New International Formulations for the Thermodynamic Properties of Light and Heavy Water

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The General Assembly of the International Association for the Properties of Steam (IAPS), meeting at the 10th International Conference on the Properties of Steam in Moscow in September 1984, adopted new formulations for the thermodynamic properties of fluid H_2O and D_2O. The new formulations have been designated as the *IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use* and the *IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance*. In this paper we present and discuss these new formulations.

Key words: equation of state; fundamental equation; heavy water; IAPS; steam; thermodynamic properties; water; water vapor.

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1. Introduction

Reliable information for the thermodynamic properties of water and steam (water substance) is needed for many industrial and scientific applications. The need for international cooperation to formulate and standardize the properties of water substance was first felt by engineers involved in the design and operation of steam turbines. This cooperation has been effected through a series of international conferences on the properties of steam, the first of which was held in London in 1929.[1-3]

As a first concrete result, the Third International Conference on the Properties of Steam, held in the USA in 1934, adopted a set of so-called skeleton tables for the specific volume and enthalpy of water substance. These tables covered temperatures up to 500 °C and pressures up to 400 bar. However, in order to arrive at the 1934 skeleton tables, it was necessary to extrapolate the available experimental data and it was recommended that additional measurements should be taken in order to increase the reliability of the skeleton tables. Several authors in different countries published extensive steam tables which were elaborations of the 1934 skeleton tables.[4-6] The work of international standardization was interrupted by World War II and taken up again at the Fourth International Conference on the Properties of Steam held in Philadelphia in 1954. The resumed activities led to the adoption of a new set of international skeleton tables for the thermodynamic properties of water substance by the Sixth International Conference on the Properties of Steam held in Providence and in New York in 1963.[7] The 1963 skeleton tables contain values and tolerances for the specific volume and specific enthalpy of water substance at temperatures up to 800 °C and pressures up to 1000 bar. The values of the 1963 skeleton tables have served as an international standard until the present.

The Sixth International Conference also appointed an International Formulation Committee (IFC) to prepare an international formulation, or set of equations, which would yield numerical values for the thermodynamic properties of water substance when programed into a computer. The IFC arrived at two such formulations, namely, the 1967 IFC Formulation for Industrial Use[8] and the *1968 IFC Formulation for Scientific and General Use*.[9] These formulations agree with the 1963 skeleton tables within the stated tolerances. The 1967 IFC Formulation for Industrial Use serves as the

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common basis for the specification of steam plants in many countries.

The IFC, having completed its tasks, was discharged at the Seventh International Conference on the Properties of Steam held in Tokyo in 1968.To provide continuity, the Seventh Conference authorized the creation of an International Association for the Properties of Steam (IAPS). In subsequent years, IAPS set up a number of working groups for the study of various properties of light and heavy water substance.

There existed a number of incentives to continue to work towards improved formulations for the properties of water and steam. First, the IFC fomulations are composites of separate equations in a number of subregions. As a consequence, these formulations do not yield a smooth representation of the derivatives of the thermodynamic surface at the boundaries of the subregions.[10,11] It thus became desirable to develop a single algebraic equation in the entire region covered by the IFC formulations. Valuable equations of this type were proposed by Keenan *et al.*[12] and subsequently by Pollak.[13] Secondly, geophysical and other technical applications generated a demand for a formulation that would be valid in wider ranges of temperatures and pressures. Finally, a significant quantity of new accurate experimental thermodynamic property data had become available since 1963 and this made it possible to develop more accurate formulations for both ordinary and heavy water. Accordingly, the General Assembly of the Ninth International Conference on the Properties of Steam held in Munich in 1979 empowered the Executive Committee (EC) of IAPS to prepare, among others, documents in the form of releases for the purpose of replacing the *IFC 1968 Formulation for Scientific and General Use*, and the 1963 skeleton tables. In addition, it authorized the EC of IAPS to issue a formulation for the thermodynamic properties of heavy water substance. The task of preparing such releases was assigned by the EC to Working Group I of IAPS, consisting of representatives from Canada, the Czechoslovak Socialist Republic, the Federal Republic of Germany, Japan, Switzerland, the Union of Soviet Socialist Republics, the United Kingdom, and the United States of America.[14] The names of the individual members of Working Group I are given in Table 1.1. Working Group I met in London in 1980, in Prague in 1981, in Ottawa in 1982, in Tokyo in 1983, and in Moscow in 1984.

