	.350	.379	.408	.438	.467	.497	.528	.559	.590	.622	.654	.687	.720	.754
56	−1.5853	.317	.346	.375	.405	.434	.464	.494	.524	.554	.586	.617	.649	.682	.715	.749
58	−1.5502	.314	.343	.373	.402	.432	.462	.492	.523	.554	.585	.616	.648	.681	.715	.749
60	−1.5163	.312	.341	.371	.401	.431	.461	.492	.523	.554	.586	.618	.650	.683	.717	.751
65	−1.4363	.305	.334	.363	.393	.424	.454	.485	.516	.548	.580	.613	.646	.679	.714	.749
70	−1.3622	.298	.326	.356	.385	.415	.445	.476	.507	.539	.571	.604	.637	.670	.705	.739
75	−1.2932	.291	.320	.348	.377	.407	.436	.467	.497	.529	.560	.593	.625	.659	.692	.727
80	−1.2286	.286	.314	.342	.370	.399	.428	.458	.488	.519	.550	.582	.614	.647	.680	.714
85	−1.1680	.281	.308	.336	.364	.392	.421	.450	.480	.510	.540	.571	.603	.635	.667	.700
90	−1.1109	.278	.304	.332	.359	.387	.416	.445	.474	.503	.534	.564	.595	.627	.659	.691
95	−1.0568	.274	.301	.328	.355	.383	.411	.440	.469	.498	.528	.558	.589	.620	.652	.684
100	−1.0055	.270	.297	.324	.351	.379	.407	.435	.464	.493	.522	.552	.583	.614	.645	.677
105	−0.9567	.267	.294	.320	.347	.375	.402	.430	.459	.487	.517	.546	.576	.607	.638	.670
110	−.9102	.264	.290	.317	.344	.371	.398	.426	.454	.482	.511	.540	.570	.600	.631	.662
115	−.8657	.262	.287	.313	.340	.367	.394	.421	.449	.477	.505	.534	.564	.594	.624	.655
120	−.8232	.259	.285	.311	.337	.364	.390	.418	.445	.473	.501	.530	.559	.589	.619	.649
125	−.7824	.258	.284	.309	.335	.361	.388	.415	.442	.470	.498	.526	.555	.584	.614	.644
130	−.7431	.257	.282	.307	.333	.359	.386	.412	.439	.467	.495	.523	.552	.580	.610	.640
135	−.7054	.255	.280	.305	.331	.357	.383	.409	.436	.463	.491	.519	.547	.576	.605	.634
140	−.6690	.253	.278	.303	.329	.354	.380	.407	.433	.460	.488	.515	.544	.572	.601	.630
145	−.6339	.252	.277	.301	.327	.352	.378	.404	.431	.457	.485	.512	.540	.568	.597	.626
150	−.6000	.251	.275	.300	.325	.351	.376	.402	.429	.455	.482	.509	.537	.565	.593	.622

155	−.5673	.249	.274	.298	.323	.349	.374	.400	.426	.453	.479	.506	.534	.561	.589	.617
160	−.5355	.248	.272	.297	.321	.346	.372	.397	.423	.450	.476	.503	.530	.557	.585	.613
165	−.5047	.246	.270	.294	.319	.344	.369	.394	.420	.446	.472	.498	.525	.552	.579	.607
170	−.4749	.244	.267	.291	.316	.340	.365	.390	.415	.441	.467	.493	.519	.546	.573	.600
180	−.4177	.240	.263	.287	.310	.334	.359	.383	.408	.433	.458	.484	.510	.537	.563	.590
190	−.3637	.237	.259	.282	.306	.329	.353	.378	.402	.427	.452	.477	.503	.529	.555	.582
200	−.3124	.234	.256	.279	.302	.326	.349	.373	.398	.422	.447	.472	.498	.523	.550	.576
210	−.2636	.232	.254	.277	.300	.323	.347	.370	.394	.419	.443	.468	.494	.519	.545	.571
220	−.2170	.230	.252	.274	.297	.320	.343	.367	.391	.415	.439	.464	.489	.514	.540	.566
230	−.1726	.227	.249	.271	.293	.316	.339	.362	.386	.410	.434	.458	.483	.508	.533	.559
240	−.1300	.224	.246	.268	.290	.3127	.335	.358	.381	.405	.428	.452	.477	.501	.526	.552
250	−.0892	.221	.243	.264	.286	.308	.331	.353	.376	.399	.423	.447	.471	.495	.519	.544
260	−.0500	.219	.240	.262	.283	.305	.327	.350	.372	.395	.418	.441	.465	.489	.513	.538
270	−.0123	.2172	.2381	.2593	.2806	.3022	.3240	.3460	.3683	.3908	.4136	.4366	.4598	.4833	.5071	.5311
280	+.0241	.2151	.2358	.2567	.2778	.2991	.3206	.3424	.3644	.3866	.4090	.4317	.4546	.4777	.5011	.5248
300	.0931	.2113	.2316	.2520	.2727	.2935	.3145	.3358	.3572	.3789	.4008	.4228	.4451	.4676	.4904	.5133
320	.1576	.2078	.2277	.2478	.2680	.2885	.3091	.3299	.3508	.3720	.3934	.4149	.4367	.4587	.4808	.5032
340	.2183	.2047	.2242	.2440	.2638	.2839	.3041	.3245	.3451	.3658	.3868	.4079	.4292	.4507	.4723	.4942
360	.2754	.2018	.2211	.2405	.2600	.2797	.2996	.3197	.3399	.3603	.3808	.4015	.4224	.4434	.4647	.4861
380	.3295	.1991	.2181	.2372	.2565	.2759	.2955	.3152	.3351	.3551	.3753	.3957	.4162	.4369	.4577	.4787
400	.3808	.197	.215	.234	.253	.272	.292	.311	.331	.350	.370	.390	.410	.431	.451	.472
420	.4296	.194	.213	.231	.250	.269	.288	.307	.327	.346	.366	.385	.405	.425	.445	.466
440	.4761	.192	.210	.229	.247	.266	.285	.304	.323	.342	.361	.381	.400	.420	.440	.460
460	.5206	.190	.208	.226	.245	.263	.282	.300	.319	.338	.357	.376	.396	.415	.435	.455
480	.5631	.188	.206	.224	.242	.260	.279	.297	.316	.335	.353	.372	.392	.411	.430	.450
500	.6039	.186	.204	.222	.240	.258	.276	.294	.313	.331	.350	.369	.388	.407	.426	.445
520	.6432	.185	.202	.220	.238	.255	.273	.291	.310	.328	.346	.365	.384	.403	.421	.441
540	.6809	.183	.200	.218	.235	.253	.271	.289	.307	.325	.343	.362	.380	.399	.418	.436
560	.7173	.182	.199	.216	.233	.251	.269	.286	.304	.322	.340	.358	.377	.395	.414	.432
580	.7524	.180	.197	.214	.231	.249	.266	.284	.302	.319	.337	.355	.374	.392	.410	.429
600	.7863	.179	.195	.212	.230	.247	.264	.282	.299	.317	.335	.352	.370	.389	.407	.425
$\frac{S^\circ_{(p=1)}-S^\circ}{R}$		5.3936	5.4806	5.5607	5.6348	5.7038	5.7683	5.8289	5.8861	5.9402	5.9915	6.0403	6.0868	6.1312	6.1738	6.2146

TABLE 23. *Enthalpy of ideal gas minus enthalpy of real gas at the same T and ρ, divided by RT, for normal H_2*

Temperature	$\frac{H^\circ - H}{RT}$														
	ρ=1Amagat	2	3	6	10	20	40	60	80	100	120	140	160	180	200
°K															
16	0.02193	0.04381	0.06568												
18	.01869	.03725	.05583	0.11144											
20	.01614	.03226	.04835	.09650	0.1604										
22	.01420	.02838	.04253	.08489	.1411										
24	.01263	.02524	.03783	.07551	.1255	0.2494									
26	.01132	.02260	.03388	.06765	.1125	.2237	0.4420								
28	.01023	.02045	.03063	.06116	.1017	.2023	.3994	0.591							
30	.00931	.01860	.02786	.05564	.0925	.1839	.3637	.538	0.708	0.872					
32	.00851	.01701	.02549	.05089	.0846	.1681	.3318	.491	.646	.797	0.943	1.085	1.222	1.355	
34	.00781	.01556	.02337	.04666	.0776	.1541	.3042	.451	.593	.731	.865	0.995	1.121	1.243	1.361
36	.00719	.01436	.02153	.04298	.0714	.1420	.2801	.414	.545	.673	.796	.916	1.032	1.145	1.253
38	.00665	.01329	.01991	.03976	.0661	.1313	.2592	.383	.504	.622	.736	.847	0.955	1.059	1.160
40	.00617	.01234	.01850	.03692	.0614	.1220	.2409	.357	.469	.578	.684	.787	.887	0.984	1.078
42	.00576	.01151	.01727	.03445	.0573	.1140	.2249	.333	.438	.539	.638	.734	.828	.918	1.005
44	.00538	.01077	.01615	.03223	.0536	.1067	.2104	.312	.410	.505	.598	.688	.775	.860	0.942
46	.00504	.01008	.01513	.03020	.0502	.1000	.1971	.292	.384	.473	.560	.645	.727	.806	.883
48	.00473	.00946	.01420	.02834	.0471	.0937	.1849	.274	.360	.444	.526	.605	.682	.757	.829
50	00445	.00889	.01324	.02665	.0443	.0881	.1739	.257	.338	.417	.494	.569	.641	.711	.779
52	.00419	.00837	.01257	.02509	.0417	.0830	.1638	.243	.319	.394	.466	.537	.605	.671	.734
54	.00396	.00792	.01188	.02371	.0393	.0784	.1548	.229	.302	.373	.441	.507	.571	.632	.692
56	.00376	.00750	.01126	.02247	.0374	.0743	.1466	.217	.286	.353	.417	.479	.540	.598	.654
58	.00356	.00710	.01066	.02127	.0354	.0704	.1389	.206	.271	.333	.394	.453	.511	.566	.619
60	.00337	.00674	.01010	.02017	.0335	.0666	.1315	.194	.256	.315	.373	.429	.483	.536	.586
65	.00296	.00592	.00887	.01771	.02943	.0584	.1153	.1706	.2242	.276	.327	.376	.423	.469	.513
70	.00261	.00522	.00782	.01542	.02595	.0515	.1017	.1503	.1974	.243	.287	.330	.371	.411	.449
75	.00231	.00461	.00692	.01382	.02297	.0456	.0900	.1330	.1747	.215	.254	.291	.327	.362	.395
80	.00205	.00411	.00616	.01230	.02043	.0406	.0799	.1182	.1552	.191	.225	.258	.290	.320	.349
85	.00184	.00368	.00551	.01101	.01828	.0363	.0714	.1055	.1384	.170	.201	.230	.257	.283	.308
90	.00165	.00330	.00495	.00987	.01639	.0325	.0639	.0942	.1235	.152	.179	.204	.229	.252	.273
95	.00148	.00296	.00444	.00884	.01469	.0291	.0571	.0842	.1101	.135	.159	.181	.203	.223	.241
100	.00133	.00265	.00398	.00793	.01316	.0261	.0511	.0752	.0983	.120	.141	.161	.179	.197	.213
105	.00119	.00238	.00357	.00712	.01182	.0234	.0458	.0673	.0878	.107	.125	.143	.159	.174	.187
110	.00107	.00215	.00322	.00642	.01065	.0210	.0412	.0603	.0785	.095	.111	.126	.140	.153	.165
115	.00097	.00194	.00290	.00579	.00960	.0190	.0370	.0540	.0701	.085	.099	.112	.124	.135	.144
120	.00088	.00175	.00262	.00523	.00867	.0171	.0333	.0485	.0628	.076	.088	.099	.109	.118	.126
125	.00079	.00158	.00236	.00472	.00781	.0154	.0299	.0434	.0561	.068	.078	.088	.097	.104	.110
130	.00071	.00143	.00213	.00425	.00704	.0139	.0268	.0388	.0499	.060	.069	.077	.084	.090	.095
135	.00064	.00128	.00193	.00382	.00632	.0124	.0239	.0345	.0442	.053	.061	.067	.073	.078	.081
140	.00057	.00115	.00172	.00341	.00563	.0110	.0212	.0305	.0389	.046	.053	.058	.063	.066	.068
145	.00051	.00102	.00154	.00304	.00502	.0098	.0186	.0269	.0340	.040	.045	.050	.053	.055	.056
150	.00045	.00090	.00136	.00269	.00444	.0087	.0165	.0235	.0295	.035	.039	.042	.044	.045	.045

155	.00040	.00081	.00121	.00239	.00393	.0076	.0144	.0204	.0254	.029	.033	.035	.036	.036	.035
160	.00035	.00071	.00106	.00209	.00344	.0067	.0125	.0174	.0214	.024	.027	.028	.028	.027	.025
165	.00031	.00061	.00092	.00180	.00295	.0057	.0105	.0145	.0176	.020	.021	.021	.020	.018	.015
170	.00026	.00052	.00076	.00152	.00248	.0047	.0087	.0117	.0139	.015	.015	.014	.012	.010	.006
180	.00017	.00034	.00050	.00100	.00161	.0030	.0052	.0066	.0070	.0065	.005	.003	−.001	−.005	−.011
190	.00010	.00019	.00028	.00053	.00085	.0015	.0022	.0021	.0011	−.0008	−.004	−.008	−.012	−.018	−.025
200	.00003	.00006	.00008	.00015	.00021	.0002	−.0003	−.0017	−.0059	−.0070	−.011	−.016	−.022	−.029	−.037
210	−.00003	−.00005	−.00009	−.00020	−.00037	−.0009	−.0026	−.0051	−.0084	−.0126	−.018	−.024	−.031	−.039	−.048
220	−.00008	−.00016	−.00024	−.00051	−.00091	−.0020	−.0047	−.0082	−.0126	−.0178	−.024	−.031	−.039	−.047	−.057
230	−.00013	−.00027	−.00041	−.00084	−.00143	−.0030	−.0068	−.0113	−.0166	−.0228	−.030	−.038	−.047	−.056	−.067
240	−.00018	−.00036	−.00056	−.00113	−.00192	−.0040	−.0088	−.0142	−.0204	−.0274	−.035	−.044	−.054	−.064	−.076
250	−.00023	−.00046	−.00068	−.00138	−.00233	−.0048	−.0104	−.0166	−.0236	−.0314	−.040	−.050	−.060	−.071	−.083
260	−.00026	−.00053	−.00078	−.00159	−.00268	−.0055	−.0118	−.0187	−.0265	−.0349	−.044	−.054	−.065	−.077	−.090
270	−.000290	−.000584	−.000877	−.001770	−.002985	−.00615	−.01299	−.02058	−.02891	−.03802	−.0479	−.0587	−.0703	−.0828	−.0962
280	−.000321	−.000645	−.000969	−.001953	−.003290	−.00675	−.01421	−.02238	−.03131	−.04099	−.0515	−.0628	−.0749	−.0879	−.1018
300	−.000375	−.000752	−.001131	−.002276	−.003827	−.00782	−.01634	−.02556	−.03549	−.04620	−.0577	−.0699	−.0830	−.0970	−.1118
320	−.000422	−.000845	−.001271	−.002556	−.004291	−.00875	−.01816	−.02826	−.03907	−.05062	−.0629	−.0760	−.0899	−.1046	−.1202
340	−.000462	−.000926	−.001390	−.002794	−.004688	−.00954	−.01973	−.03058	−.04213	−.05440	−.0674	−.0812	−.0957	−.1111	−.1273
360	−.000496	−.000994	−.001493	−.003000	−.005031	−.01022	−.02108	−.03259	−.04478	−.05766	−.0713	−.0856	−.1007	−.1166	−.1334
380	−.000526	−.001054	−.001584	−.003181	−.005332	−.01081	−.02226	−.03433	−.04707	−.06049	−.0746	−.0895	−.1051	−.1214	−.1386
400	−.00055	−.00111	−.00166	−.00334	−.00560	−.0113	−.0233	−.0359	−.0491	−.0630	−.0776	−.0928	−.1088	−.1256	−.1432
420	−.00058	−.00116	−.00174	−.00348	−.00583	−.0118	−.0242	−.0372	−.0509	−.0652	−.0801	−.0958	−.1121	−.1292	−.1471
440	−.00060	−.00120	−.00180	−.00360	−.00604	−.0122	−.0250	−.0384	−.0524	−.0671	−.0824	−.0984	−.1150	−.1324	−.1506
460	−.00062	−.00123	−.00185	−.00372	−.00622	−.0126	−.0257	−.0395	−.0538	−.0688	−.0844	−.1006	−.1176	−.1352	−.1536
480	−.00063	−.00127	−.00190	−.00382	−.00639	−.0129	−.0264	−.0404	−.0550	−.0703	−.0862	−.1027	−.1199	−.1377	−.1563
500	−.00065	−.00130	−.00195	−.00390	−.00653	−.0132	−.0270	−.0413	−.0562	−.0716	−.0877	−.1045	−.1218	−.1399	−.1587
520	−.00066	−.00132	−.00199	−.00398	−.00667	−.0135	−.0275	−.0420	−.0571	−.0728	−.0892	−.1061	−.1236	−.1419	−.1608
540	−.00067	−.00135	−.00202	−.00406	−.00679	−.0137	−.0279	−.0427	−.0580	−.0739	−.0904	−.1075	−.1252	−.1436	−.1627
560	−.00068	−.00137	−.00205	−.00412	−.00689	−.0139	−.0284	−.0433	−.0588	−.0749	−.0916	−.1088	−.1267	−.1452	−.1643
580	−.00069	−.00139	−.00208	−.00418	−.00699	−.0141	−.0287	−.0439	−.0596	−.0758	−.0926	−.1100	−.1280	−.1466	−.1658
600	−.00070	−.00141	−.00211	−.00424	−.00708	−.0143	−.0291	−.0444	−.0602	−.0766	−.0935	−.1110	−.1291	−.1478	−.1671

TABLE 23. *Enthalpy of ideal gas minus enthalpy of real gas at the same T and p, divided by RT, for normal H_2*—Continued

