

Thermophysical Properties of Fluid H₂O

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Thermophysical Properties of Fluid H₂O

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In view of the important role that water substance plays in science and industry, this paper lists the thermophysical properties of fluid H₂O which are most needed for engineering applications. The properties are described in a very compact form with the aid of explicit expressions for programming on a computer and for inclusion in data banks. The paper includes a fundamental equation in the form of the Helmholtz free energy expressed as an analytic function of temperature and density. This fundamental equation is a dimensionless version of the Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use, which enables one to calculate all equilibrium thermodynamic properties in a wide range of states, but with the exclusion of a small region near the critical point. In the latter region, the equilibrium properties are described by a scaled fundamental equation in the form of the pressure as a function of chemical potential and temperature. In addition, the paper gives equations for the viscosity, thermal conductivity, and surface tension. All equations in the paper are mutually thermodynamically consistent. The set of equations and their constants listed here represents the most reliable information according to the judgment of the authors.

Key words: critical parameters; equation of state; fundamental equation; steam; surface tension; thermal conductivity; thermodynamic properties; viscosity; water; water vapor.

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1. Introduction

Water and steam, or "water substance" as Frederick G. Keyes preferred to call it, is probably the most important substance in existence; it is used as a working fluid in many engineering devices, it is the most frequently used solvent, it plays an essential part in the vagaries of weather and climate. Last, but not least, it covers more than two-thirds of the surface of the earth, not to mention its seminal role in living organisms. It is not, therefore, surprising that the measurement of the thermophysical properties of water substance has occupied the attention of many scientists in many countries over many decades. It is, further, not surprising that a study of the most fundamental thermophysical properties of this substance became the topic of a major cooperative international effort which was initiated more than 50 years ago and which lasts to this day.

As a result of more than half a century of measurements, correlations and international exchange, augmented by a national effort centered within the National Bureau of Standards, we have now reached a point where the most important thermodynamic and transport properties of water substance can be presented for the use of science and industry in a highly concentrated and internally consistent form. The reduction of a vast mass of information on the properties of H_2O in a highly compact form was, of course, made possible by the fairly recent explosive development of computers and computation methods.

The present report lists closed-form expressions for the thermodynamic, transport, and capillary properties of water substance. The equations are easy to program on a computer and can be made into codes that fit into larger data banks. This allows the user to extend vastly the scope of the original measurements. Some equations have obtained endorsement by the International Association for the Properties of Steam.¹ It must, however, be emphasized that this publication is not issued under the authority of that body. The aim is

to supply data of maximum reliability and usefulness according to the judgment of the authors and regardless of their provenience.

All equations have been programed on computers by many scientists and calculated results were carefully checked against critically evaluated experimental data. A short numerical table is included in this paper solely for the purpose of verifying computer codes. The equations are judicious mixtures of plain curve-fitting and theoretically justified expressions. The latter played an important part in the presentation of the properties in the critical region. Present-day understanding of the thermodynamic properties of any substance, including H_2O , indicates that the thermodynamic surface becomes nonanalytic at the critical point. Thus it is convenient to exclude from the global thermodynamic surface a small near-critical region. Outside this region, the properties can be represented by an analytic function.^{2,3} Inside this region, recourse must be made to the recently discovered scaling laws for the critical behavior of substances.⁴ Equations for the equilibrium properties of water substance in the critical region have to be presented separately from the equations for the properties in the analytic region, because attempts to formulate a unified global equation have not yet been completely successful.⁵

The authors hope that this selection of formulas will be of use to all those who need computer codes for the thermophysical properties of fluid H_2O .

2. Molecular Data

$$\text{Molar mass}^6: M = 0.018\,015\,2 \text{ kg/mol, (2.1)}$$

$$\text{universal gas constant}^7: R = 8.314\,41 \text{ J/mol K, (2.2)}$$

$$\text{specific gas constant: } R = 461.522 \text{ J/kg K. (2.3)}$$

The molar mass and the specific gas constant refer to water of normal isotopic composition (natural abundance).⁶

3. Critical Constants

$$\text{Critical temperature: } T_{cr} = (647.14 + \delta) \text{ K} = (373.99 + \delta) ^\circ\text{C with } -0.10 < \delta < +0.10, \quad (3.1)$$

$$\text{critical pressure: } P_{cr} = (22.064 + 0.27\delta \pm 0.005) \text{ MPa,} \quad (3.2)$$

$$\text{critical density: } \rho_{cr} = (322 \pm 3) \text{ kg/m}^3, \quad (3.3)$$

$$\text{critical specific volume: } V_{cr} = (0.003\,11 \pm 0.000\,03) \text{ m}^3/\text{kg,} \quad (3.4)$$

as adopted by the International Association for the Properties of Steam.¹

We note that the above values for the critical constants have been obtained as results of measurements which are frequently repeated and improved. For this reason, they will be subject to change. On the other hand, critical parameters are often used as reference quantities in correlations. Once

adopted, such reference constants need not be revised, when our knowledge of the critical constants improves. In order to distinguish the reference constants from the critical constants (to which they are close), we denote the reference constants by asterisks: P^* , T^* , ρ^* and treat them as empirical correlation constants throughout the remainder of the publication.