Based on the recommendations of Working Group I, the EC of IAPS adopted in 1982 a Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use and a Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Heavy Water Substance.[15] The Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use was the result of the joint work of L. Haar and J. S. Gallagher at the National Bureau of Standards of the USA, and of the late G. S. Kell at the National Research Council of Canada. This formulation was checked carefully by various national research groups represented in Working Group I. The equation adopted as the Provisional Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance was originally published by Haar *et al.* in the *Proceedings of the 8th Symposium on Thermophysical Properties*,[16] and subsequently issued as the *NBS/NRC Steam Tables*.[17] The Provisional Formulation 1982 for the Thermodynamic Properties of Heavy Water Substance was based on an equation prepared by Hill *et al.* at the University of British Columbia in Canada and published in this journal[18]; it was also issued as *Tables of Thermodynamic Properties of Heavy Water in S.I. Units*.[19] Both formulations were adopted by IAPS in 1982 on a provisional basis with the understanding that final action was to be taken by the Tenth International Conference on the Properties of Steam in Moscow in 1984. The General Assembly of IAPS meeting at the Tenth Conference adopted the *IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use* and the *IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance*.[20] The formulations adopted in 1984 are identical with the provisional formulations earlier adopted in 1982, except that the equations have been cast in dimensionless forms as proposed by Kestin *et al.*[21,22]

TABLE 1.1. Members of Working Group I of IAPS

A. A. Aleksandrov	(USSR)
S. Angus	(UK)
J. R. Cooper	(UK)
L. Haar	(USA)
A. J. W. Hedbäck	(Switzerland)
P. G. Hill	(Canada)
J. Jůza	(CSSR)
G. S. Kell	(Canada)
E. J. Le Fèvre	(UK)
J. M. H. Levelt Sengers	(USA)
P. Z. Rosta	(Canada)
J. Straub[a]	(FRG)
M. Uematsu	(Japan)
W. Wagner	(FRG)
K. Watanabe	(Japan)
A. Nagashima[b]	(Japan)

[a] Chairman.
[b] Co-opted expert.

Thus the *IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use* replaces the *1968 IFC Formulation for Scientific and General Use.* It is emphasized that the international status of the 1967 IFC Formulation for Industrial Use[5] remains in effect and is unchanged.

At the Tenth International Conference on the Properties of Steam, the General Assembly of IAPS also approved a new set of skeleton tables for the thermodynamic properties of water substance, which the EC of IAPS will prepare for release in the near future.

2. IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance

2.1. Fundamental Equation

A verbatim copy of the *Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Wa-*

ter Substance for Scientific and General Use[a)] is attached as Appendix I to this article. The formulation is based on a fundamental equation for the specific Helmholtz free energy A as a function of temperature T and density ρ developed by Messrs. Haar, Gallagher, and by the late Dr. Kell.[16,17] The formulation in the dimensionless form adopted by IAPS in 1984 is identical with the fundamental equation presented in Sec. 5 of a previous publication in this journal.[21]

All thermodynamic properties are made dimensionless with the aid of a reference temperature T^*, a reference density ρ^*, and a reference pressure P^*. For H_2O these three reference constants are defined as

$$T^* = 647.27 \text{ K}, \tag{2.1}$$

$$\rho^* = 317.763 \text{ kg m}^{-3}, \tag{2.2}$$

$$P^* = 22.115 \times 10^6 \text{ Pa}. \tag{2.3}$$

These reference constants are close to but not identical with the critical parameters[24] of H_2O.

The fundamental equation adopted by IAPS is an equation for the dimensionless Helmholtz function $\overline{A} = A\rho^*/P^*$ in terms of the reduced temperature $\overline{T} = T/T^*$ and the reduced density $\overline{\rho} = \rho/\rho^*$. The fundamental equation has the form

$$\overline{A}(\overline{T},\overline{\rho}) = \sum_{j=0}^{4} \overline{A}_j, \tag{2.4}$$

where the functions $\overline{A}_j$ are given by

$$\overline{A}_0 = (A_{00} + A_{01}\overline{T})\ln \overline{T} + \sum_{i=2}^{17} A_{0i}\overline{T}^{i-4}, \tag{2.4a}$$

$$\overline{A}_1 = \overline{\rho} \sum_{i=0}^{4} A_{1i}(1/\overline{T})^{i-1}, \tag{2.4b}$$

$$\overline{A}_2 = A_{20}\overline{T}\left[\ln\left(\frac{\overline{\rho}}{1-y}\right) - \frac{130}{3(1-y)} + \frac{169}{6(1-y)^2} - 14y\right], \tag{2.4c}$$

with

$$y = \overline{\rho}[y_0 + y_1 \ln \overline{T} + (y_2/\overline{T}^3) + (y_3/\overline{T}^5)],$$