Temperature	$\frac{H^\circ - H}{RT}$														
	$p=220$	240	260	280	300	320	340	360	380	400	420	440	460	480	500
°K															
16															
18															
20															
22															
24															
26															
28															
30															
32															
34	1.475	1.582	1.692	1.793	1.890	1.983	2.071	2.154	2.234	2.310	2.382	2.453	2.521	2.586	2.647
36	1.359	1.461	1.559	1.653	1.743	1.830	1.912	1.991	2.065	2.136	2.204	2.269	2.331	2.390	2.446
38	1.257	1.351	1.442	1.529	1.612	1.693	1.770	1.844	1.914	1.981	2.044	2.104	2.161	2.215	2.265
40	1.168	1.256	1.340	1.421	1.499	1.574	1.646	1.715	1.781	1.843	1.902	1.958	2.010	2.059	2.104
42	1.090	1.171	1.250	1.325	1.398	1.467	1.534	1.599	1.661	1.719	1.774	1.826	1.874	1.919	1.959
44	1.021	1.097	1.170	1.241	1.308	1.373	1.436	1.496	1.553	1.608	1.659	1.707	1.752	1.792	1.829
46	0.957	1.028	1.097	1.163	1.226	1.286	1.344	1.400	1.453	1.504	1.551	1.596	1.637	1.674	1.707
48	.898	0.965	1.029	1.091	1.150	1.206	1.260	1.311	1.361	1.407	1.451	1.492	1.530	1.564	1.594
50	.844	.907	0.968	1.025	1.081	1.133	1.183	1.231	1.276	1.319	1.359	1.396	1.430	1.461	1.489
52	.796	.855	.911	0.966	1.017	1.066	1.112	1.156	1.198	1.237	1.273	1.307	1.338	1.366	1.391
54	.750	.806	.859	.910	0.958	1.003	1.046	1.087	1.125	1.161	1.195	1.225	1.253	1.279	1.301
56	.708	.761	.811	.859	.904	0.947	0.987	1.025	1.060	1.093	1.123	1.151	1.177	1.200	1.219
58	.670	.720	.767	.812	.855	.896	.934	0.969	1.002	1.033	1.061	1.087	1.110	1.130	1.148
60	.635	.682	.727	.770	.811	.849	.886	.919	0.950	0.979	1.005	1.028	1.049	1.069	1.085
65	.555	.596	.634	.671	.706	.739	.770	.799	.825	.849	0.870	0.889	0.906	0.920	0.931
70	.486	.521	.554	.586	.615	.643	.669	.692	.714	.733	.750	.764	.776	.786	.793
75	.427	.457	.485	.511	.536	.559	.580	.599	.616	.631	.644	.654	.662	.667	.669
80	.376	.401	.425	.447	.468	.487	.503	.518	.531	.542	.551	.557	.561	.562	.561
85	.331	.353	.373	.391	.408	.423	.436	.448	.457	.464	.469	.472	.472	.470	.466
90	.293	.312	.328	.344	.357	.369	.380	.388	.394	.398	.400	.400	.398	.393	.385
95	.259	.274	.289	.301	.312	.322	.329	.335	.338	.340	.340	.337	.332	.325	.315
100	.228	.241	.253	.263	.272	.279	.284	.287	.288	.288	.285	.280	.274	.264	.252
105	.200	.211	.221	.229	.235	.240	.242	.244	.243	.240	.236	.229	.220	.208	.195
110	.175	.184	.191	.197	.202	.204	.205	.204	.202	.197	.191	.182	.171	.158	.142
115	.152	.159	.165	.169	.171	.172	.172	.169	.164	.158	.150	.140	.127	.112	.095
120	.132	.137	.141	.144	.144	.144	.141	.137	.131	.123	.114	.102	.088	.072	.053
125	.115	.118	.121	.121	.121	.118	.115	.109	.102	.093	.082	.068	.053	.036	.016
130	.098	.100	.101	.101	.099	.095	.090	.083	.075	.064	.052	.038	.021	.003	−.018
135	.083	.084	.083	.081	.078	.073	.067	.059	.049	.038	.024	.009	−.008	−.028	−.050
140	.068	.068	.066	.063	.059	.053	.046	.037	.026	.014	−.001	−.017	−.036	−.056	−.079
145	.056	.054	.051	.047	.041	.035	.026	.016	.005	−.009	−.024	−.042	−.061	−.082	−.106
150	.044	.041	.037	.032	.026	.018	.009	−.002	−.015	−.029	−.045	−.064	−.084	−.106	−.130

155	.032	.029	.024	.018	.011	.002	−.008	−.020	−.033	−.048	−.066	−.084	−.105	−.128	−.154
160	.022	.017	.012	.005	−.003	−.013	−.024	−.036	−.051	−.067	−.084	−.104	−.126	−.150	−.176
165	.011	.006	−.000	−.008	−.017	−.028	−.040	−.053	−.068	−.085	−.103	−.124	−.146	−.171	−.197
170	.001	−.005	−.013	−.021	−.031	−.042	−.055	−.070	−.085	−.103	−.122	−.143	−.166	−.191	−.218
180	−.017	−.025	−.034	−.044	−.055	−.068	−.082	−.098	−.115	−.134	−.154	−.176	−.200	−.225	−.253
190	−.033	−.042	−.052	−.063	−.076	−.090	−.105	−.122	−.140	−.160	−.181	−.204	−.228	−.255	−.283
200	−.046	−.056	−.068	−.080	−.093	−.108	−.125	−.142	−.161	−.181	−.203	−.227	−.252	−.279	−.308
210	−.057	−.068	−.081	−.094	−.108	−.124	−.141	−.159	−.179	−.200	−.223	−.247	−.273	−.300	−.330
220	−.068	−.080	−.093	−.107	−.122	−.139	−.156	−.175	−.196	−.218	−.241	−.266	−.292	−.320	−.350
230	−.079	−.091	−.105	−.120	−.136	−.153	−.172	−.191	−.212	−.235	−.259	−.284	−.311	−.340	−.370
240	−.088	−.101	−.116	−.132	−.148	−.166	−.185	−.206	−.227	−.250	−.275	−.301	−.328	−.358	−.388
250	−.096	−.111	−.126	−.142	−.159	−.178	−.198	−.219	−.241	−.265	−.290	−.316	−.344	−.374	−.405
260	−.104	−.119	−.134	−.151	−.169	−.188	−.209	−.230	−.253	−.277	−.303	−.330	−.358	−.388	−.420
270	−.1105	−.1258	−.1421	−.1595	−.1780	−.1976	−.2184	−.2405	−.2638	−.2884	−.3144	−.3419	−.3709	−.4014	−.4336
280	−.1167	−.1326	−.1494	−.1673	−.1862	−.2063	−.2276	−.2500	−.2738	−.2988	−.3252	−.3530	−.3824	−.4133	−.4458
300	−.1276	−.1443	−.1619	−.1806	−.2004	−.2212	−.2432	−.2664	−.2908	−.3165	−.3436	−.3719	−.4018	−.4332	−.4662
320	−.1367	−.1541	−.1724	−.1918	−.2122	−.2336	−.2562	−.2799	−.3048	−.3310	−.3585	−.3873	−.4175	−.4492	−.4824
340	−.1444	−.1624	−.1813	−.2012	−.2220	−.2440	−.2670	−.2911	−.3164	−.3429	−.3707	−.3998	−.4302	−.4621	−.4954
360	−.1510	−.1694	−.1888	−.2091	−.2304	−.2527	−.2760	−.3005	−.3261	−.3528	−.3808	−.4100	−.4406	−.4725	−.5059
380	−.1566	−.1755	−.1952	−.2159	−.2375	−.2601	−.2837	−.3084	−.3342	−.3611	−.3892	−.4186	−.4492	−.4811	−.5144
400	−.161	−.181	−.201	−.222	−.2435	−.266	−.290	−.315	−.341	−.368	−.396	−.426	−.456	−.488	−.521
420	−.166	−.185	−.206	−.227	−.249	−.272	−.296	−.321	−.347	−.374	−.402	−.432	−.462	−.494	−.527
440	−.169	−.189	−.210	−.231	−.253	−.277	−.301	−.326	−.352	−.379	−.407	−.437	−.467	−.499	−.532
460	−.173	−.193	−.213	−.235	−.257	−.281	−.305	−.330	−.356	−.383	−.411	−.441	−.471	−.503	−.536
480	−.176	−.196	−.217	−.238	−.261	−.284	−.308	−.334	−.360	−.387	−.415	−.444	−.475	−.506	−.539
500	−.178	−.198	−.219	−.241	−.264	−.287	−.311	−.337	−.363	−.390	−.418	−.447	−.477	−.509	−.541
520	−.180	−.201	−.222	−.244	−.266	−.290	−.314	−.339	−.365	−.393	−.421	−.450	−.480	−.511	−.543
540	−.182	−.203	−.224	−.246	−.269	−.292	−.316	−.342	−.368	−.395	−.423	−.452	−.482	−.513	−.545
560	−.184	−.205	−.226	−.248	−.271	−.294	−.319	−.344	−.370	−.397	−.425	−.453	−.483	−.514	−.546
580	−.186	−.206	−.228	−.250	−.272	−.296	−.320	−.345	−.371	−.398	−.426	−.455	−.485	−.515	−.547
600	−.187	−.208	−.229	−.251	−.274	−.298	−.322	−.347	−.373	−.400	−.427	−.456	−.486	−.516	−.548

Values of F/RT, E/RT, and $\ln(f/P)$ may be obtained rather simply from values of S/R and H/RT and the Z-table in accordance with the following equations:

$$F/RT=(H/RT)-(S/R) \tag{5.13}$$

$$\ln \frac{f}{P}=\frac{F_{\rho,T\,(\mathrm{real})}-F^{\circ}_{\rho,T\,(\mathrm{ideal})}}{RT}-\ln Z \tag{5.14}$$

$$E/RT=(H/RT)-Z. \tag{5.15}$$

The value of $[F^{\circ}_{\rho,\,T\,(\mathrm{ideal})}-F_{\rho,\,T\,(\mathrm{real})}/RT]$ may be obtained by subtracting $(S^{\circ}-S)/R$, given in table 22, from $(H^{\circ}-H)/RT$, given in table 23.

The calculation of the heat capacities of the real gas involves the evaluation of

$$\int_0^{\rho}[T^2(d^2Z/dT^2)_{\rho}/\rho]d\rho.$$

This may be carried out using the $(d^2Z/dT^2)_{\rho}$ table (table 16), and a method of tabular integration. Table 23 may be used to obtain $\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]d\rho$, since from eq 5.12 it follows that

$$\int_0^{\rho}[T(dZ/dT)_{\rho}/\rho]\,d\rho=\frac{H^{\circ}-H}{RT}\,(\text{from table 23})+(Z-1). \tag{5.16}$$

In the temperature and density ranges where Z may be represented by an analytic expression,[12] these two integrals may be evaluated by using series expansions for Z and its derivatives in the integrands. The difference between the specific heats at constant pressure for the real and ideal gas states may be calculated using the equation

$$[C_{p(\mathrm{real\ gas})}-C^{\circ}_{p(\mathrm{ideal})}]/R=T\left\{\left(\frac{d}{d\rho}\left[\frac{H^{\circ}-H}{RT}\right]\right)_T\left(\frac{dP}{dT}\right)_{\rho}\Big/\left(\frac{dP}{d\rho}\right)_T-\left(\frac{d}{dT}\left[\frac{H^{\circ}-H}{RT}\right]\right)_{\rho}\right\}-\frac{H^{\circ}-H}{RT} \tag{5.17}$$

$$=-T\left(\frac{d}{dT}\left[\frac{H^{\circ}-H}{RT}\right]\right)_{\rho}-\frac{H^{\circ}-H}{RT}+\left[Z+T\left(\frac{dZ}{dT}\right)_{\rho}\right]\left[T\left(\frac{dZ}{dT}\right)_{\rho}-\rho\left(\frac{dZ}{d\rho}\right)_T\right]\Big/\left[Z+\rho\left(\frac{dZ}{d\rho}\right)_T\right] \tag{5.17a}$$

The derivatives in eq 5.17 may be calculated from tables 14 and 23, using a method of tabular differentiation. Except for the first term, the derivatives in eq 5.17a are given in tables 15 and 17.

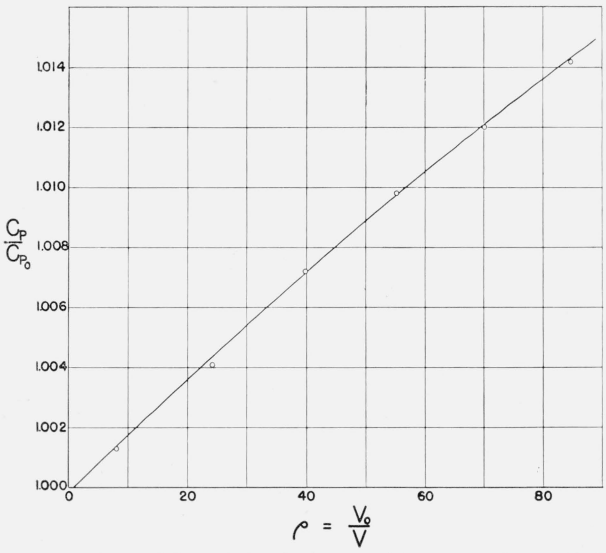

FIGURE 12. *Effect of density on specific heat of H_2 at 50° C.*

Figure 12 shows the dependence of the specific heat at constant pressure for hydrogen at 50° C upon the Amagat density ρ. The curve represents the results of the evaluation of formula 5.8, using the PVT correlation of this paper. The plotted points are observations by Workman [49]. No other direct experimental data on the effect of pressure upon the specific heat at constant pressure are available for hydrogen.

An indirect indication of the effect of pressure on the specific heat of hydrogen is found in the work of van Itterbeek [78], who used the results of van Itterbeek and Keesom [77] on the effect of pressure on the velocity of sound in hydrogen at liquid hydrogen temperatures. The results of van Itterbeek at a pressure of one-tenth of an atmosphere indicate that the increase of C_p with pressure above the zero-pressure value agrees with the PVT prediction within 3 percent at 17.5° K and at 19.0° K, but is lower by more than 30 percent at 20.5° K. At pressures above ½ atm at 20.5° K, this difference in heat capacity has become approximately 0.1 cal deg^{-1} mole^{-1}, but this discrepancy is reduced by roughly 50 percent if the data of van Itterbeek and Keesom are evaluated with values of C_p-C_v based on the PVT tables of this paper.

[12] Up to $\rho=500$ at temperatures above 0° C, the equation $Z=\exp(B\rho+C\rho^2)$ has been used. This is eq 4.8 and eq 4.9 is its series expansion. The symbols stand for functions of T, which are given by eq 4.11 and 4.12.

From $\rho=0$ to $\rho=200$ and $T=14°$ K to 56° K Z can be expressed by $Z=1-(A/T^{3/2})\rho-(C/T^{3/2})\rho^2$, which is equivalent to eq 4.14. The symbols A and C stand for functions of T, whose values are tabulated in table 19.

The specific heat of hydrogen at constant volume has been determined by Eucken [169] for various combinations of temperature and density in the ranges 35° to 110° K and 60 to 150 Amagats.

Joule-Thomson coefficients of hydrogen may be of interest. These may be calculated from eq 4.6. For this calculation there are required: the value of C_p which may be calculated using eq 5.8 or 5.17. Values of Z, $(dZ/dT)_\rho$, and $(dZ/d\rho)_T$ are given explicitly in tables 13, 15, and 17. By using values of C_p for H_2 at 50° C derived from figure 12, the following values of μ for 50° C were obtained by calculation: at $\rho=20$, $\mu=-0.0350$ deg atm^{-1}; $\rho=40, \mu=-0.0364$; $\rho=60, \mu=-0.0378$; $\rho=80$, $\mu=-0.0390$, and $\rho=100$, $\mu=-0.0402$. By extrapolation, one obtains for μ at $\rho=0$ the value -0.0335.

There are no accurate measured Joule-Thomson data for hydrogen for 50° C with which these calculated values of μ may be compared.

Results of measurements on Joule-Thomson effects in hydrogen and deuterium at liquid air and room temperatures have been published recently by Johnston and coworkers [57, 58], with curves showing calculated values for hydrogen based on the tables of this paper.* Considering that the Joule-Thomson coefficients are not obtained with great simplicity from the PVT data and depend sensitively on the trends of the representation, the agreement is considered fairly satisfactory.

The location of the inversion curve for the Joule-Thomson effect in hydrogen on a ρ-T graph may be determined from tables 15 and 17 by finding values of ρ and T for which $T(dZ/dT)_\rho = \rho(dZ/d\rho)_T$, in accordance with eq. 4.6.

An expression for μ in terms of derivatives of the enthalpy, H, is

$$\mu=\frac{(dH/d\rho)_T}{\left(\frac{dH}{d\rho}\right)_T\left(\frac{dP}{dT}\right)_\rho-\left(\frac{dH}{dT}\right)_\rho\left(\frac{dP}{d\rho}\right)_T}. \qquad (5.18)$$

In accordance with this equation the inversion curve may be determined by inspection of the $(H^\circ-H)/RT$ table (table 23), since $\mu=0$ where

$$\left(\frac{d(H^\circ-H)/RT}{d\rho}\right)_T=0. \qquad (5.19)$$

*The tables of this paper were completed before the papers by Johnston and coworkers [57, 58] on the Joule-Thomson coefficients of H_2 and D_2 appeared. Our correlation of PVT data would doubtless have been better if these Joule-Thomson data had been available at the time the correlation was made.

The heavy curve in figure 13 is the inversion curve of hydrogen as given by the correlation of this paper. In locating it, values of P were determined with the help of table 14. For temperatures below 75° K some extrapolation beyond the limit of the tables was necessary. In this extrapolated region the σ versus ρ diagram, figure 6, was worked with, and the relation for the inversion curve on this diagram was used to get the extrapolated part of the inversion curve directly from the σ versus ρ diagram.

In a Joule-Thomson expansion of hydrogen at constant temperature from a high to a very low

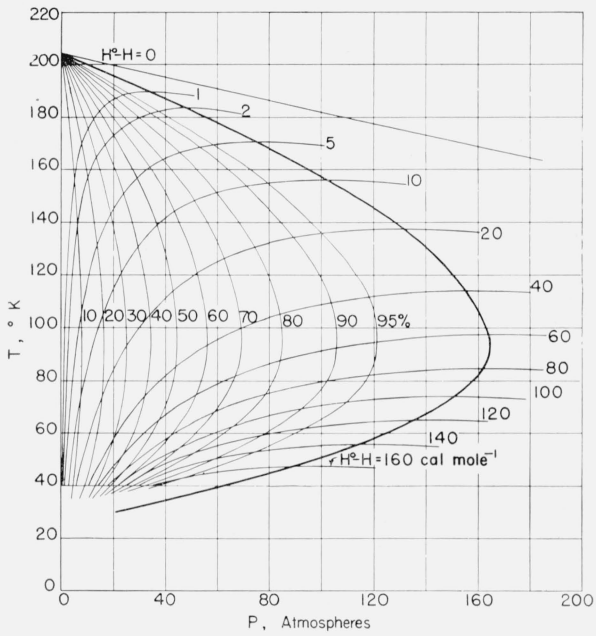

FIGURE 13. *Curves related to the Joule-Thomson cooling of H_2.*

density, approaching zero density, there is a change in enthalpy equal to $(H^\circ-H)$. In figure 13 the curves that cross the inversion curve horizontally are curves of constant $H^\circ-H$. As H° is a function of temperature, these constant $(H^\circ-H)$ curves are not isenthalpics.