4. Dimensionless Variables and Reference Constants

It is an established fact that correlation equations become simpler if for the independent variables one chooses the thermodynamic temperature T and the density ρ or the specific volume $V = \rho^{-1}$.

All equations in this publication are presented in nondimensional form. The dimensionless version of each quantity is denoted by a symbol with a bar. The reference quantities consist of two classes: six primary reference quantities (denoted by an asterisk) and three secondary reference quantities (denoted by a double asterisk) which are simple combinations of the primary reference quantities.

4.1. Primary Reference Constants

$$\text{Reference temperature: } \bar{T}^* = 647.27 \text{ K}, \quad (4.1)$$

$$\text{reference density: } \rho^* = 317.763 \text{ kg/m}^3, \quad (4.2)$$

$$\text{reference pressure: } P^* = 22.115 \times 10^6 \text{ Pa}, \quad (4.3)$$

$$\text{reference viscosity: } \eta^* = 55.071 \times 10^{-6} \text{ Pa s}, \quad (4.4)$$

$$\text{reference thermal conductivity: } \lambda^* = 0.49450 \text{ W/K m}, \quad (4.5)$$

$$\text{reference surface tension: } \sigma^* = 235.8 \times 10^{-3} \text{ N/m}. \quad (4.6)$$

It is emphasized that the three reference constants T^*, ρ^*, P^* are close to but not identical with the critical parameters $T_{\text{cr}}, \rho_{\text{cr}}, P_{\text{cr}}$.

4.2. Secondary Reference Constants

$$\begin{array}{l} \text{Reference constant for Helmholtz} \\ \text{function, energy, enthalpy,} \\ \text{Gibbs function:} \end{array} \quad A^{**} = \frac{P^*}{\rho^*} = 69\,595.89 \text{ J/kg}, \quad (4.7)$$

$$\begin{array}{l} \text{reference constant for entropy,} \\ \text{specific heats:} \end{array} \quad S^{**} = \frac{P^*}{\rho^* T^*} = 107.5222 \text{ J/kg K}, \quad (4.8)$$

$$\begin{array}{l} \text{reference constant for} \\ \text{sound velocity:} \end{array} \quad w^{**} = \left(\frac{P^*}{\rho^*} \right)^{1/2} = 263.810 \text{ m/s}. \quad (4.9)$$

4.3. Thermophysical Properties in Dimensionless Form

$$\text{temperature: } \bar{T} = T/T^*, \quad (4.10)$$

$$\text{pressure: } \bar{P} = P/P^*, \quad (4.11)$$

$$\text{density: } \bar{\rho} = \rho/\rho^*, \quad (4.12)$$

$$\text{specific volume: } \bar{V} = V/\rho^*, \quad (4.13)$$

$$\text{specific Helmholtz function: } \bar{A} = A/A^{**}, \quad (4.14)$$

$$\text{specific energy: } \bar{U} = U/A^{**}, \quad (4.15)$$

$$\text{specific enthalpy: } \bar{H} = H/A^{**}, \quad (4.16)$$

$$\text{specific Gibbs function: } \bar{G} = G/A^{**}, \quad (4.17)$$

$$\text{chemical potential: } \bar{\mu} = \mu/A^{**}, \quad (4.18)$$

$$\text{specific entropy: } \bar{S} = S/S^{**}, \quad (4.19)$$

$$\begin{array}{l} \text{specific heat at constant} \\ \text{volume:} \end{array} \quad \bar{C}_v = C_v/S^{**}, \quad (4.20)$$

$$\begin{array}{l} \text{specific heat at constant} \\ \text{pressure:} \end{array} \quad \bar{C}_p = C_p/S^{**}, \quad (4.21)$$

$$\text{isothermal compressibility: } \bar{K}_T = K_T P^*, \quad (4.22)$$

$$\text{symmetrized compressibility: } \bar{\chi}_T = \chi_T P^*/\rho^{**2}, \quad (4.23)$$

$$\text{speed of sound: } \bar{w} = w/w^{**}, \quad (4.24)$$

$$\text{viscosity: } \bar{\eta} = \eta/\eta^*, \quad (4.25)$$

$$\text{thermal conductivity: } \bar{\lambda} = \lambda/\lambda^*, \quad (4.26)$$

$$\text{surface tension: } \bar{\sigma} = \sigma/\sigma^*. \quad (4.27)$$

5. Equilibrium Thermodynamic Properties in the Analytic Range

All equilibrium thermodynamic properties in the analytic region, that is, to the exclusion of a small area near the critical point, are implied by the canonical equation

$$A = A(T, \rho), \quad (5.1)$$

in which the Helmholtz free energy A is represented as a function of temperature and density.

The equation is based on a formulation constructed by

L. Haar, J. S. Gallagher, and G. S. Kell.^{2,3} It has been provisionally adopted by the International Association for the Properties of Steam and in its original form it is known as the Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use.¹ For the present publication, the original equation has been converted to a nondimensional form for convenience of programming. In order to change the system of units in the output, it is sufficient to perform the conversion in the primary and secondary reference constants given earlier in Secs. 4.1 and 4.2.