$$\overline{A}_3 = \sum_{i=0}^{35} A_{3i}(1/\overline{T})^{l(i)} z^{k(i)}, \tag{2.4d}$$

with

$$z = 1 - \exp(-z_0\overline{\rho}),$$

$$\overline{A}_4 = \sum_{i=0}^{3} A_{4i}\delta_i^{n(i)} \exp(-\alpha_i\delta_i^{m(i)} - \beta_i\tau_i^2), \tag{2.4e}$$

with

$$\delta_i = \frac{\overline{\rho} - \overline{\rho}_i}{\overline{\rho}_i}, \quad \tau_i = \frac{\overline{T} - \overline{T}_i}{\overline{T}_i}.$$

The coefficients A_{ji}, the coefficients y_i, the exponents $k(i)$, $l(i)$, $m(i)$, $n(i)$, and the constants z_0, α_i, β_i, $\overline{\rho}_i$, and $\overline{T}_i$ are listed in Tables I.1–I.5 of Appendix I.

[a)] By ordinary water substance is meant water whose molar mass (Refs. 21 and 23) is equal to 0.018 015 2 kg/mol.

The use of this formulation for fluid H_2O has been endorsed by IAPS for temperatures between 0 and 1000 °C and pressures ranging from zero up to a maximum of 5000 bar at 0 °C and up to 15 000 bar at 150 °C and above. A small region around the critical point bounded by

$$|T - T^*| \leqslant 1 \text{ K}, \quad |\overline{\rho} - 1| \leqslant 0.3, \tag{2.5}$$

is excepted. A comparison between values of thermodynamic properties calculated from this fundamental equation with selected experimental data is included in the *NBS/NRC Steam Tables*.[17] The uncertainties in the values of the density and enthalpy calculated from this fundamental equation can be estimated from the information presented in Figs. 1–3 of Appendix I.

2.2. Thermodynamic Derivatives

All thermodynamic properties can be expressed in terms of the function $\overline{A}(\overline{T},\overline{\rho})$ and its first and second derivatives with respect to $\overline{T}$ and $\overline{\rho}$ as indicated in Secs. 1.3 and 2.3 of Appendix I. These derivatives can be written in the form

$$\left(\frac{\partial \overline{A}}{\partial \overline{T}}\right)_{\overline{\rho}} = \sum_{j=0}^{4} \overline{A}_{T,j}, \tag{2.6}$$

$$\left(\frac{\partial^2 \overline{A}}{\partial \overline{T}^2}\right)_{\overline{\rho}} = \sum_{j=0}^{4} \overline{A}_{TT,j}, \tag{2.7}$$

$$\left(\frac{\partial \overline{A}}{\partial \overline{\rho}}\right)_{\overline{T}} = \sum_{j=0}^{4} \overline{A}_{\rho,j}, \tag{2.8}$$

$$\left(\frac{\partial^2 \overline{A}}{\partial \overline{\rho}^2}\right)_{\overline{T}} = \sum_{j=0}^{4} \overline{A}_{\rho\rho,j}, \tag{2.9}$$

$$\frac{\partial^2 \overline{A}}{\partial \overline{T}\,\partial \overline{\rho}} = \sum_{j=0}^{4} \overline{A}_{T\rho,j}. \tag{2.10}$$

For the convenience of the user we present in Tables 2.1–2.5 the explicit expressions for the functions $\overline{A}_{T,j}$, $\overline{A}_{TT,j}$, $\overline{A}_{\rho,j}$, $\overline{A}_{\rho\rho,j}$, and $\overline{A}_{T\rho,j}$. In particular, the dimensionless specific entropy $\overline{S} = \rho^* T^* S/P^*$ and dimensionless specific energy $\overline{U} = \rho^* U/P^*$ are given by

$$\overline{S} = -\sum_{j=0}^{4} \overline{A}_{T,j}, \tag{2.11}$$

$$\overline{U} = \sum_{j=0}^{4} (\overline{A}_j - \overline{T}\overline{A}_{T,j}). \tag{2.12}$$

When the expressions for $\overline{A}_0$ and $\overline{A}_{T,0}$ are substituted into Eqs. (2.11) and (2.12), we note that the coefficients A_{04} and A_{05} enter as additive constants in the expressions for $\overline{U}$ and $\overline{S}$, respectively. These constants are fixed by the convention that the energy and the entropy of the liquid phase at the triple point are taken to be zero. In the liquid region small changes in density along an isotherm cause large changes in pressure. For this reason values calculated for the entropy and energy at the triple-point density may depend on the particular computer code. Hence, it is advisable to adjust the constants A_{04} and A_{05} in a given computer code so as to guarantee that the calculated energy and entropy vanish at the reference point with the desired accuracy.