The horizontal crossing of the inversion curve by the $(H^\circ-H)$ curve is related to the fact that μ, which is zero along the inversion curve, is equal to $(dH/dP)_T/C_p$, which means that along the inversion curve $(dH/dP)_T$ is zero. The enthalpy change $(H^\circ-H)$ is equal, very nearly, to the amount of refrigeration, per mole of gas, available for the liquefaction of hydrogen in a Hampson or Linde low pressure type of hydrogen liquefier in which a

continuous flow of gaseous hydrogen is allowed to expand from a high to a low pressure without doing work against an external force system. The fraction x of the high pressure hydrogen flow that might, theoretically, be liquefied is

$$x=\frac{H'-H}{H'-H_{liq}}=\frac{H'-H}{(H'-H_{vap})+L_v}, \qquad (5.20)$$

where H and H' are the enthalpies of the compressed and expanded hydrogen at the temperature at which the compressed hydrogen leaves the precooler and enters the last stage interchanger before expansion; L_v is the heat of vaporization of liquid hydrogen at the boiling temperature determined by the pressure of the expanded hydrogen; and $(H_{vap}-H_{liq})=L_v$ is the difference in enthalpies of saturated vapor and liquid in equilibrium at the pressure of the expanded hydrogen. Only a relatively small error is made in x if in place of H' and H_{vap} for the real gas at atmospheric pressure one uses the enthalpies $H°$ and $H°_{vap}$ of hydrogen in the ideal gas state at the same temperatures as would be used for H' and H_{vap}.

$$x=\frac{H°-H}{H°-H°_{vap}+L_v}. \qquad (5.21)$$

For a temperature of precooling equal to 65° K, the error introduced by the approximation is about 0.5 percent.

The lines of figure 13 that are roughly parallel to the inversion curve and converge with it at the inversion point, 204.6° K, are lines showing the pressure at which $H°-H$ has reached a given fraction of its maximum value for the given temperature. As the inversion curve is the line of maximum values of $(H°-H)$ it is also the 100-percent line in this family of constant percentage lines.

In the free expansion of a continuous flow of gas not doing work against an external force system, the maximum refrigeration is obtained by expanding from the inversion pressure for the given temperature of the compressed gas. The curves of constant percentage of maximum values of $(H°-H)$ are also curves of constant percentage of the maximum available refrigeration in an expansion to low pressure.

Figure 13 makes apparent how greatly the refrigeration and the fraction of hydrogen liquefied (eq 5.21) by a Hampson type liquefier are increased by lowering the temperature of the compressed hydrogen before it enters the final interchanger from which expansion of the hydrogen takes place. It is also seen that the condition of highest inversion pressure (92° K and 165 atm) is by no means the most favorable condition for liquefaction; a further cooling of the compressed hydrogen by 32 degrees nearly doubles the refrigeration produced and more than doubles the fraction liquefied. It is also seen from figure 13 that for the usual range of temperatures (55° to 90° K) to which compressed hydrogen is precooled before expansion in a Hampson-type liquefier, about 95 percent of the maximum refrigeration is obtained when the pressure of the compressed gas is only 75 percent of the inversion pressure.

VI. Viscosity and Thermal Conductivity

1. Viscosity and Thermal Conductivity of the Gas Near Atmospheric Pressure

(a) Hydrogen

Values for the viscosity of gaseous normal hydrogen at atmospheric pressure for temperatures above the boiling point and at saturation pressure for two temperatures below the boiling point are given in table 24. These were calculated using the empirical equation

$$\eta=85.558\times10^{-7}\frac{T^{3/2}}{T+19.55}\frac{T+650.39}{(T+1175.9)}\text{ poises} \qquad (6.1)$$

for the viscosity at very low pressure,[13] together with values for the small differences between viscosities at atmospheric or saturation pressure and at very low pressure (see eq 6.17 and 6.16). The four constants of eq 6.1 were chosen on the basis of experimental data near 20°, 90°, 300°, and 685° K. The value used for the viscosity of hydrogen at 685° K was 0.55 percent larger than the experimental values of Trautz and Zink [99], as their value was based on Millikan's value for the viscosity of air which is now known to be low by about this amount.

In figure 14 are plotted deviations of recent experimental viscosity data from eq 6.1. No changes were made in the experimental data for

[13] This viscosity at very low pressure is a true or bulk viscosity. The pressure effect mentioned here is not the familiar low pressure effect on the apparent experimental viscosity involving the accommodation coefficient and the limited size of experimental apparatus.

TABLE 24. *Viscosity of gaseous hydrogen* (H_2)

T	η	T	η	T	η
°K	*Poises*	°K	*Poises*	°K	*Poises*
10	51.0×10^{-7}	260	813.6×10^{-7}	620	$1,461\times10^{-7}$
20	109.3	270	834.6	640	1,493
30	160.7	280	855.3	660	1,524
40	206.8	290	875.8	680	1,555
50	248.9	300	896.0	700	1,585
60	287.6	310	916.0	720	1,616
70	323.8	320	935.8	740	1,646
80	357.9	330	955.4	760	1,675
90	390.3	340	974.8	780	1,705
100	421.1	350	994.0	800	1,734
110	450.8	360	1,013	820	1,763
120	479.3	370	1,032	840	1,792
130	507.0	380	1,051	860	1,820
140	533.8	390	1,069	880	1,848
150	559.8	400	1,087	900	1,876
160	585.2	420	1,124	920	1,904
170	610.0	440	1,160	940	1,932
180	634.3	460	1,195	960	1,959
190	658.1	480	1,230	980	1,986
200	681.4	500	1,264	1,000	2,013
210	704.3	520	1,298	1,020	2,040
220	726.9	540	1,331	1,040	2,066
230	749.0	560	1,364	1,060	2,092
240	770.9	580	1,397	1,080	2,118
250	792.4	600	1,429	1,100	2,144

the differences in density. Deviations of table 24 values from eq 6.1 are represented in figure 14 by the peaked curve, which is appreciably above the zero line between 10° K and 100° K and in very close agreement with it at higher temperatures. This peaked curve represents the viscosity at atmospheric pressure above the boiling point and at saturation vapor pressure below the boiling point. Different reported values of viscosity at low temperatures are so poorly in agreement that their comparison does not indicate the magnitude of the peak, which has accordingly been obtained from theory, using data of state. To limit the crowding of experimental points in the figure, those plotted represent only data published since 1928, but a few data obtained after 1928 have been omitted. The data of Trautz and co-workers [94 to 102] would be in better agreement with the zero line if increased by about one half percent for the revision in the value for the viscosity of air.

It has been pointed out by others that the Sutherland formula

$$\eta=\eta'\left(\frac{T}{T'}\right)^{3/2}\frac{T'+C}{T+C} \qquad (6.2)$$

does not fit the data for hydrogen over an extended range of temperature. This may be seen in figure 14 in which the deviations of the Sutherland formula from eq 6.1 are represented by the curve below the zero line. The constant C was evaluated at 300° K to represent the trend of the best data.

Values of the thermal conductivity of gaseous normal hydrogen are given in table 25.

TABLE 25. *Thermal conductivity of gaseous hydrogen at 1 atm*

T	K	T	K
°K	*cal cm*$^{-1}$ *sec*$^{-1}$ °*C*$^{-1}$	°K	*cal cm*$^{-1}$ *sec*$^{-1}$ °*C*$^{-1}$
10	14.3×10^{-6}	260	397.0×10^{-6}
20	34.6	270	409.7
30	53.5	280	422.1
40	70.7	290	434.2
50	86.5	300	446.3
60	101.4	320	469.8
70	116.1	340	492.8
80	130.8	360	515
90	145.9	380	537
100	161.3	400	559
110	177.0	420	580
120	192.9	440	601
130	208.8	460	622
140	224.6	480	643
150	240.4	500	664
160	256.0	520	684
170	271.4	540	705
180	286.5	560	725
190	301.1	580	745
200	315.4	600	766
210	329.6		
220	343.5		
230	357.2		
240	370.7		
250	384.0		

They were calculated from the equation

$$k=[1.8341-0.004458T+(1.1308+0.0008973T)C_p^\circ]\frac{\eta}{M}\frac{1}{\left(1+\frac{3.2}{T}\right)} \qquad (6.3)$$

In principle, a correction from low pressure to one atmosphere would be applicable, but it has been omitted because the uncertainty of the experimental values is much greater. In eq 6.3, M is the molecular weight, η the viscosity given by eq 6.1, C_p° the specific heat in calories per mole per degree at constant pressure, and T the temperature in degrees Kelvin. This equation is an empirical representation of the data and was

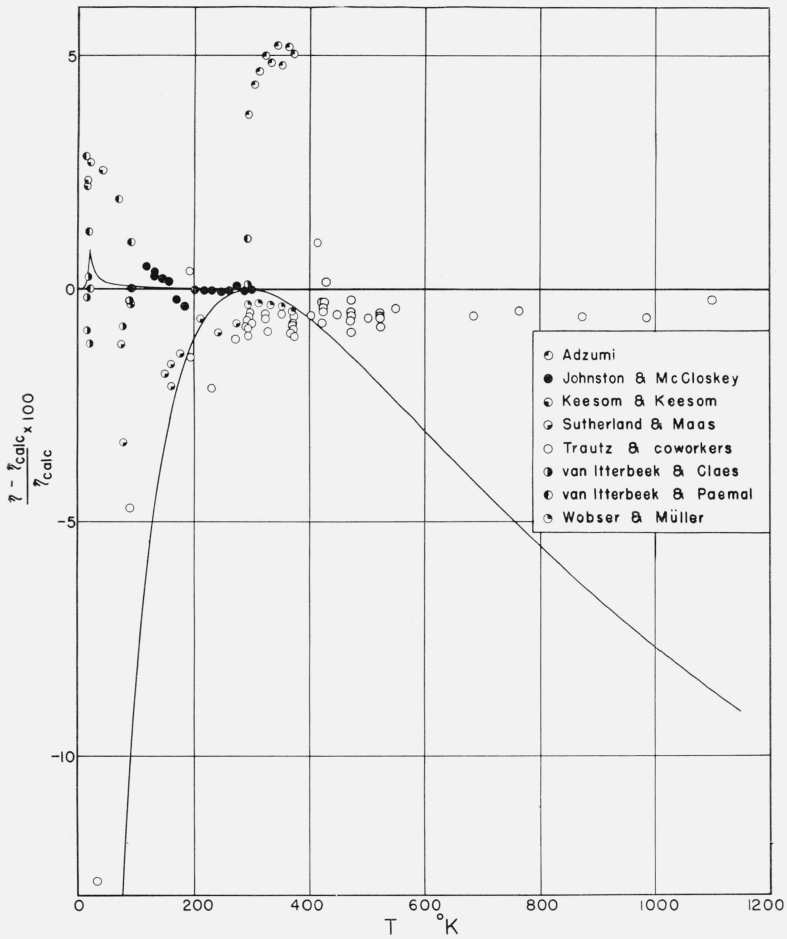

FIGURE 14. *Viscosity of hydrogen.*

obtained in several steps, which will be explained in the discussion that follows.

In figure 15, curve A represents eq 6.3, whereas curves B and C are theoretical and are given for comparison. Curve C is for Eucken's relation

$$k=(9\gamma-5)C_v^\circ\eta/(4M), \tag{6.4}$$

or its equivalent

$$k=(C_p^\circ+1.25R)\eta/M. \tag{6.5}$$

Chapman and Cowling [137] proposed the formula

$$k=\left[\frac{15}{4}(\gamma-1)+\frac{1}{2}U_{11}(5-3\gamma)\right]\eta C_v^\circ/M, \tag{6.6}$$

which is equivalent to

$$k=[U_{11}C_p^\circ+(3.75-2.5U_{11})R]\eta/M. \tag{6.7}$$

The transport of internal molecular energy of a gas is supposed to be represented better theoretically as a result of including the quantity U_{11}, which is the ratio of mean free path lengths for diffusion and viscosity.

U_{11} is a pure number whose value was determined theoretically for (1) smooth elastic spheres and (2) for molecules repelling as the inverse fifth power of the distance (Maxwellian molecules), the values being 1.204 and 1.55, respectively.

For U_{11} equal to 1, curve C is obtained, as eq 6.6 and 6.7 then reduce to eq 6.4 and 6.5. Curve B of figure 15 is a graph of eq 6.7 with $U_{11}=1.4$, a value indicated by a group of measurements of the conductivity near 300° K. It is evident that the main body of the experimental data is not consistent with a constant value of U_{11}. On the basis of a value of 1.4 for U_{11} near 300° K and a higher value at 700° K, as indicated by a curve representing the data, the relation

$$U_{11}=1.1308+0.0008973T \tag{6.8}$$

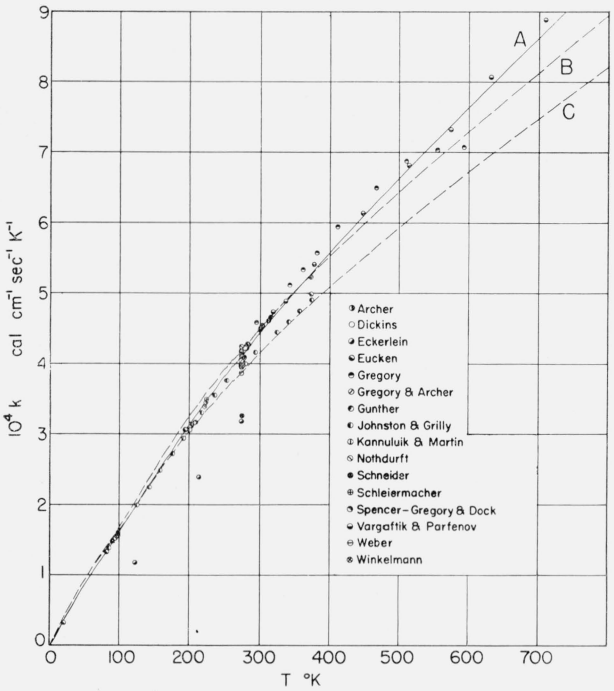

FIGURE 15. *Thermal conductivity of hydrogen.*

was adopted. It was found that the curve was not critically dependent on the functional form of U_{11} as a change to $U_{11}=a+b\sqrt{T}$ altered the final curve negligibly between 300° and 700° K.

At temperatures somewhat below 100° K, the ideal gas specific heat of hydrogen at constant pressure approaches the value $(5/2)R$ characteristic of a monatomic gas. For this value of C_p°, the U_{11} terms in eq 6.7 cancel and eq 6.4 to 6.7 reduce to

$$k=\frac{5}{2}\eta(C_v/M). \tag{6.9}$$

This equation has been derived exactly for a force that at all distances is repulsive and proportional to $1/r^5$. Enskog [132] has shown that for attracting rigid spheres (Sutherland molecules),

$$k=[2.522/1(1+0.03C/T)]\eta C_v/M,$$

where C is the Sutherland constant in eq 6.2. Thermal conductivities of hydrogen measured at liquid air temperatures are a few percent lower than equations 6.4 to 6.9 would indicate. No theoretical explanation of this is at hand, but the agreement of the three independent investigations in this region indicates that the lower value is to be accepted. To take account of this, a correction factor $1/(1+3.2/T)$ has been included, having a form suggested by Enskog's theoretical result for attracting rigid spheres but with the constant chosen to fit these experimental data. The inclusion of this factor also brings the final curve closer to Eucken's experimental value at 20.96° K, which is still almost 12 percent lower than the curve.

The curve as chosen to fit the thermal conductivity data is not regarded as completely satisfactory. In the temperature range 270° to 400° K, the experimental data appear to fall into two groups, one quite close to the curve adopted and the other lower by about 7 percent. The lower group includes the most recent data.

Equation 6.4 to 6.9 make it evident that at low-temperatures where the specific heats of ortho and para hydrogen differ, their thermal conductivities differ also. This difference in thermal conductivity was the basis of the method of ortho-para analysis used by Bonhoeffer and Harteck [121]. The temperature or electrical resistance of an electrically heated wire carrying a given current determines, after calibration, the ortho-para composition of the hydrogen that surrounds the wire in a tube externally thermostated at liquid air temperature. A small difference is to be expected in the viscosities of ortho and para hydrogen by reason of small differences in their intermolecular forces manifested by small differences in vapor pressure, and density of the condensed states.

This difference in viscosities is small and was not detected in the experiment undertaken by Harteck and Schmidt [122], in which an accuracy of 1 percent was attained. In later developments of the so-called thermal conductivity method of ortho-para analysis, the pressure of the gas was reduced to make the mean free path large compared with the diameter of the heated wire. For this condition the ordinary thermal conductivity is not the controlling factor.

(b) Deuterium

Several investigations have been made of the viscosity of deuterium at atmospheric pressure, the most recent being that of Van Itterbeek and Van Paemel [106, 107], published in 1940. Table 26, which gives values for the ratio between viscosities of deuterium and hydrogen for several temperatures, was taken from the paper by Van Itterbeek and Van Paemel.

TABLE 26. *Ratio of viscosities for gaseous* D_2 *and* H_2

T	$\eta(D_2)/\eta(H_2)$
° K	
293	1.40
90	1.38
80	1.37
70	1.36
20	1.24
15	1.24
12.5	1.24

The ratio of the thermal conductivity of deuterium at 0° C to the thermal conductivity of hydrogen also at 0° was determined by C. T. Archer [127] and by W. G. Kannuluik [130], who obtained respectively, the values 0.736_5 and 0.732_4. By using the mean of these values with appropriate values of C_p and η, one obtains for U_{11} in eq 6.7 for the thermal conductivity of D_2 at 0° C the value 1.55. Archer also measured the thermal conductivity of various equilibrium mixtures of H_2, HD, and D_2.