5.1. The Fundamental Equation in Canonical Form

$$\bar{A}(\bar{T}, \bar{\rho}) = \bar{A}_0(\bar{T}) + \bar{A}_1(\bar{T}, \bar{\rho}) + \bar{A}_2(\bar{T}, \bar{\rho}) + \bar{A}_3(\bar{T}, \bar{\rho}) + \bar{A}_4(\bar{T}, \bar{\rho}). \quad (5.2)$$

$$\bar{A}_0(\bar{T}) = (A_{00} + A_{01}\bar{T})\ln \bar{T} + \sum_{i=2}^{17} A_{0i}\bar{T}^{i-4}. \quad (5.3)$$

$$\bar{A}_1(\bar{T}, \bar{\rho}) = \bar{\rho} \sum_{i=0}^4 A_{1i} \left(\frac{1}{\bar{T}} \right)^{i-1}. \quad (5.4)$$

$$\bar{A}_2(\bar{T}, \bar{\rho}) = A_{20}\bar{T} \left[\ln \left(\frac{\bar{\rho}}{1-y} \right) - \frac{130}{3(1-y)} + \frac{169}{6(1-y)^2} - 14y \right], \quad (5.5)$$

with

$$y = \bar{\rho} \left[y_0 + y_1 \ln \bar{T} + \frac{y_2}{\bar{T}^3} + \frac{y_3}{\bar{T}^5} \right]. \quad (5.5a)$$

$$\bar{A}_3(\bar{T}, \bar{\rho}) = \sum_{i=0}^{35} A_{3i} \left(\frac{1}{\bar{T}} \right)^{i(i)} z^{k(i)}, \quad (5.6)$$

with

$$z = 1 - e^{-z_0 \bar{\rho}}. \quad (5.6a)$$

$$\bar{A}_4(\bar{T}, \bar{\rho}) = \sum_{i=0}^3 A_{4i} \delta_i^{m(i)} \exp[-\alpha_i \delta_i^{m(i)} - \beta_i \tau_i^2], \quad (5.7)$$

with

$$\delta_i = \frac{\bar{\rho} - \bar{\rho}_i}{\bar{\rho}_i}, \quad \tau_i = \frac{\bar{T} - \bar{T}_i}{\bar{T}_i}. \quad (5.7a)$$

The fundamental Eq. (5.2) covers the temperature range from 273.15 to 1273.15 K and covers the range of pressures described by the conditions

$$P \leq 1500 \text{ MPa}$$

for 423.15 K $\leq T \leq$ 1273.15 K,

$$P \leq 100 \left[5 + \frac{T - 273.15 \text{ K}}{15 \text{ K}} \right] \text{ MPa} \quad (5.8)$$

for 273.15 K $\leq T \leq$ 423.15 K.

The formulation is valid everywhere in this range except for an excluded region around the critical point bounded by

$$|T - T^*| \leq 1 \text{ K}, \quad |\bar{\rho} - 1| \leq 0.3. \quad (5.9)$$

It is possible to extrapolate the fundamental equation beyond the range specified by Eq. (5.8) as agreed upon by the International Association for the Properties of Steam and use it in the extended range of temperatures up to 2500 K

and pressures up to 3000 MPa.⁴ The behavior of the surface in the widened range does not seem to be unphysical. The few experimental data that exist in the extended range support the extrapolated equation. The reliability of the results of calculations, however, is reduced and the uncertainties are increased in the extended range outside that specified by Eq. (5.8).

5.2. Coefficients in the Equations for the Helmholtz Function $\bar{A}(\bar{T}, \bar{\rho})$

The coefficients in the equations for the Helmholtz function are listed in Tables 1–5. In all tables presented in this paper, we have adopted the “E-notation.” That is, the integer which follows E indicates the power of ten by which the listed coefficient value should be multiplied. Thus E + 2 represents the factor $10^2 = 100$, etc.

TABLE 1. Coefficients for $\bar{A}_0(\bar{T})$

<i>i</i>	<i>A</i> _{0<i>i</i>}
0	− 0.130840393653E + 2
1	− 0.857020420940E + 2
2	0.765192919131E − 2
3	− 0.620600116069E + 0
4	− 0.106924329402E + 2
5	− 0.280671377296E + 1
6	0.119843634845E + 3
7	− 0.823907389256E + 2
8	0.555864146443E + 2
9	− 0.310698122980E + 2
10	0.136200239305E + 2
11	− 0.457116129409E + 1
12	0.115382128188E + 1
13	− 0.214242224683E + 0
14	0.282800597384E − 1
15	− 0.230384152737E − 2
16	0.132952679669E − 3
17	− 0.319277411208E − 5

TABLE 2. Coefficients for $\bar{A}_1(\bar{T}, \bar{\rho})$

<i>i</i>	<i>A</i> _{1<i>i</i>}
0	0.15383053E + 1
1	− 0.81048367E + 0
2	− 0.68305748E + 1
3	0.00000000
4	0.86756271E + 0

TABLE 3. Coefficients for $\bar{A}_2(\bar{T}, \bar{\rho})$

<i>A</i> ₂₀ = 0.42923415E + 1	
<i>i</i>	<i>y</i> _{<i>i</i>}
0	0.59402227E − 1
1	− 0.28128238E − 1
2	0.56826674E − 3
3	− 0.27987451E − 3