TABLE 2.1. The functions $\overline{A}_{T,j}$ for H_2O

$$\overline{A}_{T,0} = \frac{A_{00}}{\overline{T}} + A_{01}\ln\overline{T} + A_{01} + \sum_{i=2}^{17} A_{0i}(i-4)\overline{T}^{i-5} \tag{2.1.1}$$

$$\overline{A}_{T,1} = -\overline{\rho}\sum_{i=0}^{4} A_{1i}(i-1)\left(\frac{1}{\overline{T}}\right)^{i} \tag{2.1.2}$$

$$\overline{A}_{T,2} = \frac{\overline{A}_2}{\overline{T}} + A_{20}\overline{T}\left[\frac{1}{1-y} - \frac{130}{3(1-y)^2} + \frac{169}{3(1-y)^3} - 14\right]\left(\frac{\partial y}{\partial \overline{T}}\right)_{\overline{\rho}} \tag{2.1.3}$$

$$\overline{A}_{T,3} = -\sum_{i=0}^{35} A_{3i}l(i)\left(\frac{1}{\overline{T}}\right)^{l(i)+1} z^{k(i)} \tag{2.1.4}$$

$$\overline{A}_{T,4} = -2\sum_{i=0}^{3} \frac{A_{4i}\delta_i^{n(i)}\beta_i\tau_i}{\overline{T}_i}\exp(-\alpha_i\delta_i^{m(i)} - \beta_i\tau_i^2) \tag{2.1.5}$$

Note: $$\left(\frac{\partial y}{\partial \overline{T}}\right)_{\overline{\rho}} = \overline{\rho}\left(\frac{y_1}{\overline{T}} - \frac{3y_2}{\overline{T}^4} - \frac{5y_3}{\overline{T}^6}\right) \tag{2.1.6}$$

TABLE 2.2. The functions $\overline{A}_{TT,j}$ for H_2O

$$\overline{A}_{TT,0} = -\frac{A_{00}}{\overline{T}^2} + \frac{A_{01}}{\overline{T}} + \sum_{i=2}^{17} A_{0i}(i-4)(i-5)\overline{T}^{i-6} \tag{2.2.1}$$

$$\overline{A}_{TT,1} = +\overline{\rho}\sum_{i=0}^{4} A_{1i}i(i-1)\left(\frac{1}{\overline{T}}\right)^{i+1} \tag{2.2.2}$$

$$\overline{A}_{TT,2} = A_{20}\left[\frac{1}{1-y} - \frac{130}{3(1-y)^2} + \frac{169}{3(1-y)^3} - 14\right]\left[2\left(\frac{\partial y}{\partial \overline{T}}\right)_{\overline{\rho}} + \overline{T}\left(\frac{\partial^2 y}{\partial \overline{T}^2}\right)_{\overline{\rho}}\right] + A_{20}\overline{T}\left[\frac{1}{(1-y)^2} - \frac{260}{3(1-y)^3} + \frac{169}{(1-y)^4}\right]\left(\frac{\partial y}{\partial \overline{T}}\right)_{\overline{\rho}}^2 \tag{2.2.3}$$

$$\overline{A}_{TT,3} = \sum_{i=0}^{35} A_{3i}l(i)\,[l(i)+1]\left(\frac{1}{\overline{T}}\right)^{l(i)+2} z^{k(i)} \tag{2.2.4}$$

$$\overline{A}_{TT,4} = -2\sum_{i=0}^{3} \frac{A_{4i}\delta_i^{n(i)}(\beta_i - 2\beta_i^2\tau_i^2)}{\overline{T}_i^2}\exp(-\alpha_i\delta_i^{m(i)} - \beta_i\tau_i^2) \tag{2.2.5}$$

Note: $$\left(\frac{\partial^2 y}{\partial \overline{T}^2}\right)_{\overline{\rho}} = \overline{\rho}\left(-\frac{y_1}{\overline{T}^2} + \frac{12y_2}{\overline{T}^5} + \frac{30y_3}{\overline{T}^7}\right) \tag{2.2.6}$$