For two isotopic gases with identically the same intermolecular forces, the classical theory values for the ratio of their viscosities, and the ratio of their thermal conductivities at temperatures where their heat capacities are equal are

$$\eta_1/\eta_2 = \sqrt{M_1/M_2} \text{ and } k_1/k_2 = \sqrt{M_2/M_1} \quad (6.10)$$

For H_2 and D_2 these ratios have the values: $\eta_{D_2}/\eta_{H_2} = 1.414$ and $k_{D_2}/k_{H_2} = 0.707$, and are independent of the intermolecular force field so long as it is the same for the two isotopes. The difference between the rotational heat capacities of H_2 and D_2 at low temperatures by itself makes the ratio k_{D_2}/k_{H_2} larger and thus has an effect opposite to but less than that of the smaller mean velocity of D_2 molecules caused by the greater mass. Using Eucken's eq 6.4 for k and making allowance for the difference in heat capacities of H_2 and D_2, one obtains 0.718 for k_{D_2}/k_{H_2} at 0° C. The classical theory values for these ratios of thermal conductivities and viscosities are approached closely at room temperatures. The effect of quantum mechanical interaction in transport phenomena can be described in terms of increase in the apparent size of the molecules. In classical theory the size of the molecule plays an important role, the viscosity and thermal conductivity decreasing as the size increases. For hydrogen and deuterium, the quantum mechanical increase in apparent size is small at room temperature but becomes large at low temperature. The increase depends also upon the masses of the colliding molecules and is larger for H_2 than for D_2 at the same temperature. It was pointed out in the section on the PVT data for deuterium that the quantum theory of second virial coefficients includes an effect interpretable classically as an increase in apparent size of molecules, becoming very large at low temperatures. The quantum mechanically obtained increase in apparent size with lowering of temperature is not the same for viscosity as that associated with the second virial coefficient, however. This is not surprising when one considers that the increase in the mean de Broglie wave length with decreasing temperature increases the diffraction behind a scattering molecule; an effect that does not enter in the determination of the second virial coefficient, but which taken by itself would decrease the apparent size of a scattering molecule for viscosity.

2. Viscosity and Thermal Conductivity of the Gas at High Pressures

There are no experimental data on the thermal conductivity of gaseous H_2 at high pressures. For viscosity, however, experimental data obtained by Boyd [134] and Gibson [135] are available. Gibson's data, which are for 25° C, are more precise than those of Boyd and are plotted in figure 16. It will be seen that there is fairly good agreement between these better experimental data and the curve representing the theoretical formula due to Enskog. Differing approaches to the problem of relating viscosity and variables of state will be found elsewhere [133, 136].

In elementary theory, the viscosity and thermal conductivity for a given gas are proportional to the product of V, ρ, and Λ, where V is the mean molecular velocity, ρ is the density, and Λ is a suitable mean path length for the transfer of momentum or energy. Although Λ is often taken as identical with the ordinary free path of molecular motion, it is actually greater by a small distance of the order of magnitude of a molecular diameter, as at each collision the momenta and energies are transferred an additional distance related to the diameters of the molecules involved. Thus instead of Λ decreasing as $1/\rho$ when ρ is increased, which would make $\rho\Lambda$ independent of

ρ, Λ decreases a little less slowly so as to make $\rho\Lambda$ increase slightly as ρ is increased. Accordingly, both the thermal conductivity and the viscosity of a gas would be expected to increase with increasing density, particularly when multiple encounters between molecules occur frequently as in the case of high densities.

Enskog's theory was developed for a gas whose molecules were assumed to be mutually attracting rigid spheres, for which the equation of state has the form

$$P+a\rho^2=RT\rho(1+b\rho\chi), \tag{6.11}$$

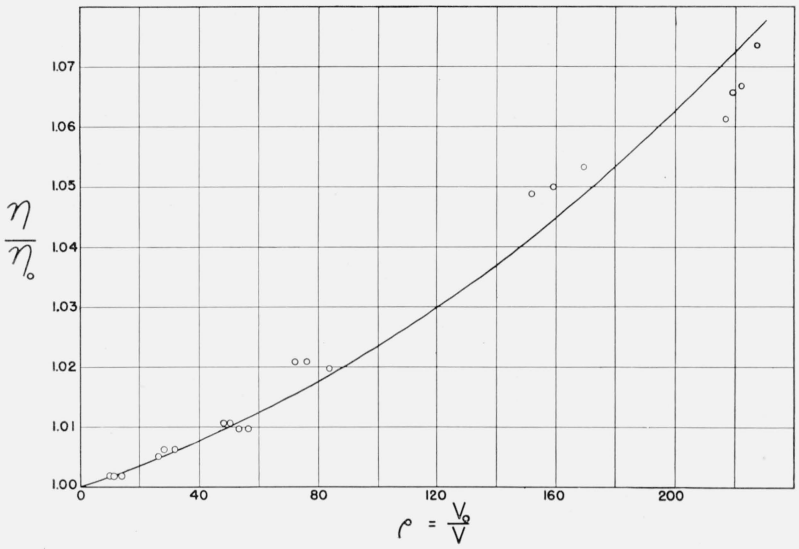

FIGURE 16. *Effect of density on viscosity of hydrogen at 25° C.*

where the constants a and b are assumed to be independent of T and ρ, and χ is a function of ρ expressed in the form of a power series in $b\rho$. The equation of state that was used is thus almost the same as the Van der Waals equation

$$P+a\rho^2=RT\rho(1-b\rho)^{-1}=RT\rho [1+b\rho(1+b\rho+b^2\rho^2+\ldots)] \tag{6.12}$$

except for the details of the dependence of χ upon ρ. The Van der Waals equation is derived on the basis that simultaneous encounters of three or more molecules are rare enough to be neglected. Only at low pressures is this valid and under this condition terms of the second degree and higher in $b\rho$ are neglected in the derivation. The function

$$\chi=1+0.625b\rho+0.2869b^2\rho^2+\ldots \tag{6.13}$$

used by Enskog takes account of simultaneous encounters of three and four molecules as treated by Boltzmann and Clausius.

According to Enskog's theory, the viscosity and thermal conductivity of a compressed gas are related to the viscosity η_0 and conductivity k_0 at low pressure by the equations

$$\eta/\eta_0=b\rho[1/(b\rho\chi)+0.8+0.7614b\rho\chi\ \ldots\ ] \tag{6.14}$$

and

$$k/k_0=b\rho[1/(b\rho\chi)+1.2+0.7574b\rho\chi\ \ldots\ ] \tag{6.15}$$

It follows from eq 6.11, the equation of state assumed for Enskog's theory, that

$$b\rho\chi=\frac{T}{P}\left(\frac{dP}{dT}\right)_\rho\left(\frac{PV}{RT}\right)-1=Z-1+T\left(\frac{dZ}{dT}\right)_\rho. \tag{6.16}$$

Thus, the value of $b\rho\chi$ may be calculated from the tables of Z and $(dZ/dT)_\rho$ and the value of $b\rho$ may then be found with the help of eq 6.13.

Over the range of Gibson's experimental viscosity data very little change is made in the values predicted if simple power series expansions in $b\rho\chi$, obtained from equations 6.14 and 6.15, are used:

$$\eta/\eta_0=1+0.175b\rho\chi+0.7557(b\rho\chi)^2-0.405(b\rho\chi)^3 \tag{6.17}$$

$$k/k_0=1+0.575b\rho\chi+0.5017(b\rho\chi)^2-0.204(b\rho\chi)^3 \tag{6.18}$$

The coefficient of the last term of each equation would be changed if higher order terms were added to eq 6.13, 6.14, and 6.15. Dropping the last term of eq 6.17 for η/η_0 does not significantly change the agreement with Gibson's experimental data.

In order to show the general magnitude of the theoretical effect of pressure on the viscosity and thermal conductivity of hydrogen the preceding equations have been evaluated for several additional combinations of temperature and pressure, using data from the PVT tables. Table 27 gives the values thus obtained. It is seen that the calculated relative change in η and k with pressure is much more pronounced at the lower temperatures, for which large deviations from the ideal gas law occur even at moderate pressures.

TABLE 27. *Effect of pressure on viscosity and thermal conductivity of hydrogen*

T	P	η/η_0	k/k_0
°K	atm		
18	0.455	1.0045	1.0138
20	.889	1.0077	1.0225
22	1.565	1.0126	1.0347
30	1	1.0037	1.0114
30	2.04	1.0086	1.0248
38	30.4	1.53	1.76
40	1	1.0021	1.0068
40	2.80	1.0067	1.0199
40	37.2	1.53	1.76
50	1	1.0015	1.0048
50	3.55	1.0060	1.0178
50	50	1.31	1.49
60	1	1.0012	1.0037
70	1	1.0009	1.0030
70	5.06	1.0051	1.0155
70	50	1.11	1.22
80	1	1.00075	1.0024
90	1	1.00065	1.0021
90	6.56	1.0047	1.0141
90	50.0	1.06	1.13
100	1	1.00056	1.0018
110	1	1.00049	1.0016
150	1	1.00034	1.0011
250	1	1.00018	1.0006
400	1	1.00010	1.0003
600	1	1.00006	1.0002

3. The Viscosity of Liquid Hydrogen

The first determination of the viscosity of liquid hydrogen was made in 1917 by Verschaffelt and Nicaise [138] from measurements of the logarithmic decrement of the oscillatory rotation of a sphere in liquid hydrogen at 20.36° K. Later, determinations were made of the viscosity of liquid hydrogen from 15° to 20° K, in 1938 by Keesom and Mac Wood [139] from measurements of the logarithmic decrement of an oscillating disc, and in 1939 by Johns [140], using the capillary flow method. The reported viscosities are

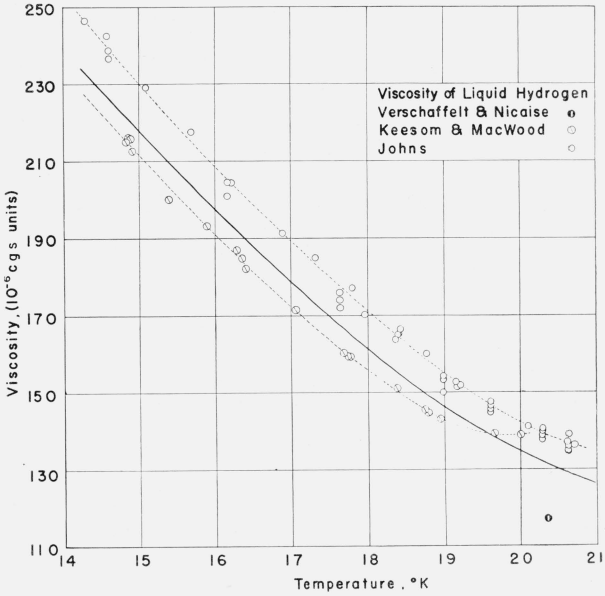

FIGURE 17. *Viscosity of liquid hydrogen.*

shown in figure 17. The values obtained by Johns are roughly 10 percent greater than those of Keesom and Mac Wood except near the boiling point, 20.4° K. There seems to be no clear indication in the papers reporting the measurements that either of these two later sets is less dependable than the other. Accordingly a curve to represent the present most probable values of the viscosity of liquid hydrogen was drawn principally between the two sets. Near the boiling point the curve was drawn approximately parallel to that of Johns because it was felt that the lower value of Verschaffelt and Nicaise supported the more regular variation of viscosity with temperature as reported by Johns.

VII. Pressure Temperature Relations for Two-Phase Equilibria for H_2, HD, and D_2 as Single Components

In this section are presented data on (1) vapor pressures of solid and liquid H_2, HD, and D_2 with such derived constants as normal boiling temperatures and triple-point temperatures and pres-

sures; differences between the vapor pressures of different mixtures of o- and p-H_2; and changes in vapor pressures of ortho-para H_2 mixtures resulting from self conversion; (2) the pressure-temperature relations for the solid-liquid equilibrium of H_2, HD, and D_2. The data are presented in the form of equations, tables, and graphs.

1. Vapor Pressures, Boiling, and Triple Points [14]

The present vapor-pressure data on the hydrogens can be fitted with equations of the form

$$\log_{10}P = A + B/T + CT \qquad (7.1)$$

to within the accuracy of the experimental data. The millimeter of Hg at 0° C and standard gravity is used in this section as the unit of vapor pressure. Temperatures are on the Kelvin Scale.

In tables 28 and 29 the vapor pressures, boiling points, and triple points of the different isotopic and ortho-para modifications of hydrogen are compared.

(a) H_2

The differences between the hydrogen vapor-pressure data reported in the literature [143 to 146, 148] are the result, principally, of differences in the temperature scales used by different observers and of unknown differences in the ortho-para composition of the hydrogen.

The vapor-pressure data recently obtained [146] at the National Bureau of Standards are on the low-temperature scale established at the National Bureau of Standards and are for known ortho-

[14] Boiling-point and triple-point data from this section have been used in advance of publication in the "Tables of Selected Values of Chemical Thermodynamic Properties" prepared by the National Bureau of Standards in conjunction with the Office of Naval Research of the U. S. Navy Department.

TABLE 28. *Vapor pressures of the several isotopic varieties of hydrogen at integral temperatures and at their triple points and boiling points.*

[Values marked (*) were obtained by extrapolation of the vapor-pressure equation to temperatures at which no data were available. The o-H_2 table is based on an extrapolation with respect to composition.]

T	20.4° K Equilibrium hydrogen 0.21 percent o-H_2		Normal hydrogen 75 percent o-H_2		Orthohydrogen 100 percent o-H_2		Normal deuterium 66.67 percent o-D_2		20.4° K Equilibrium deuterium 97.8 percent o-D_2		Hydrogen deuteride	
	P	State	P	State	P	State	P	State	P	State	P	State
° K	mm Hg		mm Hg		mm Hg		mm Hg		mm Hg		mm Hg	
10	1.93	Solid*	1.7_3	Solid*		Solid	0.05	Solid*	0.05	Solid*	0.28	Solid.*
11	5.62	Solid	5.0_9	Solid		do	.20	do	.21	do	.99	Solid.
12	13.9	do	12.7	do		do	.73	do	.75	do	2.94	Do.
13	30.2	do	27.9	do		do	2.14	do	2.20	do	7.46	Do.
13.81_3	52.8	Triple point.	49.1	do		do	4.61	do	4.73	do	14.6	Do.
13.95_7	57.4	Liquid	54.0	Triple point		do	5.24	do	5.37	do	16.3	Do.
14	58.8	do	55.4	Liquid		do	5.44	Solid	5.57	Solid	16.8	Do.
14.05	60.5	do	57.0	do	55.1	Triple point*	5.68	do	5.82	do	17.5	Do.
15	100.4	do	95.0	do	92.2	Liquid*	12.3	do	12.6	do	34.4	Do.
16	161.2	do	153.3	do	149.1	do	25.4	do	26.0	do	65.2	Do.
16.60_4	209.3	do	199.7	do	194.4	do	37.9	do	38.7	do	92.8	Triple point.
17	246.2	do	235.2	do	229.2	do	48.6	do	49.6	do	112.5	Liquid.
18	360.6	do	345.9	do	337.8	do	87.2	do	88.7	do	176.4	Do.
18.69_1	459.8	do	442.0	do	432.3	do	126.3	do	128.5	Triple point	234.5	Do.
18.72_3	464.9	do	446.9	do	437.1	do	128.5	Triple point	130.3	Liquid	237.5	Do.
19	510.1	do	490.8	do	480.7	do	145.1	Liquid	147.2	do	264.7	Do.
20	700.3	do	675.7	do	662.6	do	219.9	do	223.1	do	382.8	Do.
20.27_3	760	do	733.9	do	720.0	do	244.9	do	248.4	do	420.9	Do.
20.39_0	786.8	do	760	do	745.7	do	256.2	do	259.9	do	438.1	Do.
20.45_4	801.7	Liquid*	774.4	Liquid*	760	do	262.5	Liquid*	266.2	Liquid*	447.7	Liquid.*
21	937.0	do	906.4	do	890.6	do	322.2	do	326.9	do	536.2	Do.
22	1226.6	do	1189.0	do	1170.4	do	458.5	do	465.1	do	730.5	Do.
22.13_3	1269.4	do	1230.8	do	1211.8	do	479.6	do	486.5	do	760	Do.
23	1574.9	do	1529.6	do	1508.4	do	636.2	do	645.3	do	972.0	Do.
23.52_7	1784.4	do	1734.5	do	1712.2	do	749.3	do	760	do	1120.1	Do.
23.57_3	1803.5	do	1753.3	do	1730.8	do	760	do	770.6	do	1133.8	Do.

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TABLE 29. *Boiling points and triple points of the hydrogens*

	Boiling point	Triple point	
		T	P
	° K	° K	mm Hg
20.4° K equilibrium hydrogen (0.21% o-H_2)	20.27_3	13.81_3	52.8
38 percent o-H_2, 62 percent p-H_2	20.32	13.86	53.0
Normal hydrogen (75% o-H_2)	20.39_0	13.95_7	54.0
Orthohydrogen	20.45	14.05	55.1
Normal deuterium (66.67% o-D_2)	23.57_3	18.72_3	128.5
20.4° K equilibrium deuterium (97.8% o-D_2)	23.52_7	18.69_1	128.5
Paradeuterium	23.66	18.78	128.5
Hydrogen deuteride	22.13_3	16.60_4	92.8

para compositions. Only the NBS results are given here.

Normal hydrogen (75 percent o-H_2, 25 percent p-H_2):

$$\text{Liquid: } \log_{10}P(\text{mm Hg})=4.66687-\frac{44.9569}{T}+0.020537T. \tag{7.2}$$

$$\text{Solid: } \log_{10}P(\text{mm Hg})=4.56488-\frac{47.2059}{T}+0.03939T. \tag{7.3}$$

20.4°K-equilibrium hydrogen (99.79 percent p-H_2, 0.21 percent o-H_2:

$$\text{Liquid: } \log_{10}P(\text{mm Hg})=4.64392-\frac{44.3450}{T}+0.02093T. \tag{7.4}$$

$$\text{Solid: } \log_{10}P(\text{mm Hg})=4.62438-\frac{47.0172}{T}+0.03635T. \tag{7.5}$$

The triple-point temperatures and pressures were determined experimentally with a low-temperature calorimeter with a platinum resistance thermometer for the temperature measurements. Equations 7.2 to 7.5 were made to fit these triple points, and are based on vapor pressure data extending from 10.5° to 20.4° K. Although the equation for liquid normal H_2 is based only on National Bureau of Standards data below 20.4° K, the equation represents, within the limits of experimental accuracy, the Leiden data that extend nearly to the critical point, 33.19° K. As mentioned in section IV, the vapor-pressure equation for normal hydrogen was used in constructing the PVT relations for hydrogen. The experimentally determined triple-point temperatures and pressures for n-H_2 and e-H_2 are given in tables 28 and 29.

Figure 18 is a diagram of differences between the vapor pressures of a 20.4°K equilibrium mixture of o- and p-H_2 (0.21 percent o-H_2) and five different mixtures of o- and p-H_2 in the liquid state. The vapor pressure of the 20.4°K equilibrium mixture is denoted by $P_{(e-H_2)}$ and that of any other mixture by $P_{(\text{mixture})}$. Each curve of the graph is for a single mixture whose composition is indicated on the graph by its o-H_2 composition. The 75 percent curve is for normal hydrogen. The vapor pressure differences ΔP are plotted as a function of the vapor pressure of the 20.4°K equilibrium hydrogen. The circles represent the experimental data.