TABLE 4. Coefficients for $\bar{A}_3(\bar{T}, \bar{\rho})$

$z_0 = 0.317763\text{E} + 0$			
i	$k(i)$	$l(i)$	A_{3i}
0	1	1	-0.76221190138079E + 1
1	1	2	0.32661493707555E + 2
2	1	4	0.11305763156821E + 2
3	1	6	-0.10015404767712E + 1
4	2	1	0.12830064355028E + 3
5	2	2	-0.28371416789846E + 3
6	2	4	0.24256279839182E + 3
7	2	6	-0.99357645626725E + 2
8	3	1	-0.12275453013171E + 4
9	3	2	-0.23077622506234E + 4
10	3	4	-0.16352219929859E + 4
11	3	6	0.58436648297764E + 3
12	4	1	0.42365441415641E + 4
13	4	2	-0.78027526961828E + 4
14	4	4	0.38855645739589E + 4
15	4	6	-0.91225112529381E + 3
16	5	1	-0.90143895703666E + 4
17	5	2	0.15196214817734E + 5
18	5	4	-0.39616651358508E + 4
19	5	6	-0.72027511617558E + 3
20	6	1	0.11147126705990E + 5
21	6	2	-0.17412065252210E + 5
22	6	4	0.99918281207782E + 3
23	6	6	0.33504807153854E + 4
24	7	1	-0.64752644922631E + 4
25	7	2	0.98323730907847E + 4
26	7	4	0.83877854108422E + 3
27	7	6	-0.27919349903103E + 4
28	9	1	0.11112410081192E + 4
29	9	2	-0.17287587261807E + 4
30	9	4	-0.36233262795423E + 3
31	9	6	0.61139429010144E + 3
32	3	0	0.32968064728562E + 2
33	3	3	0.10411239605066E + 3
34	1	3	-0.38225874712590E + 2
35	5	3	-0.20307478607599E + 3

Note: The specific internal energy of the liquid at the triple point U_{tr} and the specific entropy of the liquid at the triple point S_{tr} have been set equal to zero. As a consequence the specific enthalpy of the liquid at the triple point becomes different from zero. Thus for the liquid at the triple point,⁸

$$T_{tr} = 273.16 \text{ K}, \quad P_{tr} = 611.73 \text{ Pa}, \quad (5.10)$$

$$U_{tr} = 0, \quad S_{tr} = 0, \quad (5.11)$$

$$H_{tr} = 0.61187 \text{ J/kg}. \quad (5.12)$$

In the liquid-water region, small changes in density along an isotherm cause large changes in pressure. For this reason, due to an accumulation of small errors, a particular computer code may fail to return the zeros [Eq. (5.11)] at the triple-

point density which corresponds to the above values of P_{tr} and T_{tr} . In order to avoid this blemish, it is advisable to adjust the constants A_{04} and A_{05} in Eq. (5.3) by imposing condition (5.11) with the desired accuracy.

5.3. Thermodynamic Relations

All thermodynamic properties of interest can be derived from the fundamental Eq. (5.2) by the use of the following thermodynamic relations

$$\bar{V} = \bar{\rho}^{-1}, \quad (5.13)$$

$$\bar{P} = \bar{\rho}^2 \left(\frac{\partial \bar{A}}{\partial \bar{\rho}} \right)_{\bar{T}}, \quad (5.14)$$

$$\left(\frac{\partial \bar{P}}{\partial \bar{\rho}} \right)_{\bar{T}} = \frac{2\bar{P}}{\bar{\rho}} + \bar{\rho}^2 \left(\frac{\partial^2 \bar{A}}{\partial \bar{\rho}^2} \right)_{\bar{T}}, \quad (5.15)$$

$$\bar{K}_T^{-1} = \bar{\rho} \left(\frac{\partial \bar{P}}{\partial \bar{\rho}} \right)_{\bar{T}}, \quad (5.16)$$

$$\bar{\chi}_T = \bar{\rho}^2 \bar{K}_T, \quad (5.17)$$

$$\left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\rho}} = \bar{\rho}^2 \frac{\partial^2 \bar{A}}{\partial \bar{\rho} \partial \bar{T}}, \quad (5.18)$$

$$\bar{S} = - \left(\frac{\partial \bar{A}}{\partial \bar{T}} \right)_{\bar{\rho}}, \quad (5.19)$$

$$\bar{U} = \bar{A} + \bar{T} \bar{S}, \quad (5.20)$$

$$\bar{H} = \bar{U} + \frac{\bar{P}}{\bar{\rho}}, \quad (5.21)$$

$$\bar{G} = \bar{\mu} = \bar{A} + \frac{\bar{P}}{\bar{\rho}}, \quad (5.22)$$

$$\bar{C}_v = - \bar{T} \left(\frac{\partial^2 \bar{A}}{\partial \bar{T}^2} \right)_{\bar{\rho}}, \quad (5.23)$$

$$\bar{C}_p = \bar{C}_v + \frac{\bar{T}}{\bar{\rho}^2} \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\rho}}^2, \quad (5.24)$$

$$\bar{w} = \left[\frac{\bar{C}_p}{\bar{C}_v} \left(\frac{\partial \bar{P}}{\partial \bar{\rho}} \right)_{\bar{T}} \right]^{1/2}. \quad (5.25)$$