Figure 19 shows the vapor pressure differences of figure 18 extended into the solid range, for mixtures of 38 and 75 percent ortho composition. At the extreme right of the figure, these mixtures and the e-H_2 with which they are compared are all liquid. Passing to the left, the first sharp break encountered on either curve corresponds to the triple point of the mixture. The second sharp break corresponds to the triple point of e-H_2. To the left of the last break, both materials are solid. Between the two breaks on either curve, the mixture is solid but the e-H_2 is liquid.

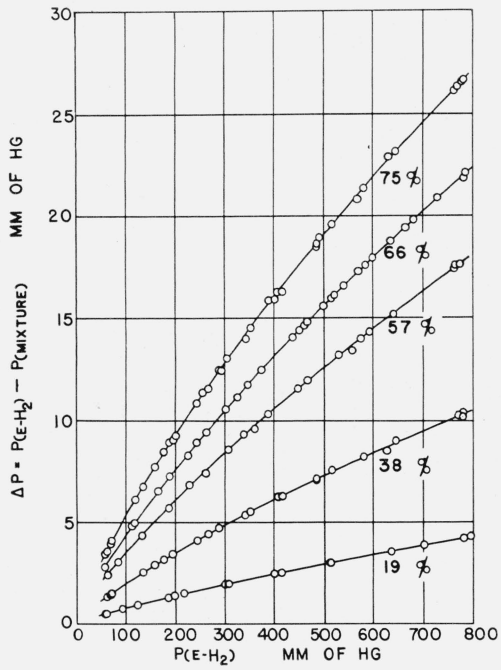

FIGURE 18. *Vapor pressure differences for liquid ortho-para H_2 mixtures.*

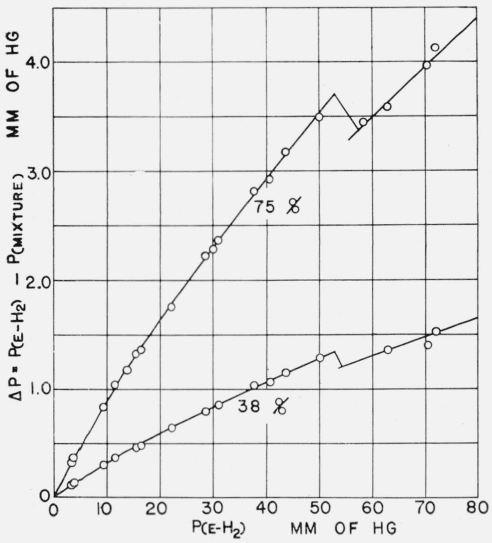

FIGURE 19. *Vapor pressure differences for solid ortho-para* H_2 *mixtures.*

A comparison of the ΔP's for different mixtures of o- and p-H_2 in figures 18 and 19 shows that the ΔP's are not proportional to their corresponding differences in composition.

For ideal solutions the ratio $\Delta P/\Delta x$, where Δx is the difference in composition, is independent of the composition at constant temperature. In figure 20 this ratio is plotted for four temperatures, the circles representing the experimental vapor pressure data as given by points on the smooth curves of figure 18. Figure 20 shows that the vapor pressures of ortho-para mixtures differ greatly from ideal solution predictions.

The vapor pressure differences ($P_{e-H_2}-P_m$) for mixtures of o- and p-H_2 of any composition at 14.00°, 16.00°, 18.00° and 20.39° K may be calculated from the isotherms of figure 20. Other isotherms may be determined with the help of figures 18 and 19. By extending the isotherms of figure 20 to 100 percent o-H_2, the vapor pressure of pure liquid o-H_2 was determined. The following equation represents the vapor pressures of pure liquid o-H_2 obtained in this way:

$$\text{liquid: } \log_{10}P(\text{mm Hg})=4.65009-\frac{45.0439}{T}+0.021168T \qquad (7.6)$$

The triple-point temperature and pressure of o-H_2 were determined by a quadratic extrapolation of the triple point temperatures and pressures of e-H_2(20.4° K), m-H_2(38 percent o-H_2) and n-H_2. The values thus obtained for o-H_2 were 14.05° K and 55.1 mm Hg. These are in agreement with eq 7.6 for the vapor pressure of liquid o-H_2.

If linear extrapolation is used, omitting the values for m-H_2, one obtains 14.00° K and 54.4 mm Hg as lower limiting values of the triple point constants for o-H_2. The triple point constants of m-H_2 were obtained by reading the values $P(e\text{-}H_2)$ and ΔP corresponding to the upper break in the 38 percent curve. The difference of these is the triple point pressure of m-H_2. By substituting $P(\text{e-}H_2)$ into the vapor pressure equation (eq 7.4) for liquid e-H_2, the triple point temperature of m-H_2 is obtained. The uncertainties in these derived triple point constants of m-H_2 and o-H_2 are greater than for the experimentally determined values for e-H_2 and n-H_2.

The vapor pressure of a nonequilibrium mixture of o- and p-H_2 changes slowly with time because of the slow conversion of a nonequilibrium mixture, liquid or solid, to the equilibrium composition. At its normal boiling point, the vapor pressure of n-H_2 changes at the rate of 0.23 mm Hg per hour [148]. Paramagnetic substances increase the rate of conversion. The rate of increase of the vapor pressure at 20.4° K of a sample of hydrogen containing 0.01 percent oxygen was about three times that for pure hydrogen.

The interconversion of ortho and parahydrogen in the absence of molecular dissociation is the result of an intra-molecular rearrangement of pro-

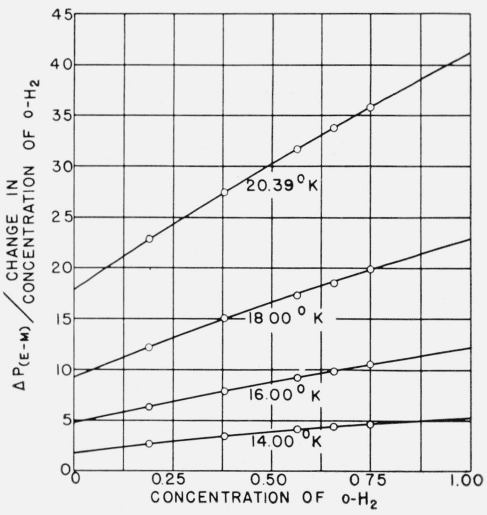

FIGURE 20. *Deviations of vapor pressure of ortho-para* H_2 *mixtures from law of ideal solutions.*

tons in the presence of a strong magnetic field, inhomogeneous on a scale of molecular dimensions.

As p-H_2 has no net nuclear magnetic moment, the self conversion of nonequilibrium mixtures results only from the interaction of o-H_2 molecules, which do have a nuclear magnetic moment, with each other and with p-H_2 molecules. Hence, the ortho-para conversion in liquid and solid H_2 is a bimolecular change.

$$-d[o\text{-}H_2]/dt = k_1[o\text{-}H_2]^2 - k_2[o\text{-}H_2]\,[p\text{-}H_2] \quad (7.7)$$

The velocity constant k_2 is much smaller than k_1 in accord with the small equilibrium proportion of o-H_2. At equilibrium, where $d[o\text{-}H_2]/dt$ is zero, $k_2/k_1 = [o\text{-}H_2]/[p\text{-}H_2]$. Values of equilibrium concentrations are given in table 12. For liquid hydrogen the velocity constant k_1 for conversion is 0.0114 per hour when concentrations are expressed in mole fractions. The value of k_1 for solid H_2, 0.019 hr^{-1} [147], is larger than for liquid H_2 but decreases with time due to the immobility of molecules in the solid. The initial value of k_1 is restored however by melting and freezing.

(b) D_2

The vapor pressures of normal and equilibrium deuterium were measured [149] relative to the vapor pressure of liquid n-H_2 from 14° to 20.4° K. As these measurements are independent of a temperature scale their functional relations are given. Vapor pressures are expressed in terms of mm of Hg at standard conditions.

Normal deuterium (66.67 percent o-D_2, 33.33 percent p-D_2):

$$\text{Liquid: } \log_{10} P(n\text{-}D_2) = -1.3376 + 1.3004 \log_{10} P\,(n\text{-}H_2). \quad (7.8)$$

$$\text{Solid: } \log_{10} P(n\text{-}D_2) = -1.9044 + 1.5143 \log_{10} P(n\text{-}H_2). \quad (7.9)$$

20.4K Equilibrium deuterium (97.8 percent o-D_2, 2.2 percent p-D_2):

$$\text{Liquid: } \log_{10} P(e\text{-}D_2) = -1.3302 + 1.3000 \log_{10} P\,(n\text{-}H_2). \quad (7.10)$$

$$\text{Solid: } \log_{10} P(e\text{-}D_2) = -1.8873 + 1.5106 \log_{10} P\,(n\text{-}H_2). \quad (7.11)$$

Substituting for $\log_{10} P(n\text{-}H_2)$ values given by eq. 7.2 for liquid n-H_2 the following equations for $\log_{10} P(D_2)$ are obtained:

Normal deuterium (66.67 percent o-D_2, 33.33 percent p-D_2):

$$\text{Liquid: } \log_{10} P(\text{mm Hg}) = 4.7312 - \frac{58.4619}{T} + 0.02671\,T. \quad (7.12)$$

$$\text{Solid: } \log_{10} P(\text{mm Hg}) = 5.1626 - \frac{68.0782}{T} + 0.03110\,T. \quad (7.13)$$

20.4°K equilibrium deuterium (97.8 percent o-D_2, 2.2 percent p-D_2)

$$\text{Liquid: } \log_{10} P(\text{mm Hg}) = 4.7367 - \frac{58.4440}{T} + 0.02670\,T. \quad (7.14)$$

$$\text{Solid: } \log_{10} P(\text{mm Hg}) = 5.1625 - \frac{67.9119}{T} + 0.03102\,T. \quad (7.15)$$

The triple-point temperatures and pressures for D_2 given in tables 28 and 29 were obtained by simultaneous solution of the vapor pressure equations for solid and liquid.

The self conversion of nonequilibrium mixtures of o- and p-D_2 proceeds at a very much slower rate than for H_2. Thus no increase in the vapor pressure of liquid n-D_2 resulting from self conversion was observed at 20.4° K over a period of 100 hours [149]. The estimated probable error of two observations extending over 100-hour periods was ±0.27 mm Hg. The small rate of self conversion of D_2, compared with H_2, is a result of the smaller magnetic moment of the deuteron compared with the proton. The ratio of nuclear magnetic moments D/H is 0.26. The relative rate of self conversion for the same displacements of D_2 and H_2 from the equilibrium ortho-para composition is proportional, *as to order of magnitude only*, to the fourth power of their relative magnetic moments, that is to 0.005. Allowing for the smaller displacement of n-D_2 from equilibrium composition and the smaller difference between the vapor pressures of the ortho and para varieties of D_2, the expected ratio of the rates of vapor pressure change, n-D_2 to n-H_2, is of the order of 10^{-3}. For a more detailed discussion see reference [149].

(c) HD

As the two nuclei of the HD molecule are dissimilar, hydrogen deuteride does not have ortho and para varieties. Measurements of the vapor

pressure of HD extend from 10.4° to 20.4° K [150]. The following vapor-pressure equations were made to fit the triple-point temperature 16.60_4° K measured with a platinum resistance thermometer in a calorimeter in which the solid and liquid phases were in equilibrium.

HD:

$$\text{Liquid: } \log_{10} P \text{ (mm Hg)} = 5.04964 - \frac{55.2495}{T} + 0.01479\,T \qquad (7.16)$$

$$\text{Solid: } \log_{10} P \text{ (mm Hg)} = 4.70260 - \frac{56.7154}{T} + 0.04101\,T \qquad (7.17)$$

The triple-point pressure of HD given in tables 28 and 29 can be obtained from either of these equations.

(d) HT and DT

Tritium, T, the hydrogen isotope of atomic weight 3 is radioactive and has a half-lifetime of 31 ± 8 years [151]. Its disintegration products are a negative β-particle and He^3. Because of its comparatively short half-life, the natural abundance of T in hydrogen is extremely small. Libby and Barter [152] determined the vapor pressures of HT and DT using T made by the irradiation of a block of metallic Li with neutrons ($Li^6 + n \rightarrow He^4 + T^3$). The tritium held by the Li as LiT was liberated by the reaction of H_2O or D_2O with the Li block. Gaseous H_2 or D_2 with a trace of HT or DT was obtained. The gas was liquefied and then evaporated, and the radioactivity of the evaporated vapor was measured as a function of the volume of the remaining unevaporated liquid. From a comparison of the radioactivity of the vapor leaving the liquid during different periods of the evaporation, Libby and Barter calculated the vapor pressures of HT and DT, making use of ideal solution laws for this purpose. They obtained for the vapor pressures of HT and DT, 254 ± 16 and 123 ± 6 mm Hg, respectively, at the normal boiling temperature of hydrogen (20.39° K). By extrapolation, they estimated that the vapor pressure of T_2 at 20.39° K is 45 ± 10 mm Hg.

2. Pressure-Temperature Relations for Solid-Liquid Equilibrium

The melting, or freezing pressures, of n-H_2, HD, and n-D_2 given in table 30 are based on smooth curves drawn through the experimental data (H_2, [153 to 157]; HD [150]; D_2 [174]) and cover the same ranges of pressure and temperature as the data. Figure 21 is a diagram of the deviations of the data for n-H_2 from the table. The dashed line shows a 1-percent deviation from the table and the full-line curve represents the deviation from the table of the equation

$$\log_{10}(237.1 + P) = 1.85904 \log_{10} T + 0.24731, \qquad (7.18),$$

where P is in kg cm^{-2}.

TABLE 30. *Melting temperature-pressure relations for n-H_2, HD, and n-D_2*

T	P		
	n-H_2	HD	n-D_2
°K	kg cm^{-2}	kg cm^{-2}	kg cm^{-2}
13.96	0.07	--------	--------
14	1.4	--------	--------
15	33.2	--------	--------
16	67.3	--------	--------
16.60	--------	0.13	--------
17	103.5	14.2	--------
18	142.3	52.6	--------
18.72	--------	--------	0.17
19	183.6	92.9	13.9
20	227.1	--------	56.0
21	272.3	--------	100.0
22	318.6	--------	--------
23	366.0	--------	--------
24	415.0	--------	--------
25	465.6	--------	--------
26	518	--------	--------
27	572	--------	--------
28	628	--------	--------
29	685	--------	--------
30	744	--------	--------
32	867	--------	--------
34	996	--------	--------
36	1,131	--------	--------
38	1,274	--------	--------
40	1,422	--------	--------
45	1,821	--------	--------
50	2,258	--------	--------
55	2,735	--------	--------
60	3,249	--------	--------
65	3,801	--------	--------
70	4,389	--------	--------
75	5,014	--------	--------
80	5,674	--------	--------

Figure 22 is intended to show the relation between the melting pressures of n-H_2, HD, and n-D_2. The curve for n-H_2 is a graph of table values. The curves through the experimental

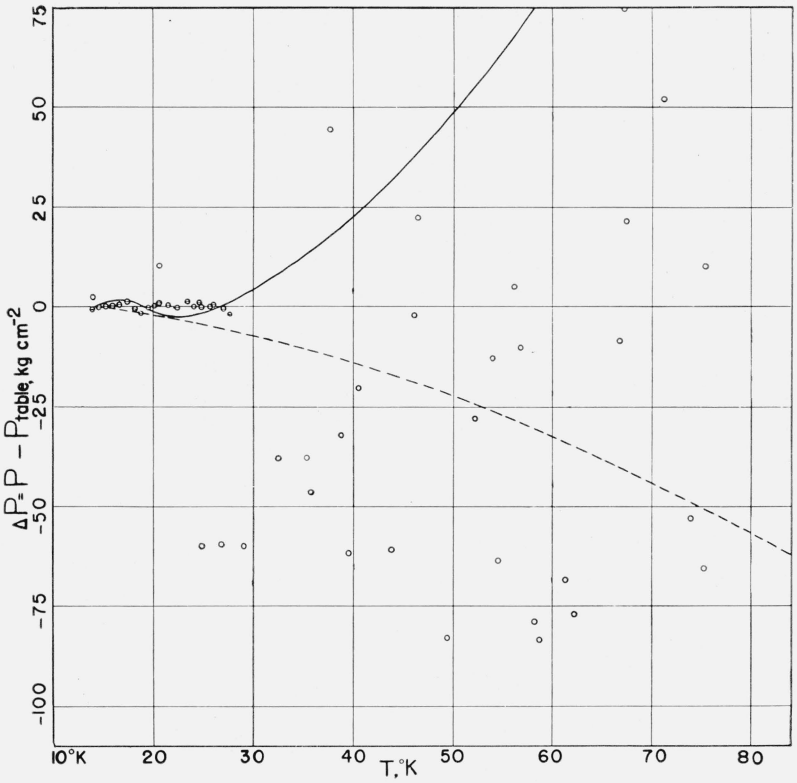

FIGURE 21. *Melting pressure of n-H_2 as a function of temperature.*

data for HD and D_2 were obtained by a simple vertical displacement of the H_2 curve and show that the differences in melting pressures of the three isotopic varieties are only slightly dependent upon the temperature. These differences in pressure are 89.6 kg cm^{-2} for H_2 and HD and 170.6 kg cm^{-2} for H_2 and D_2. As the change of melting pressure with temperature, dP/dT, has nearly the same value for H_2, HD, and D_2, if compared at the same temperature, it follows from the Clapeyron equations that $L_f/\delta V$, the ratio of the heat of fusion to the change in volume on melting, also has nearly the same value for the three isotopes when compared at the same value of T. A similar statement can be made for $S_f/\delta V$, the ratio of the entropy of fusion to the change in volume on melting.

The table values of melting pressure for HD and D_2 were obtained from curves drawn through the experimental data and not from the curves of figure 22.

VIII. PVT Data for the Condensed States

The available date of state for the condensed phases of H_2, HD, and D_2 are meager [158 to 166] and in general not accurate enough for the calculation of reliable values of thermodynamical properties. The data on the liquid, however, were used in the construction of the liquid regions of the σ versus ρ diagrams, figure 6, and the T versus S diagram, figures 31, 32, and 33.

1. Liquid H_2, HD, and D_2

In table 31 are given the molar volumes of liquid n-H_2, p-H_2, HD, and n-D_2 in equilibrium

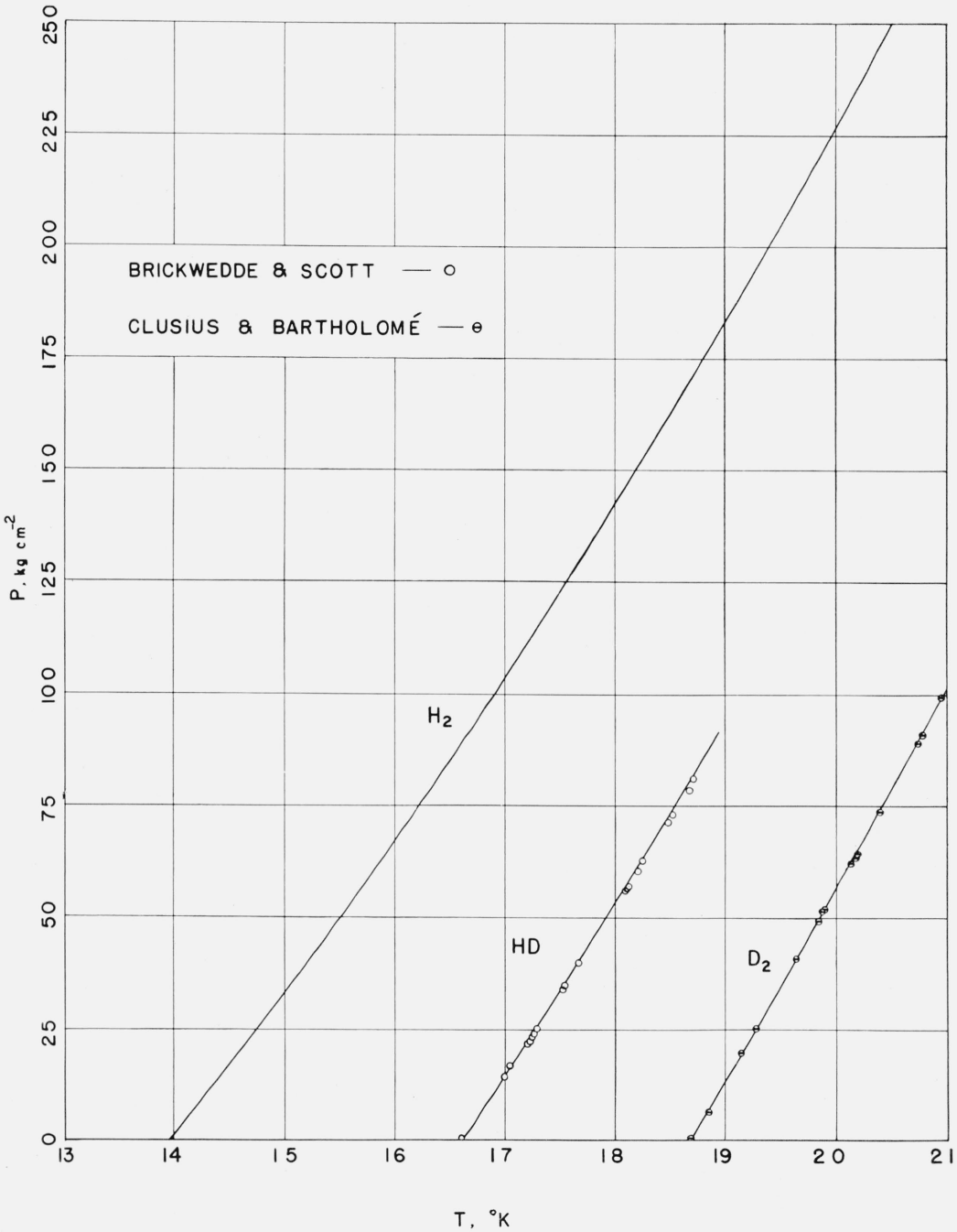

FIGURE 22. *Melting pressures of* n-H_2, HD, *and* n-D_2.

TABLE 31. *Molar volumes of normal hydrogen, parahydrogen, normal deuterium, and hydrogen deuteride, in the liquid state*

T	Volume of liquid at saturation pressure			
	n-H_2	p-H_2	n-D_2	HD
°K	*cm³ mole⁻¹*	*cm³ mole⁻¹*	*cm³ mole⁻¹*	*cm³ mole⁻¹*
13.813	--------	26.176	--------	--------
13.96	26.108	--------	--------	--------
14	26.119	26.227	--------	--------
15	26.407	26.518	--------	--------
16	26.721	26.836	--------	--------
16.604	--------	--------	--------	24.487
17	27.061	27.179	--------	24.594
18	27.426	27.549	--------	24.885
18.723	--------	--------	23.162	--------
19	27.816	27.945	23.237	25.211
20	28.232	28.368	23.525	25.572
20.39	28.401	--------	--------	--------
22	29.233	--------	--------	--------
24	30.451	--------	--------	--------
26	31.995	--------	--------	--------
28	34.059	--------	--------	--------
30	37.138	--------	--------	--------
32	43.211	--------	--------	--------
33.19	66.95	--------	--------	--------

with vapor from the triple point to the highest temperature of measurement. From the triple point to 20.4° K, these equilibrium molar volumes have been represented by the following equations, in which temperatures are on the Kelvin scale:

Normal hydrogen [163]:

$$V(\text{cm}^3\ \text{mole}^{-1})=24.747-0.08005T+0.012716T^2. \tag{8.1}$$

Parahydrogen [163]:

$$V(\text{cm}^3\ \text{mole}^{-1})=24.902-0.0888T+0.013104T^2. \tag{8.2}$$

Hydrogen deuteride [150]:

$$V(\text{cm}^3\ \text{mole}^{-1})=24.886-0.30911T+0.01717T^2. \tag{8.3}$$

Normal deuterium [174]:

$$V(\text{cm}^3\ \text{mole}^{-1})=22.965-0.2460T+0.0137T^2. \tag{8.4}$$

Table values at 20.39° K and lower were calculated from these equations. Values of the molar volume of liquid normal hydrogen above 20.4° K were obtained from the experimental data of Mathias, Crommelin, and Onnes [161] with the help of a sensitive interpolation method based upon the use of an empirical equation and a deviation graph. A change was made in the experimental data because the value used by Mathias, Crommelin, and Onnes for the density of gaseous hydrogen at standard conditions differs from that recommended in this paper on page 396.

Bartholomé [177] measured the molar volumes of liquid n-H_2 and n-D_2 as a function of pressure at three temperatures between 16° and 21° K. The measurements extended from the vapor pressure to nearly the freezing pressure. Smoothed values of molar volumes are given in tables 32 and 33. Bartholomé showed that isothermal changes in volume to about 9 percent of the volume of "saturated" liquid can be represented to within the precision of his measurements, ± 0.05 cm³ mole⁻¹ by Eucken's equation

$$\frac{1}{V^3}=\frac{1}{2}\left[\frac{1}{v_0^3}+\sqrt{\frac{1}{v_0^6}+aP}\right], \tag{8.5}$$

in which V, the molar volume of the liquid, is expressed as a function of the pressure P. v_0 is the molar volume extrapolated to zero pressure, and a is an empirical constant dependent upon the temperature. Tables 32 and 33 include values of the molar volumes of liquid n-H_2 and n-D_2 at freezing pressure for the three temperatures of Bartholomé's measurements.

TABLE 32. *Molar volumes of liquid n-H_2 for various temperatures and pressures.*

Pressure	T=16.43° K	T=18.24° K	T=20.33° K
kg cm⁻²	*cm³ mole⁻¹*	*cm³ mole⁻¹*	*cm³ mole⁻¹*
0[a]	26.87	27.54	28.43
10	26.59	27.18	27.97
25	26.20	26.72	27.40
50	25.66	26.10	26.62
75	25.20	25.59	25.98
82.6	25.08	--------	--------
100	--------	25.14	25.42
125	--------	24.71	24.91
150	--------	24.30	24.47
151.98	--------	24.27	--------
175	--------	--------	24.09
200	--------	--------	23.76
225	--------	--------	23.48
241.83	--------	--------	23.31
	$a=3.80\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{kg}}$	$a=3.93\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{kg}}$	$a=4.16\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{kg}}$

[a] The values at zero pressure were obtained by extrapolation consistent with the molar volumes at saturation vapor pressure given by eq. 8.1.

TABLE 33. *Molar volumes of liquid n-D_2 for various temperatures and pressures*

Pressure	T=19.70° K	T=20.31° K	T=20.97° K
kg cm⁻²	*cm³ mole⁻¹*	*cm³ mole⁻¹*	*cm³ mole⁻¹*
0[a]	23.44	23.63	23.84
10	23.24	23.37	23.59
20	23.06	23.16	23.35
30	22.89	22.97	23.14
40	22.74	22.79	22.95
43.18	22.70		
50		22.63	22.77
60		22.49	22.60
69.46		22.36	
70			22.45
80			22.30
90			22.16
98.67			22.05
	$a=6.75\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{ kg}}$	$a=7.20\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{ kg}}$	$a=7.37\times10^{-11}\frac{\text{mole}^6}{\text{cm}^{16}\text{ kg}}$

[a] The values at zero pressure were obtained by extrapolation consistent with the molar volumes at saturation vapor pressure given by eq 8.4.

2. Solid H_2, HD, and D_2

The crystal structure of solid hydrogen is thought to be hexagonal close-packed, on the basis of an X-ray investigation of solid parahydrogen by the Debye-Scherrer method at the temperature of liquid helium, conducted by Keesom, de Smedt, and Mooy [162].

Tables 34 and 35 contain all the available experimental data of state on solid H_2, HD, and D_2. Molar volumes at 0° K were obtained by calculation.

Molar volumes of the solid at the triple point given in table 34 were obtained by subtracting the volume changes on fusion from the triple point volumes of the liquid calculated from eq 8.1, 8.3, and 8.4. The volume changes on fusion, given in table 34, were calculated using the Clapeyron equation with the calorimetrically measured heats of fusion (section IX, 3), and dP/dT for the solid-liquid equilibrium at the triple point (section VII, 2).

Molar volumes of the solid in table 34 above the triple-point temperature were obtained from Bartholome's measurements of the change in volume on fusion at the temperatures given in table 34, and the volumes of the liquid at melting pressure given in tables 32 and 33.

The molar volumes of solid H_2 and D_2 at 4.2° K in table 34 were measured by Megaw [165] with a picnometer in which the solid H_2 or D_2 was surrounded with liquid helium, the volume of which had previously been measured as a function of pressure at this temperature. The compressibilities of solid H_2 and D_2 at 4.2° K, given in table 35, were calculated by Miss Megaw from the results of these measurements.

TABLE 34. *Molar volumes of solid n-H_2, HD and n-D_2 and volume changes upon fusion*

T	P	n-H_2		HD		n-D_2		Remarks
		Volume of solid	Volume change on fusion	Volume of solid	Volume change on fusion	Volume of solid	Volume change on fusion	
°K	*kg/cm²*	*cm³/mole*	*cm³/mole*	*cm³/mole*	*cm³/mole*	*cm³/mole*	*cm³/mole*	
20.97	98.7					20.07	1.98	T and P for solid-liquid equilibrium.
20.31	69.5					20.20	2.16	
18.72	0.17_4					20.48	2.66	n-D_2 triple point.
16.60	.126			21.84	2.65			HD triple point.
18.24	152.0	22.24	2.03					T and P for solid-liquid equilibrium.
16.43	82.6	22.78	2.30					
13.96	0.07_3	23.25	2.85					n-H_2 triple point.
4.2		22.65				19.56		Solid-vapor equilibrium.
4.2	0	22.65				19.56		Smoothed values based on direct experimental determination.
4.2	10	22.49				19.50		
4.2	25	22.30				19.41		
4.2	50	22.03				19.28		
4.2	75	21.80				19.16		
4.2	100	21.60				19.06		
0	0	22.57				19.49		By calculation.

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TABLE 35. *Experimentally determined compressibilities,* $\frac{1}{V}\left(\frac{dV}{dP}\right)_T$, *of solid* H_2 *and* D_2 *at 4.2° K*

Compressibility	H_2 compressibility	D_2 compressibility
	kg⁻¹ cm²	*kg⁻¹ cm²*
At pressure 0 kg cm⁻²	$(6.8 \pm 1.5)\times 10^{-4}$	$(4.5 \pm 2)\times 10^{-4}$
At pressure 100 kg cm⁻²	3.2×10^{-4}	2.1×10^{-4}
Average for range 0 to 100 kg cm⁻²	$(5.0 \pm 0.5)\times 10^{-4}$	$(3.3 \pm 0.7)\times 10^{-4}$

Miss Megaw calculated the expansivities of solid H_2 and D_2 at 4.2° and 11° K, given in table 36, using the formula

$$C_p - C_v = TV\left(\frac{dV}{dT}\right)_P^2 \Big/ \left(\frac{dV}{dP}\right)_T, \qquad (8.6)$$

with the calorimetrically determined specific heats at constant pressure and volume, and the compressibility measured at 4.2° K (table 35).

TABLE 36. *Expansivities,* $\frac{1}{V}\left(\frac{dV}{dT}\right)_P$, *of solid* H_2 *and* D_2 *calculated from* $C_p - C_v$

T	H_2	D_2
° K	*° K⁻¹*	*° K⁻¹*
4.2	0.24×10^{-2}	0.17×10^{-2}
11	$.51\times 10^{-2}$	$.37\times 10^{-2}$

The compressibilities and expansivities of solid H_2 and D_2 are large when compared with values of these properties for other substances. This is ascribed to the zero-point vibrational energy of the lattice which for hydrogen is an unusually large fraction of the negative potential energy of the lattice. This accounts also for an unusually large variation in the compressibilities of H_2 and D_2 with pressure (see table 35), and for the variation with T and V of $d \ln \theta / d \ln V$, which derivative of the Debye θ is usually regarded as a constant for other solids [165].

IX. The Thermal Properties of the Condensed Phases

In this section are included the calorimetrically measured properties: specific heats and heats of fusion and vaporization.

1. Specific Heats of the Solids and Liquids

(a) Hydrogen

The specific heats at saturation pressure of solid and liquid hydrogen were measured (1923) by Simon and Lange [171] between 10° and 20° K, before the discovery of parahydrogen. Clusius and Hiller [172] measured (1929) the specific heats of solid and liquid parahydrogen over the same range of temperatures and obtained the same values, within experimental error, for the specific heats of parahydrogen as had been obtained by Simon and Lange for supposedly normal hydrogen. Mendelsohn, Ruhemann, and Simon [173] measured (1931) the specific heats of several mixtures of ortho- and parahydrogen between 2.5° and 11.5° K. Their results on pure parahydrogen were in agreement with the earlier measurements of Clusius and Hiller, the data from 2.5° to

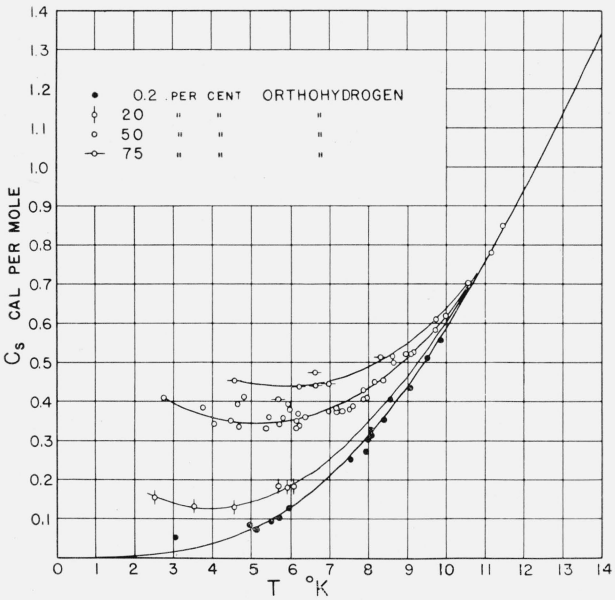

FIGURE 23. *Specific heat,* C_s, *of solid* H_2 *for various ortho-para compositions.*

14° K fitting rather closely a Debye function with $\Theta = 91°$ K.

The data of Mendelsohn, Ruhemann, and Simon are shown in figure 23. It is seen that, at temperatures below 11° K, the specific heats of mixtures containing orthohydrogen are larger than for pure parahydrogen. This difference in specific heats is connected with the multiplicity of states belonging to the lowest o-H_2 rotational level, $J=1$. The different states, three in number, correspond to three different orientations of the angular momentum vector of an o-H_2 molecule relative to the electric field in the hydrogen crystal. At 0° K, all o-H_2 molecules are in the orientation state of lowest energy. At tempera-

tures of the order of $\Delta E/k$, where ΔE is the difference in the energy of the states, the distribution of o-H_2 molecules over the three states changes rapidly with change of temperature. Along with this there is an absorption of energy and an increase in specific heat. As temperatures are approached that are high compared with $\Delta E/k$, the distribution of o-H_2 molecules becomes uniform over the three orientation states, and the specific heat of orientation approaches zero. It may be seen from figure 23 that 12° K is effectively a high temperature for this distribution, and that at temperatures above 12° K the distribution over the three $J=1$ states must be practically uniform.

The specific heats, C_s, of liquid and solid hydrogen along the saturated vapor lines are given in table 37. The C_s curves of figures 24, 25, and 26 for n-H_2 at temperatures above 11° K represent this table.

In figures 25 and 26 the heat capacity, C_v, of solid and of liquid n-H_2 at constant specified values of the density are compared with the heat capacity, C_s, of solid and liquid n-H_2 in equilibrium with saturated vapor. It is to be noted that the C_v curves of these two figures are not for C_v of solid and liquid H_2 along a line of equilibrium of vapor and condensed phase. The C_v measurements on the solid were made by Bartholomé and Eucken [176] at the density of solid H_2 at a melting temperature of about 19° K. The C_v measurements for the liquid were made by Eucken [169] and by Bartholomé and Eucken at densities ranging from 0.034 to 0.077 g cm^{-3} (380 Amagats to 860 Amagats). The density of liquid n-H_2 at its normal boiling point is 0.07097 g cm^{-3} (789.7 Amagats).

The difference between C_v in figure 25 for the solid at constant density and C_v at densities of the solid along the solid-vapor equilibrium line is small. The corresponding difference for the liquid is larger and, at the critical temperature 33.19° K, is of the order of 1 or 2 cal mole^{-1} °K^{-1}

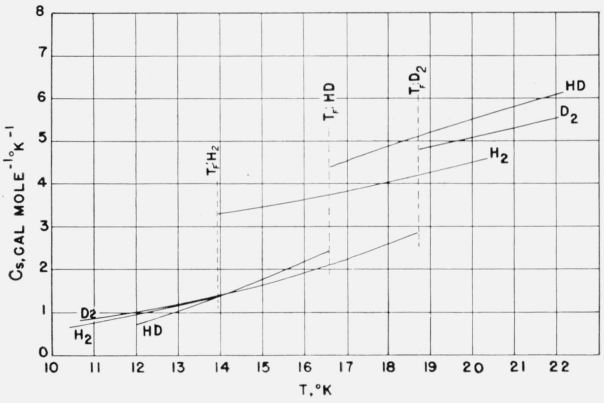

FIGURE 24. *Specific heat, C_s, of solid and liquid* H_2, HD, *and* D_2.