6. Ideal-Gas Properties

The ideal-gas properties of gaseous H₂O are obtained from

$$\bar{A}_{id} = \bar{A}_0(\bar{T}) + A_{20} \bar{T} \ln \bar{\rho}, \quad (6.1)$$

as a function of temperature and density, or

$$\bar{A}_{id} = \bar{A}_0(\bar{T}) - A_{20} \bar{T} \ln \bar{T} - A_{20} \bar{T} \ln A_{20} + A_{20} \bar{T} \ln \bar{P}, \quad (6.2)$$

as a function of temperature and pressure. These equations are based on a formulation of the ideal-gas properties pro-

TABLE 5. Coefficients for $\bar{A}_4(\bar{T}, \bar{\rho})$

i	$m(i)$	$n(i)$	α_i	β_i	$\bar{\rho}_i$	\bar{T}_i	A_{4i}
0	2	0	34	20000	0.10038928E + 1	0.98876821E + 0	-0.32329494E - 2
1	2	2	40	20000	0.10038928E + 1	0.98876821E + 0	-0.24139355E - 1
2	2	0	30	40000	0.10038928E + 1	0.99124013E + 0	0.79027651E - 3
3	4	0	1050	25	0.48778492E + 1	0.41713659E + 0	-0.13362857E + 1

posed by Woolley⁹ and cover a range of temperatures from 50 to 2000 K. An alternative equation, which can be extrapolated to higher temperatures, has been proposed by Cooper.¹⁰

7. Equilibrium Thermodynamic Properties in the Critical Region

In the critical region, it is more convenient to represent the thermodynamic properties by means of a canonical equation among the intensive variables P , T , and μ . The form chosen here is⁴

$$\frac{P}{T} = \frac{P}{T} \left(\frac{1}{T}, \frac{\mu}{T} \right). \quad (7.1)$$

7.1. Revised Dimensionless Variables for Critical Region

For a representation of the thermodynamic properties in the critical region, it is convenient to transform the reference temperature, density, and pressure to the value of these parameters at the critical point of the thermodynamic surface. Its coordinates now assume the role of revised reference constants and are defined by

$$T_c = 647.067 \text{ K} \quad \text{or} \quad \bar{T}_c = 0.999\,686, \quad (7.2)$$

$$\rho_c = 322.778 \text{ kg/m}^3 \quad \text{or} \quad \bar{\rho}_c = 1.015\,782, \quad (7.3)$$

$$P_c = 22.0460 \times 10^6 \text{ Pa} \quad \text{or} \quad \bar{P}_c = 0.996\,880. \quad (7.4)$$

The canonical equation is so structured that its critical point is located at T_c, ρ_c, P_c .

The reduced variables employed in the canonical equation for the critical region are defined by

$$\bar{T} = -\frac{\bar{T}_c}{T}, \quad (7.5)$$

$$\bar{\mu} = \frac{\bar{\mu}}{\bar{T}} \cdot \frac{\bar{\rho}_c \bar{T}_c}{\bar{P}_c}, \quad (7.6)$$

$$\bar{P} = \frac{\bar{P}}{\bar{T}} \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.7)$$

$$\bar{\rho} = \frac{\bar{\rho}}{\bar{\rho}_c}, \quad (7.8)$$

$$\bar{U} = \bar{\rho} \bar{U} \cdot \frac{1}{\bar{P}_c}, \quad (7.9)$$

$$\bar{S} = \bar{\rho} \bar{S} \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.10)$$

$$\bar{A} = \frac{\bar{\rho} \bar{A}}{\bar{T}} \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.11)$$

$$\bar{H} = \frac{\bar{\rho} \bar{H}}{\bar{T}} \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.12)$$

$$\bar{\chi}_T = \bar{T} \bar{\chi}_T \cdot \frac{\bar{P}_c}{\bar{T}_c \bar{\rho}_c^2}, \quad (7.13)$$

$$\bar{C}_v = \bar{\rho} \bar{C}_v \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.14)$$

$$\bar{C}_p = \bar{\rho} \bar{C}_p \cdot \frac{\bar{T}_c}{\bar{P}_c}, \quad (7.15)$$

$$\bar{w} = \frac{\bar{w}}{\bar{T}^{1/2}} \left(\frac{\bar{\rho}_c \bar{T}_c}{\bar{P}_c} \right)^{1/2}. \quad (7.16)$$

7.2. Fundamental Equation in the Critical Region

The canonical equation in the critical region is written in two parts, a regular part and a nonanalytic part which accounts for the critical anomalies. The former is expressed in terms of the natural variables \bar{T} and $\bar{\mu}$, defined in Eqs. (7.5) and (7.6). The latter part is parametrized with the aid of the following transformation:

$$\Delta \bar{\mu} \equiv \bar{\mu} - \bar{\mu}_0(\bar{T}) = r^{\beta\delta} a \theta (1 - \theta^2), \quad (7.17a)$$

$$\Delta \bar{T} \equiv \bar{T} + 1 = r(1 - b^2 \theta^2) - c r^{\beta\delta} a \theta (1 - \theta^2), \quad (7.17b)$$

where a , b , and c are constants. The variables r and θ replace the original variables \bar{T} and $\bar{\mu}$ in the nonanalytic part in such a way that there are no singularities in the single-phase region except at the critical point itself.