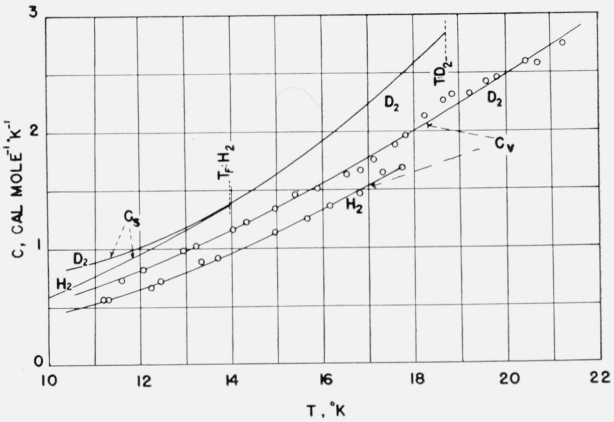

FIGURE 25. *Specific heats, C_s and C_v, of solid* H_2 *and* D_2.

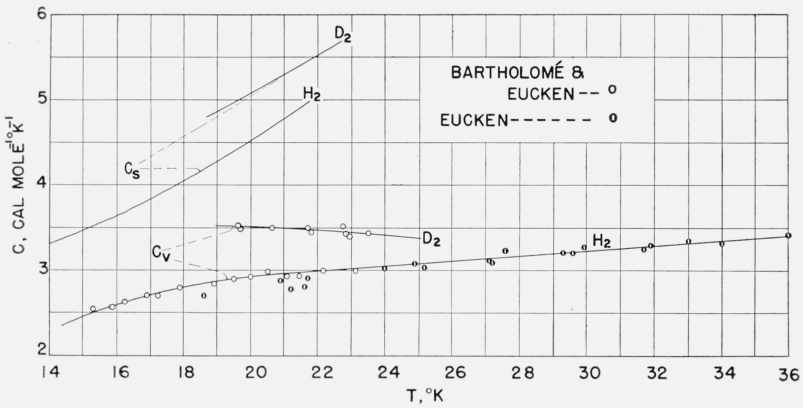

FIGURE 26. *Specific heats, C_s and C_v, of liquid* H_2 *and* D_2.

TABLE 37. *Specific heats at saturation pressure of normal hydrogen, normal deuterium, and hydrogen deuteride in the solid and liquid states*

T	Hydrogen		Deuterium		Hydrogen deuteride	
	C_s	State	C_s	State	C_s	State
° K	*cal mole*$^{-1}$ *deg*$^{-1}$		*cal mole*$^{-1}$ *deg*$^{-1}$		*cal mole*$^{-1}$ *deg*$^{-1}$	
10	0.58	Solid				
11	.76	do	0.88	Solid		
12	.95	do	1.00	do	0.69	Solid
13	1.16	do	1.18	do	1.03	Do.
13.96	1.37	do				
13.96	3.31	Liquid				
14	3.31	do	1.39	do	1.39	Do.
15	3.46	do	1.63	do	1.76	Do.
16	3.63	do	1.90	do	2.17	Do.
16.60					2.42	Do.
16.60					4.40	Liquid
17	3.83	do	2.21	do	4.53	Do.
18	4.04	do	2.56	do	4.88	Do.
18.72			2.84	do		
18.72			4.80	Liquid		
19	4.27	do	4.86	do	5.20	Do.
20	4.50	do	5.08	do	5.49	Do.
21			5.30	do	5.79	Do.
22			5.52	do	6.09	Do.

C_v along the liquid-vapor line being greater [176].

The difference between C_s and C_v for hydrogen is large when compared with the differences for other substances having higher boiling temperatures. In general, $(C_s—C_v)$ is large for low-boiling substances because of their larger expansivities.

The Debye Θ in the Debye specific heat function that fits the C_v data on solid H_2 is 105° K. This may be compared with 91° K for C_s.

The specific heats at constant pressure of compressed liquid hydrogen and gaseous hydrogen were measured by Gutsche [178] for temperatures from 16° K to 38° K and for pressures of about 10, 25, 40, 60, 80, and 100 kg cm^{-2}, using a calorimeter so arranged that approximate constancy of pressure was maintained by manual operation of valves permitting fluid to pass from the calorimeter. As a result of this experimental procedure, the mass of hydrogen in the calorimeter was smaller at the higher temperatures, and consequently the accuracy of measurement is probably lower at the higher temperatures.

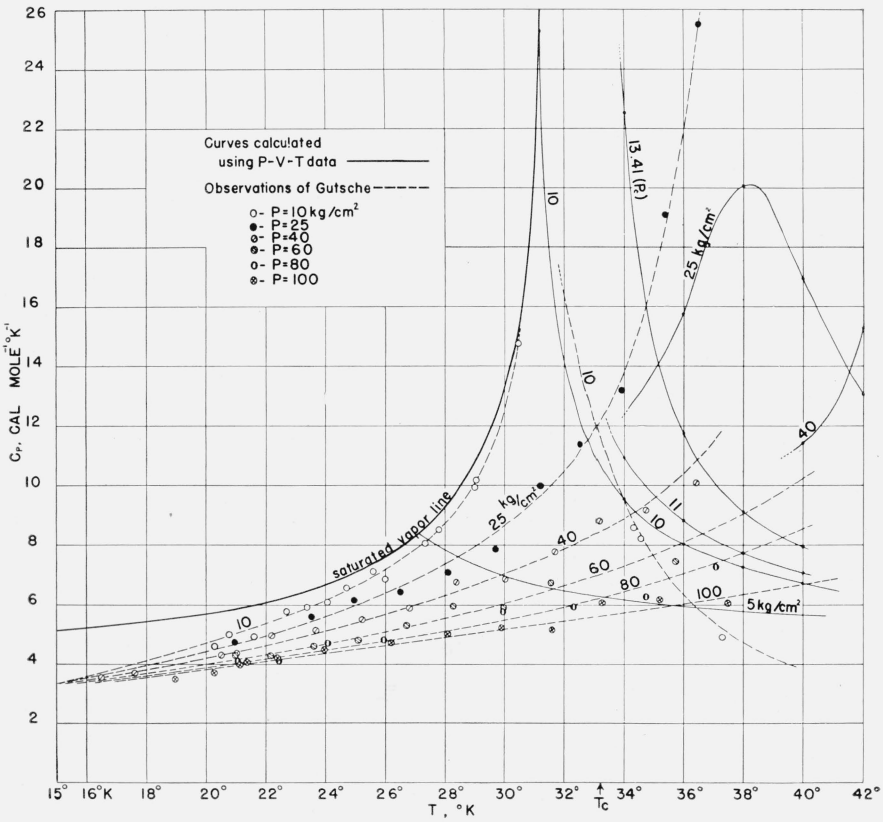

FIGURE 27. *Specific heat, C_p, of compressed liquid and gaseous* H_2.

In figure 27 are plotted Gutsche's experimental data with dotted curves as drawn by Gutsche in his paper to represent the experimental data. The full line curves apply only to the vapor and were obtained by calculation from the PVT correlations of preceding sections of the paper and specific heats in the ideal gas state, table 8. The heavy curve shows C_p for saturated vapor. The full-line curves beginning on this heavy curve, or saturated vapor line, sloping downward toward the right represent the specific heats, C_p, for the vapor at pressures of 5 and 10 kg cm^{-2}. Parts of similar curves also based on the PVT data are shown for 11 and for 13.41 kg cm^{-2}, the critical pressure.

For temperatures above the critical, the dashed curves of Gutsche for 10, 25, and 40 kg cm^{-2} are quite different from the full line curves based on PVT data. The dashed curve for the gas at 10 kg cm^{-2} is certainly incorrect at the highest temperatures, as the actual deviation from the ideal gas law for hydrogen is such as to increase C_p above the approximately 5 cal deg^{-1} mole^{-1} of the ideal gas at these temperatures.

It is seen in figure 27 that Gutsche's experimental values for the liquid scatter considerably. It is believed that Gutsche's recommended values of C_p for liquid hydrogen, represented by the dashed lines in figure 27, are too high. In figure 30 are shown two sets of isobars, E and E', on a temperature-entropy diagram for liquid hydrogen. The full-line curves, E, were calculated from Gutsche's C_p data; the dashed curves, E', are the best fit for all the thermal and state data on liquid hydrogen and are the ones used in the construction of the temperature-entropy diagram. As $(dS/dT)_P = C_p/T$, the two sets of isobars, E and E', imply different C_p's and show that Gutsche's values of C_p are too high to be consistent with the other data on liquid hydrogen. The differences are of the order of 15 percent in the C_p's of liquid hydrogen. The ratio C_p/C_v for liquid hydrogen in equilibrium with vapor was calculated from the velocity of sound in liquid hydrogen, and C_p was obtained by combining this calculated value of the ratio (C_p/C_v), with C_v from figure 26. Pitt and Jackson [175] obtained the value 1,127 m sec^{-1} for the velocity of sound in liquid hydrogen at 20.46° K. Using this with a value of (dV/dP) extrapolated from Bartholomé's data (VIII), one obtains a value of 5.07 cal deg^{-1} mole^{-1} for C_p for liquid hydrogen in equilibrium with vapor ($\sim$1 atm) at 20.46° K.

This is slightly lower than would probably be obtained by extrapolating Gutsche's curves to 1 atm.

(b) D_2 and HD

In figure 24 the specific heats C_s at saturation pressure of liquid and solid n-D_2 and HD are compared with C_s for H_2. The D_2 measurements were made by Clusius and Bartholomé [174] and the HD measurements by Brickwedde and Scott [150]. The solid D_2 data are fitted, within experimental accuracy, by a Debye function with $\Theta = 89°$. The data on solid HD, however, can not be fitted over the range of measurement with a single value of Θ. Thus Θ for C_s of HD at 16.3° K is 79°, whereas for 12.5° K, Θ is 98°. As the Debye function is intended to represent C_v, this failure to fit the C_s data is not surprising.

In figures 25 and 26 the specific heat C_v at constant volume of solid and liquid D_2 is compared with C_s for D_2 and C_v for H_2. A Debye function with $\Theta = 97°$ fits within experimental accuracy the C_v data for solid D_2. This value of Θ for solid D_2 may be compared with 105° for solid H_2. According to the simple theory of lattice vibrations, which assumes simple harmonic restoring forces in the lattice, Θ would be proportional to $1/\sqrt{M}$ and the Θ's for H_2 and D_2 would be in the ratio $\sqrt{4/2} = 1.41$. The ratio of the experimental values however, is 1.08. This is evidence that the lattice restoring forces in solid H_2 and D_2 are strongly anharmonic.

2. Latent Heats of Vaporization

(a) Normal Hydrogen

Simon and Lange [171] measured the heat of vaporization of normal hydrogen at several temperatures between the triple point and the boiling point. They found that heat of vaporization, in calories per mole, was given by

$$L_v = 219.7 - 0.27\ (T - 16.6)^2, \qquad (9.1)$$

where T is the Kelvin temperature.

(b) Mixtures of o-H_2 and p-H_2

As orthohydrogen and parahydrogen are very closely related, it might be expected that their mixtures would have properties related very simply to those of the pure components. Never-

theless, the H_2 vapor-pressure data of Brickwedde and Scott [146] given by the equations and graphs of Section 7 show that the ortho-para H_2 mixtures do not follow Raoult's law for ideal solutions. A simple application of the Clapeyron equation in the form applying to a pure substance indicates that the latent heat of vaporization and the internal energy of the liquid and solid do not follow a linear, but rather an approximately quadratic dependence upon the composition. This same qualitative result is obtained when account is taken of change of composition by fractionation during vaporization. Functions approximately linear in x, the ortho mole fraction, are obtained when $L_{mix}-L_{eq}$, the difference in latent heats, and $E_{eq}-E_{mix}$, the difference in the internal energy, are divided by $x_{mix}-x_{eq}$, the corresponding difference in the ortho mole fraction. The subscript "eq" indicates the ortho-para mixture that is at equilibrium at 20.4° K, containing 0.21 percent of ortho- and 99.79 percent of parahydrogen. The subscript "mix" refers to any other mixture for which data were obtained. When the line for $\Delta E/\Delta x$ is horizontal, it indicates that ideal solution laws apply. The line has a clear indication of slope, as shown by the continuous lines in figure 28, indicating that ideal solution laws do not apply. In the graph for $\Delta E/\Delta x$, the points for the liquid include a contribution of about 7 percent related to change of composition due to fractionation. The lower dashed line shows the result when this correction is omitted. For the solid it was thought proper to omit the correction for this effect because departure from equilibrium due to slowness of diffusion in the solid would make it too uncertain. The upper dashed line shows the result for the solid when such a correction for fractionation is included.

The use of straight lines for $\Delta E/\Delta x$, the divided difference of the internal energy, has a theoretical justification apart from the fact that the scattering of individual values is so great as to obscure the exact shape of the curve for the liquid. If the internal energy of the liquid is a simple sum of independent energies of different molecular pairs, all of essentially equal probability of formation, then the energy has the form

$$E=x^2E_{oo}+2x(1-x)\ E_{op}+(1-x)^2\ E_{pp}. \quad (9.2)$$

In this case, the differences $E_{eq}-E_{mix}$ divided by the corresponding differences in x for the mixtures of different compositions will be linearly dependent on x. The slope of this line is $2\ E_{op}-E_{oo}-E_{pp}$ and the value of the ordinate at $x=-x_{eq}$ is $2\ (E_{pp}-E_{op})$. From the curves in figure 28, it will thus be found that $E_{pp}-E_{op}$ is 0.7 cal mole^{-1} and $E_{pp}-E_{oo}$ is 4.2 cal mole^{-1} for the liquid. For the solid the corresponding values are 0.6 cal mole^{-1} and 5.4 cal mole^{-1}, respectively. The relative size of $E_{pp}-E_{oo}$ as compared to $E_{pp}-E_{op}$ suggests that most of the deviation from ideal solution laws is due to special effects between o-H_2 molecules.

From the scattering of the points plotted, it appears that ordinates are uncertain to 0.2 or 0.3 cal mole^{-1} for the liquid and possibly to 1 cal mole^{-1} for the solid. The use of the straight line for $\Delta L/\Delta x$ in figure 29 is very nearly consistent with its use for $\Delta E/\Delta x$ and is allowed within the scattering of the data. Combining the results for the dependence upon composition with the results of Simon and Lange for normal hydrogen, the latent heat of vaporization of liquid hydrogen in calories per mole is approximately

$$217.0-0.27\ (T-16.6)^2+1.4x+2.9x^2 \quad (9.3)$$

for any mixture of o-H_2 and p-H_2, where x is the orthohydrogen mole fraction.

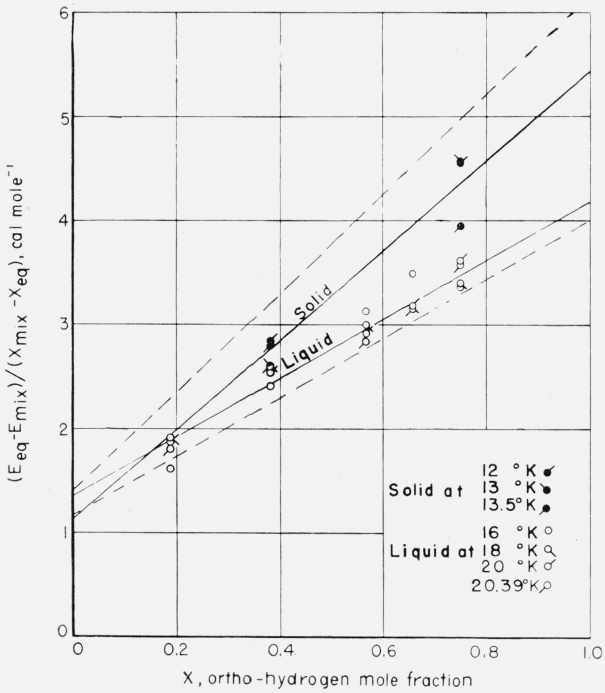

FIGURE 28. *Dependence of internal energy of solid and liquid* H_2 *upon the ortho-para composition.*

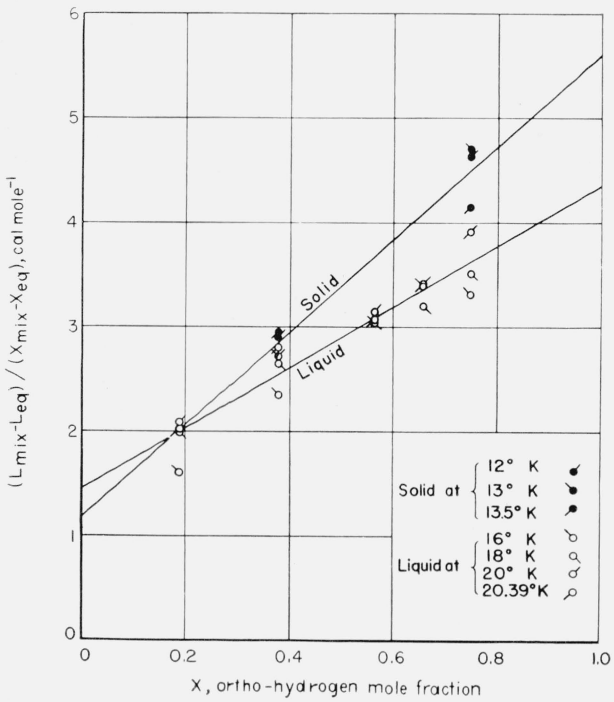

FIGURE 29. *Dependence of latent heats of vaporization and sublimation of hydrogen upon the ortho-para composition.*

The heats of fusion of para- and normal hydrogen are reported in table 38 as being equal within 0.03 cal mole^{-1}. On the basis of the two distinct straight lines for liquid and solid hydrogen in figure 29, it would be expected that the difference would be about 0.7 cal mole^{-1}. The reason for this discrepancy is not known, though it may suggest that the lines for the liquid and solid should be more nearly identical.

TABLE 38. *Latent heats of fusion*

Substance	Heat of fusion	T	P
	cal mole^{-1}	°*K*	*mm* Hg
Normal hydrogen	28.0	13.95_7	54.0
Parahydrogen	28.0_3	13.81_3	52.8
Normal deuterium	47.0	18.72_3	128.5
Hydrogen deuteride	38.1	16.60_4	92.8

The manner in which the vapor pressures depend on composition and temperature has formed the basis for the treatment of latent heats of vaporization given in this section. Cohen and Urey [166] and Schäfer [164] have given theoretical discussions of the vapor pressures of ortho and para H_2 and D_2. Cohen and Urey did not expect deviations from the law of perfect solutions. Schäfer suggested that forces connected with rotation within the crystal lattice might account for vapor-pressure differences.

(c) Normal Deuterium

Clusius and Bartholomé [174] measured the heat of vaporization of normal deuterium, obtaining the value 302.3 cal mole^{-1} at 19.70° K.

(d) Mixtures of o-D_2 and p-D_2

The difference in latent heats of vaporization and the approximate difference in internal energies have been calculated from the vapor pressures of the normal and the 20.4° K equilibrium mixtures of ortho- and paradeuterium measured by Brickwedde, Scott, and Taylor [149]. PVT data for deuterium as determined by Schäfer were also used in the calculation. As there are data for only two compositions, giving only one difference of composition, it is not possible either to correct for fractionation or to test for deviation from Raoult's Law. It seems improbable that the law holds for deuterium, as it does not hold for hydrogen. The indicated differences in latent heats of vaporization are smaller than for hydrogen. Thus, $L_{norm}-L_{eq}=0.3$ cal mole^{-1} for the liquid and 1.0 cal mole^{-1} for the solid. The same values are obtained for the differences in internal energies, $E_{eq}-E_{norm}$. Cohen and Urey [166] on the basis of their theoretical calculations, concluded that differences in binding energy between corresponding forms should be half as great for D_2 as for H_2. Considering that the uncertainties in the data for D_2 are comparable with the magnitudes themselves, the data can not be said to conflict with the theoretical preduction.

(e) Hydrogen Deuteride

Brickwedde and Scott [146] measured the heat of vaporization of hydrogen deuteride, obtaining the value 257 cal mole^{-1} at 22.54° K.

3. Latent Heats of Fusion

The latent heats of fusion of hydrogen, parahydrogen, normal deuterium, and hydrogen deuteride were measured by Simon and Lange [171], Clusius and Hiller [172], Clusius and Bartholomé [174], and by Brickwedde and Scott [150], respec-

tively, and are listed in table 38 with corresponding vapor pressures and temperatures.

X. The Temperature-Entropy Diagram

1. Data

Data of several different types were used in determining the temperature-entropy diagram. For the vapor, and for the gas below a density of 500 Amagats, values of the various quantities were obtained by interpolation from tables 14, 22, and 23. The particular difficulties encountered in treating the liquid region will be evident from the

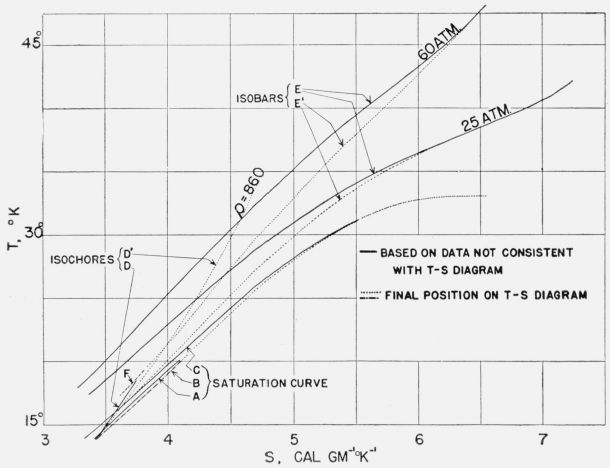

FIGURE 30. *Discrepancies in the thermal data for* H_2 *in the region of the liquid.*

following discussion. Discrepancies between the various data for the liquid are shown in figure 30.

Between the triple point and the boiling point, the entropy of liquid normal hydrogen at saturation pressure was obtained using calorimetric data for the solid and liquid and adding a theoretical value for the entropy of mixing. The result is shown as line B in figure 30. The entropy of the liquid was also calculated using the theoretical entropy of the ideal gas, correcting to the state of saturated vapor and subtracting the latent heat of vaporization. The latent heat of vaporization was determined in two ways—by direct calorimetric measurement and by using vapor pressures and other data with the Clapeyron equation. Line A is based on calorimetric latent heats and line C on latent heats from vapor pressures. At 20° K, line B indicates values 0.03 cal deg^{-1} g^{-1} greater than line A and 0.08 cal deg^{-1} g^{-1} greater than line C.

Lines of constant density could be obtained for the compressed liquid by integrating C_v/T, beginning at line B. Values of C_v from figure 26 were used. The results indicate that these constant density lines are approximately parallel at a given temperature for densities less than 500 Amagats. Data of table 14 indicate that there is a similar parallelism for higher densities near the critical temperature.

Values of entropy of the liquid for various pressures along the 17.34° K and 19.28° K isotherms were obtained by integration of the equation

$$(dS/dP)_T = -(dV/dT)_P. \qquad (10.1)$$

The values used for $(dV/dT)_P$ were based on smoothed values of volume for the liquid as given in table 32 for the temperatures 16.43° K, 18.24° K, and 20.33° K. The constant of integration was chosen to fit line B. From the results, a set of constant pressure lines, of which the segment F is typical, was obtained for various pressures. In addition, a point that should have been on the 860 Amagat density line was obtained by interpolation and a line D was drawn through it and through the 860 Amagat density point on line B as determined by eq 8.1. The line marked D' represents the final correlation.

An unsatisfactory set of values of entropy for the liquid along constant pressure lines was obtained by integrating the C_p data of Gutsche, figure 27. Curves E are the results for 25 and 60 atm, while the final correlation gave curves E'.

2. Final Correlation

In the final correlation, the saturation curve B was accepted and the isochores were considered parallel. The isochores at high density were given by integration of C_v/T, beginning on line B. The isochores at intermediate density were obtained by interpolation between values at high density and values below 500 Amagats. The interpolation was made along the 35° K isotherm from an entropy-density plot extending from $\rho=860$ Amagats to $\rho=340$ Amagats.

The extension of curve B to temperatures higher than were given by calorimetric data for the liquid was made from the lower parts of the interpolated isochores and the temperature-density relations for the liquid at saturation pressure given by eq 8.1.

The constant pressure lines were determined mainly from the vapor-pressure equation and the equation

$$(dS/dV)_T = (dP/dT)_V. \qquad (10.2)$$

At lower temperatures the lines were in fair agreement with Bartholome's PVT data, which served to locate them more closely.

The lines of constant enthalpy were determined from integrals of TdS under the constant pressure lines and were checked by integration along the isochores based on the equation

$$(dH/dT)_v = T(dS/dT)_V + V(dS/dV)_T. \qquad (10.3)$$

The location of the curves within the dome is quite straightforward, as the fractionation of the ortho-para mixture is too small to affect these curves significantly.

The resulting temperature-entropy diagram for normal hydrogen is presented in composite form in figures 31, 32, and 33. The thermal units used are based on the calorie, the Kelvin degree, and the gram, with pressures in atmospheres and densities in Amagat units.

The diagram shows lines of constant enthalpy, pressure and density and, in the region of coexistance of liquid and vapor, lines of constant "quality." The painstaking construction of the curves pertaining to the liquid region, amounting to a correlation of the data for the liquid, has been made by Robert N. Schwartz, who has also drawn the remainder of the diagram on the basis of the tables of this paper.

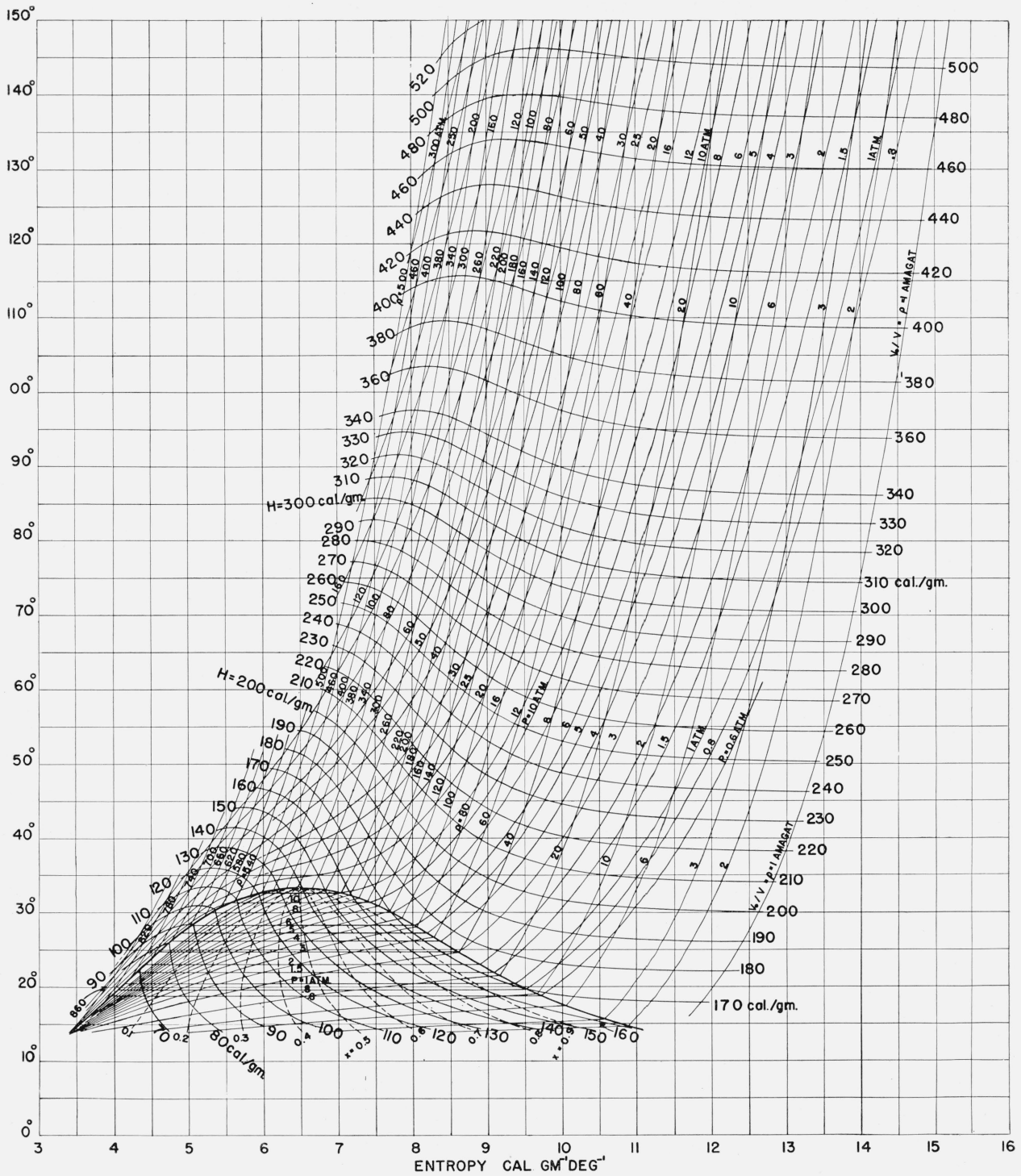

FIGURE 31. *Temperature-entropy diagram for* H_2 *in the region 0° to 150° K.*

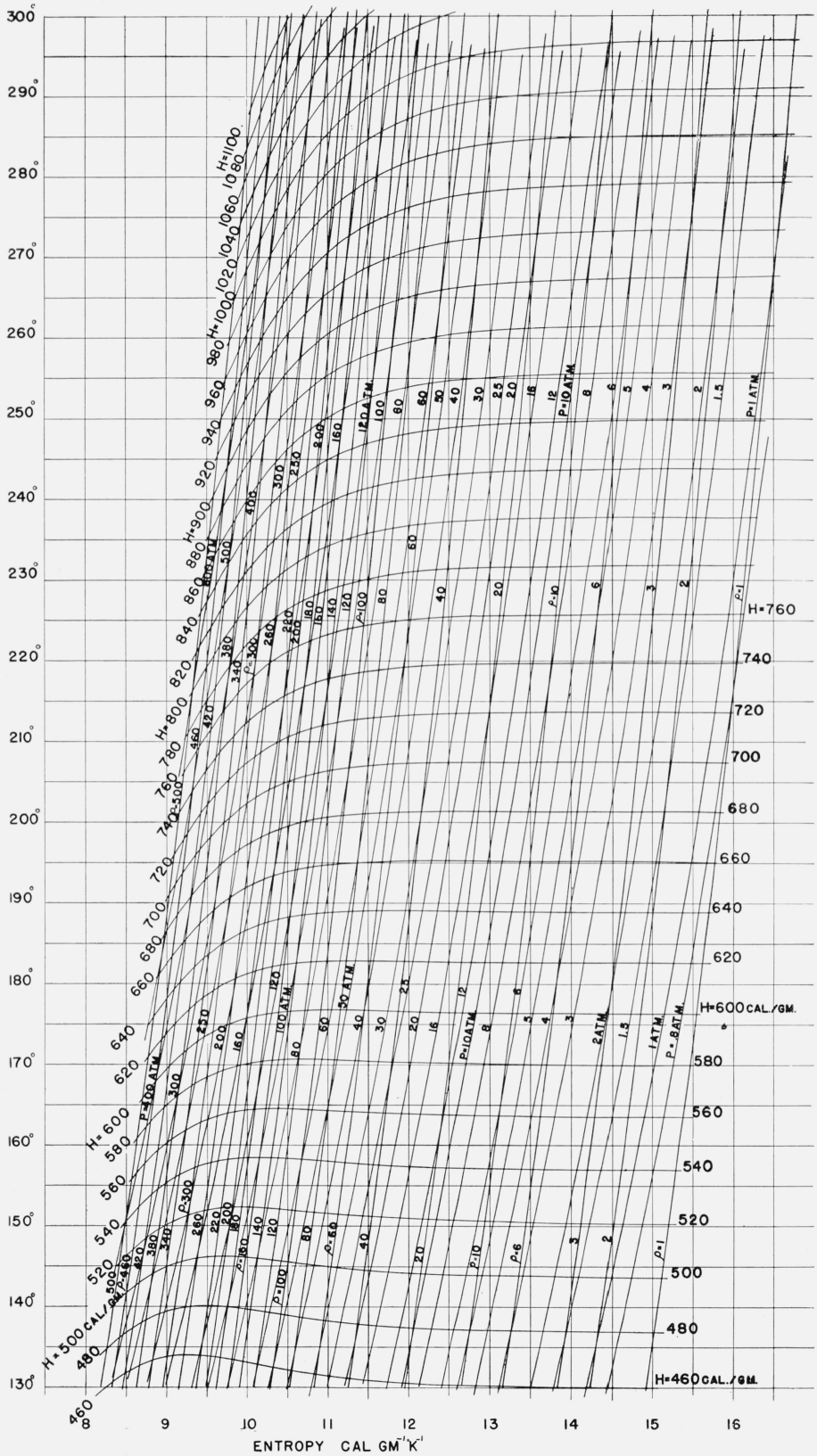

FIGURE 32. *Temperature-entropy diagram for* H_2 *in the region 130° to 300° K.*

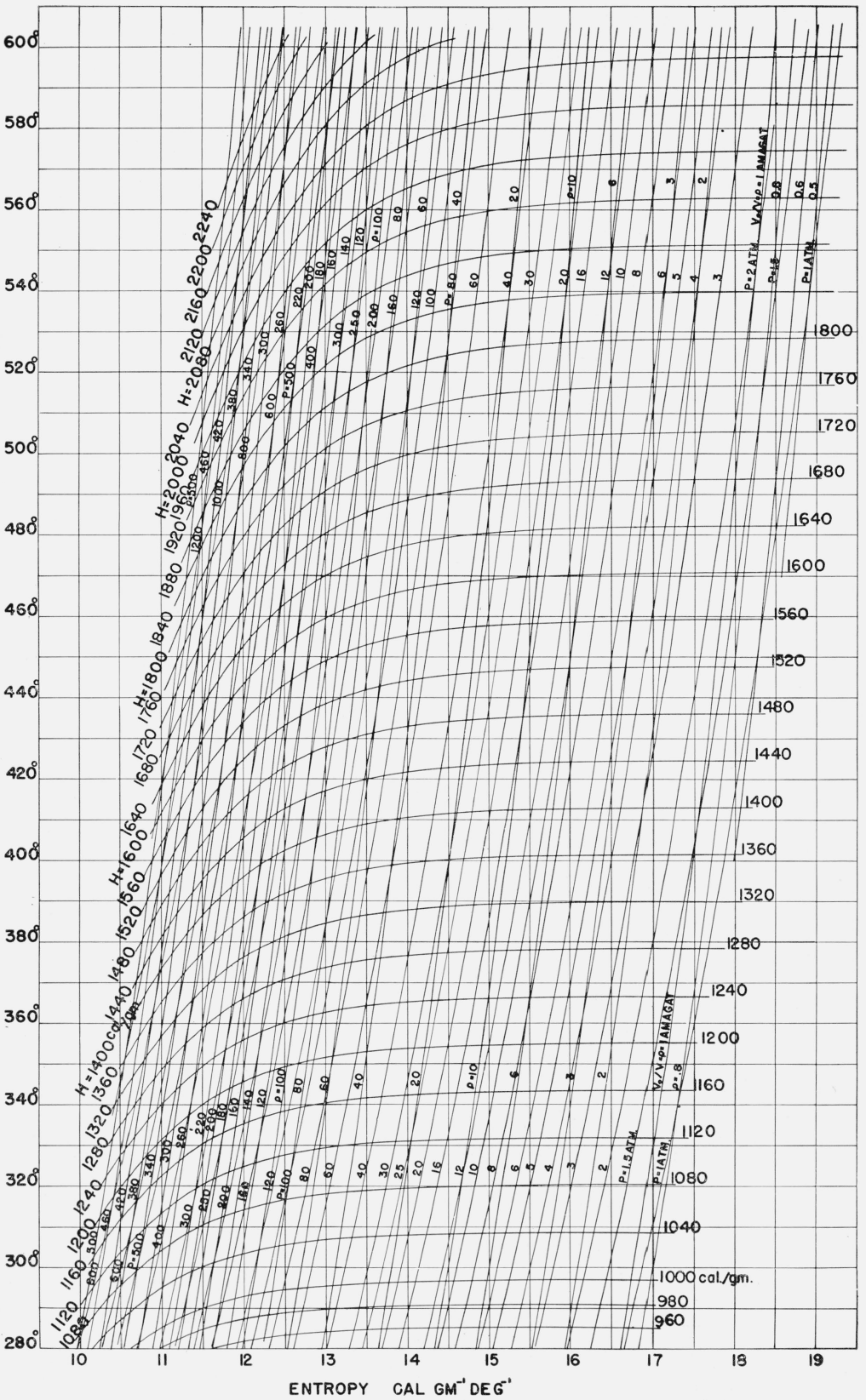

FIGURE 33. *Temperature-entropy diagram for* H_2 *in the region 280° to 600° K.*

XI. References

1. Thermodynamic Properties of the Hydrogens in the Ideal Gas State

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WASHINGTON, August 7, 1947.