The fundamental equation reads

$$\bar{P} = \bar{P}_{\text{reg}} + \bar{P}_{\text{sc}}, \quad (7.18)$$

with

$$\bar{P}_{\text{reg}} = \bar{P}_0(\bar{T}) + \Delta \bar{\mu} + \bar{P}_{11} \Delta \bar{\mu} \Delta \bar{T}, \quad (7.18a)$$

$$\bar{P}_{\text{sc}} = a k_0 r^{\beta(\delta+1)} p_0(\theta) + a k_1 r^{\beta(\delta+1)+\Delta} p_1(\theta). \quad (7.18b)$$

The functions $\bar{\mu}_0(\bar{T})$ and $\bar{P}_0(\bar{T})$ are defined by

$$\bar{\mu}_0(\bar{T}) = \bar{\mu}_c + \sum_{j=1}^3 \bar{\mu}_j (\Delta \bar{T})^j, \quad (7.19)$$

$$\bar{P}_0(\bar{T}) = 1 + \sum_{j=1}^3 \bar{P}_j (\Delta \bar{T})^j. \quad (7.20)$$

The functions $p_0(\theta)$ and $p_1(\theta)$ are polynomials of the form

$$p_i(\theta) = p_{0i} + p_{2i} \theta^2 + p_{4i} \theta^4 \quad (i = 0, 1). \quad (7.21)$$

The critical exponents are

$$\beta = 0.325, \quad \delta = 4.82, \quad \Delta = 0.50. \quad (7.22)$$

The values of the other constants in Eqs. (7.17)–(7.21) are listed in Table 6. The coefficients p_{0i} of the polynomials $p_i(\theta)$ defined in Eq. (7.21) are related to the critical exponents β , δ , Δ and the constant b^2 as discussed elsewhere²; the numerical values of the coefficients p_{0i} are given in Table 7.

TABLE 6. Coefficients for the fundamental equation in the critical region

$a =$	23.667
$k_0 =$	1.4403
$k_1 =$	0.2942
$c =$	-0.01776
$b^2 =$	1.3757
$\bar{P}_1 =$	6.8445
$\bar{P}_2 =$	-25.4915
$\bar{P}_3 =$	5.238
$\bar{P}_{11} =$	0.4918
$\bar{\mu}_c =$	-11.233
$\bar{\mu}_1 =$	-22.655
$\bar{\mu}_2 =$	-17.888
$\bar{\mu}_3 =$	-4.933

TABLE 7. Coefficients for the polynomials $p_i(\theta)$

$p_{00} =$	0.586 535
$p_{20} =$	-1.026 243
$p_{40} =$	0.612 903
$p_{01} =$	0.103 25
$p_{21} =$	0.160 32
$p_{41} =$	-0.169 86

The scaled fundamental Eq. (7.18) is valid in the range

$$0.63 \leq \bar{\rho} \leq 1.32,$$

(7.23)

$$0.995 \leq \bar{T} \leq 1.07.$$

This range overlaps in part with the range of the analytic fundamental equations as specified by Eqs. (5.8) and (5.9). In the range of overlap, one has the option of either using the analytic fundamental Eq. (5.2) or the scaled fundamental Eq. (7.18); the scaled fundamental equation is recommended in cases where it is important that the surface, and in particular its derivatives, display the physical behavior predicted by the modern theory of critical phenomena.

7.3. Thermodynamic Relations

The various thermodynamic properties can be deduced from the fundamental Eq. (7.18) with the aid of the following thermodynamic relations.⁴

$$\bar{\rho} = \left(\frac{\partial \bar{P}}{\partial \bar{\mu}} \right)_{\bar{T}}, \quad (7.24)$$

$$\bar{U} = \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\mu}}, \quad (7.25)$$

$$\bar{A} = \bar{\rho} \bar{\mu} - \bar{P}, \quad (7.26)$$

$$\bar{H} = \bar{P} - \bar{T} \bar{U}, \quad (7.27)$$

$$\bar{S} = \bar{H} - \bar{\rho} \bar{\mu} = -\bar{A} - \bar{T} \bar{U}, \quad (7.28)$$

$$\bar{\chi}_T = \left(\frac{\partial^2 \bar{P}}{\partial \bar{\mu}^2} \right)_{\bar{T}}, \quad (7.29)$$

$$\left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\rho}} = \bar{U} - \frac{\bar{\rho}}{\bar{\chi}_T} \frac{\partial^2 \bar{P}}{\partial \bar{T} \partial \bar{\mu}}, \quad (7.30)$$

$$\bar{C}_v = \bar{T}^2 \left[\left(\frac{\partial^2 \bar{P}}{\partial \bar{T}^2} \right)_{\bar{\mu}} - \frac{1}{\bar{\chi}_T} \left(\frac{\partial^2 \bar{P}}{\partial \bar{T} \partial \bar{\mu}} \right)^2 \right], \quad (7.31)$$

$$\bar{C}_p = \bar{C}_v + \frac{\bar{\chi}_T}{\bar{\rho}^2} \left[\bar{P} - \bar{T} \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\rho}} \right]^2, \quad (7.32)$$

$$\bar{w} = \left[\frac{\bar{C}_p}{\bar{C}_v} \left(\frac{\partial \bar{P}}{\partial \bar{\rho}} \right)_{\bar{T}} \right]^{1/2}. \quad (7.33)$$

Note: Explicit expressions for the derivatives of the canonical equation can be found in Ref. 4.

8. Viscosity

The viscosity is represented by the equation^{11,12}

$$\bar{\eta} = \bar{\eta}_0(\bar{T}) \times \bar{\eta}_1(\bar{T}, \bar{\rho}) \times \bar{\eta}_2(\bar{T}, \bar{\rho}). \quad (8.1)$$

The first terms of the product gives the viscosity of steam in

TABLE 8. Coefficients H_i for $\bar{\eta}_0(\bar{T})$

$H_0 =$	1.000 000
$H_1 =$	0.978 197
$H_2 =$	0.579 829
$H_3 =$	-0.202 354

the ideal-gas limit and has the form

$$\bar{\eta}_0(\bar{T}) = \frac{\sqrt{\bar{T}}}{\sum_{i=0}^3 \frac{H_i}{\bar{T}^i}} \quad (8.2)$$

with the coefficients H_i given in Table 8. The second multiplicative factor is

$$\bar{\eta}_1(\bar{T}, \bar{\rho}) = \exp \left[\bar{\rho} \sum_{i=0}^5 \sum_{j=0}^6 H_{ij} \left(\frac{1}{\bar{T}} - 1 \right)^i (\bar{\rho} - 1)^j \right] \quad (8.3)$$

with the coefficients H_{ij} given in Table 9. Outside a very narrow near-critical range circumscribed by

$$\begin{aligned} 0.9970 \leq \bar{T} \leq 1.0082, \\ 0.755 \leq \bar{\rho} \leq 1.290, \end{aligned} \quad (8.4)$$

we put

$$\bar{\eta}_2 = \bar{\eta}_2'(\bar{T}, \bar{\rho}) = 1. \quad (8.5)$$

Inside the near-critical region [Eq. (8.4)], we first calculate $\bar{\chi}_T$ from the data in Sec. 7 and then identify $\bar{\eta}_2$ with

$$\begin{aligned} \bar{\eta}_2 = \bar{\eta}_2''(\bar{T}, \bar{\rho}) = 0.922 \bar{\chi}_T^{0.0263}, \quad \text{if } \bar{\chi}_T \geq 22, \\ \bar{\eta}_2 = \bar{\eta}_2'(\bar{T}, \bar{\rho}) = 1, \quad \text{if } \bar{\chi}_T < 22. \end{aligned} \quad (8.6)$$

The domain of validity of Eq. (8.1) for the viscosity is given by

$$\begin{aligned} P \leq 500 \text{ MPa} \quad \text{for} \quad 0^\circ \text{C} \leq T \leq 150^\circ \text{C}, \\ P \leq 350 \text{ MPa} \quad \text{for} \quad 150^\circ \text{C} \leq T \leq 600^\circ \text{C}, \\ P \leq 300 \text{ MPa} \quad \text{for} \quad 600^\circ \text{C} \leq T \leq 900^\circ \text{C}. \end{aligned} \quad (8.7)$$

TABLE 9. Coefficients H_{ij} for $\bar{\eta}_1(\bar{T}, \bar{\rho})$

i	j	H_{ij}
0	0	$H_{00} = 0.513 204 7$
1	0	$H_{10} = 0.320 565 6$
4	0	$H_{40} = -0.778 256 7$
5	0	$H_{50} = 0.188 544 7$
0	1	$H_{01} = 0.215 177 8$
1	1	$H_{11} = 0.731 788 3$
2	1	$H_{21} = 1.241 044$
3	1	$H_{31} = 1.476 783$
0	2	$H_{02} = -0.281 810 7$
1	2	$H_{12} = -1.070 786$
2	2	$H_{22} = -1.263 184$
0	3	$H_{03} = 0.177 806 4$
1	3	$H_{13} = 0.460 504 0$
2	3	$H_{23} = 0.234 037 9$
3	3	$H_{33} = -0.492 417 9$
0	4	$H_{04} = -0.041 766 10$
3	4	$H_{34} = 0.160 043 5$
1	5	$H_{15} = -0.015 783 86$
3	6	$H_{36} = -0.003 629 481$

Note: Coefficients H_{ij} omitted from the table are all equal to zero identically.

TABLE 10. Coefficients L_i for $\bar{\lambda}_0(\bar{T})$

$L_0 =$	1.000 000
$L_1 =$	6.978 267
$L_2 =$	2.599 096
$L_3 =$	-0.998 254

9. Thermal Conductivity

The thermal conductivity is represented by the equation^{13,14}

$$\lambda = \bar{\lambda}_0(\bar{T}) \times \bar{\lambda}_1(\bar{T}, \bar{\rho}) + \bar{\lambda}_2(\bar{T}, \bar{\rho}). \quad (9.1)$$

The factor $\bar{\lambda}_0(\bar{T})$ gives the thermal conductivity of steam in the ideal-gas limit and has the form

$$\bar{\lambda}_0(\bar{T}) = \frac{\sqrt{\bar{T}}}{\sum_{i=0}^3 \frac{L_i}{\bar{T}^i}} \quad (9.2)$$

with the coefficients L_i given in Table 10. The factor $\bar{\lambda}_1(\bar{T}, \bar{\rho})$ is

$$\bar{\lambda}_1(\bar{T}, \bar{\rho}) = \exp \left[\bar{\rho} \sum_{i=0}^4 \sum_{j=0}^5 L_{ij} \left(\frac{1}{\bar{T}} - 1 \right)^i (\bar{\rho} - 1)^j \right], \quad (9.3)$$

with the coefficients L_{ij} given in Table 11. The additive term $\bar{\lambda}_2(\bar{T}, \bar{\rho})$ which accounts for an enhancement of the thermal conductivity in the critical region, is defined by

$$\bar{\lambda}_2(\bar{T}, \bar{\rho}) = \frac{0.001\,384\,8}{\bar{\eta}_0(\bar{T}) \cdot \bar{\eta}_1(\bar{T}, \bar{\rho})} \left(\frac{\bar{T}}{\bar{\rho}} \right)^2 \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{\rho}}^2 \bar{\chi}_T^{0.4678} \bar{\rho}^{1/2} \times \exp[-18.66(\bar{T} - 1)^2 - (\bar{\rho} - 1)^4]. \quad (9.4)$$

The derivatives $(\partial \bar{P} / \partial \bar{T})_{\bar{\rho}}$ and $\bar{\chi}_T$ are to be calculated from the fundamental equations presented in Secs. 5 and 7; the

functions $\bar{\eta}_0(\bar{T})$ and $\bar{\eta}_1(\bar{T}, \bar{\rho})$ are to be calculated from the equations presented in Sec. 8.

Equation (9.1) for the thermal conductivity covers the range

$$\begin{aligned} P < 400 \text{ MPa} & \text{ for } 0^\circ\text{C} \leq T \leq 125^\circ\text{C}, \\ P < 200 \text{ MPa} & \text{ for } 125^\circ\text{C} \leq T \leq 250^\circ\text{C}, \\ P < 150 \text{ MPa} & \text{ for } 250^\circ\text{C} \leq T \leq 400^\circ\text{C}, \\ P < 100 \text{ MPa} & \text{ for } 400^\circ\text{C} \leq T \leq 800^\circ\text{C}. \end{aligned} \quad (9.5)$$

10. Surface Tension

The surface tension is correlated by the equation^{15,16}

$$\bar{\sigma} = \left(\frac{\bar{T}_c - \bar{T}}{\bar{T}_c} \right)^v \left[1 + B \left(\frac{\bar{T}_c - \bar{T}}{\bar{T}_c} \right) \right], \quad (10.1)$$

with

$$\begin{aligned} \bar{T}_c &= 0.999\,686, \\ v &= 1.256, \\ B &= -0.625. \end{aligned} \quad (10.2)$$

This equation covers the entire liquid range from the triple point to the critical point.

11. Computer-Program Verification

To assist the user in computer-program verification, we present a short table of values calculated for a number of thermophysical properties. The numerical values in Table 12 are given to six digits which is considered adequate for all practical purposes.

TABLE 11. Coefficients L_{ij} for $\bar{\lambda}_1(\bar{T}, \bar{\rho})$

$j \backslash i$	0	1	2	3	4
0	+1.329 304 6	+1.701 836 3	+5.224 615 8	+8.712 767 5	-1.852 599 9
1	-0.404 524 37	-2.215 684 5	-10.124 111	-9.500 061 1	+0.934 046 90
2	+0.244 094 90	+1.651 105 7	+4.987 468 7	+4.378 660 6	0.0
3	+0.018 660 751	-0.767 360 02	-0.272 976 94	-0.917 837 82	0.0
4	-0.129 610 68	+0.372 833 44	-0.430 833 93	0.0	0.0
5	+0.044 809 953	-0.112 031 60	+0.133 338 49	0.0	0.0

TABLE 12. Thermophysical property values calculated for selected values of \bar{T} and $\bar{\rho}$

\bar{T}	$\bar{\rho}$	\bar{A}	\bar{P}	\bar{C}_v	$\bar{\eta}$	$\bar{\lambda}$
0.50	3.20	-0.250554E+0	0.324936E+1	0.359788E+2	0.101430E+2	0.136939E+1
0.75	2.85	-0.400493E+1	0.391145E+1	0.299897E+2	0.263154E+1	0.146879E+1
0.90	0.08	-0.127371E+2	0.260476E+0	0.196868E+2	0.366753E+0	0.113441E+0
1.00	1.50	-0.116979E+2	0.105315E+1	0.306178E+2	0.998110E+0	0.820132E+0
1.20	0.40	-0.237304E+2	0.146688E+1	0.214850E+2	0.589682E+0	0.243784E+0
1.20	1.20	-0.203908E+2	0.304551E+1	0.248417E+2	0.926072E+0	0.573946E+0
1.40	0.20	-0.383216E+2	0.108246E+1	0.182170E+2	0.647290E+0	0.214271E+0
1.40	0.90	-0.309982E+2	0.387225E+1	0.218535E+2	0.889235E+0	0.459263E+0
1.60	0.10	-0.551985E+2	0.664893E+0	0.178744E+2	0.722462E+0	0.226297E+0
1.60	0.70	-0.429449E+2	0.408739E+1	0.206189E+2	0.908446E+0	0.436321E+0

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