TABLE 2.3. The functions $\overline{A}_{\rho,j}$ for H_2O

$$\overline{A}_{\rho,0} = 0 \tag{2.3.1}$$

$$\overline{A}_{\rho,1} = \sum_{i=0}^{4} A_{1i}\left(\frac{1}{\overline{T}}\right)^{i-1} = \frac{\overline{A}_1}{\overline{\rho}} \tag{2.3.2}$$

$$\overline{A}_{\rho,2} = \frac{A_{20}\overline{T}}{\overline{\rho}}\left[\frac{1}{1-y} - \frac{130y}{3(1-y)^2} + \frac{169y}{3(1-y)^3} - 14y\right] \tag{2.3.3}$$

$$\overline{A}_{\rho,3} = z_0(1-z)\sum_{i=0}^{35} A_{3i}\left(\frac{1}{\overline{T}}\right)^{l(i)} k(i)z^{k(i)-1} \tag{2.3.4}$$

$$\overline{A}_{\rho,4} = \sum_{i=0}^{3} \frac{A_{4i}\delta_i^{n(i)-1}}{\overline{\rho}_i}[n(i) - \alpha_i m(i)\delta_i^{m(i)}]\exp[-\alpha_i\delta_i^{m(i)} - \beta_i\tau_i^2] \tag{2.3.5}$$

TABLE 2.4. The functions $\overline{A}_{\rho\rho,j}$ for H_2O

$$\overline{A}_{\rho\rho,0} = 0 \tag{2.4.1}$$

$$\overline{A}_{\rho\rho,1} = 0 \tag{2.4.2}$$

$$\overline{A}_{\rho\rho,2} = \frac{A_{20}\overline{T}}{\overline{\rho}^2}\left[-\frac{1}{1-y} + \frac{y}{(1-y)^2} - \frac{260y^2}{3(1-y)^3} + \frac{169y^2}{(1-y)^4}\right] \tag{2.4.3}$$

$$\overline{A}_{\rho\rho,3} = -z_0\overline{A}_{\rho,3} + z_0^2(1-z)^2\sum_{i=0}^{35} A_{3i}\left(\frac{1}{\overline{T}}\right)^{l(i)} k(i)[k(i)-1]z^{k(i)-2} \tag{2.4.4}$$

$$\overline{A}_{\rho\rho,4} = \sum_{i=0}^{3} \frac{A_{4i}\delta_i^{n(i)-2}}{\overline{\rho}_i^2}\{n(i)[n(i)-1] - \alpha_i m(i)[2n(i)+m(i)-1]\delta_i^{m(i)} + \alpha_i^2 m^2(i)\delta_i^{2m(i)}\}\exp[-\alpha_i\delta_i^{m(i)} - \beta_i\tau_i^2] \tag{2.4.5}$$

TABLE 2.5. The functions $\overline{A}_{T\rho,j}$ for H_2O

$$\overline{A}_{T\rho,0} = 0 \tag{2.5.1}$$

$$\overline{A}_{T\rho,1} = \frac{\overline{A}_{T,1}}{\overline{\rho}} \tag{2.5.2}$$

$$\overline{A}_{T\rho,2} = \frac{\overline{A}_{\rho,2}}{\overline{T}} + \frac{A_{20}\overline{T}}{\overline{\rho}}\left[-\frac{127}{3(1-y)^2} + \frac{169-260y}{3(1-y)^3} + \frac{169y}{(1-y)^4} - 14\right]\left(\frac{\partial y}{\partial \overline{T}}\right)_{\overline{\rho}} \tag{2.5.3}$$

$$\overline{A}_{T\rho,3} = -z_0(1-z)\sum_{i=0}^{35} A_{3i}l(i)k(i)\,(1/\overline{T})^{l(i)+1}z^{k(i)-1} \tag{2.5.4}$$

$$\overline{A}_{T\rho,4} = -2\sum_{i=0}^{3}\frac{A_{4i}\delta_i^{n(i)-1}\beta_i\tau_i}{\overline{T}_i\overline{\rho}_i}\left[n(i)-\alpha_i m(i)\delta_i^{m(i)}\right]\exp\left[-\alpha_i\delta_i^{m(i)}-\beta_i\tau_i^2\right] \tag{2.5.5}$$

3. IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance

3.1. Fundamental Equation

A verbatim copy of the *Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance*[b)] is attached as Appendix II to this article. The formulation is based on a fundamental equation developed by Hill, MacMillan, and Lee.[18,19] The formulation in the dimensionless form adopted by IAPS in 1984 is identical with the fundamental equation presented in Sec. 6 of a previous publication in this journal.[22]

For D_2O, the reference temperature T^*, the reference density ρ^*, and the reference pressure P^* are defined as

$$T^* = 643.89\ \text{K}, \tag{3.1}$$

$$\rho^* = 358\ \text{kg/m}^3, \tag{3.2}$$

$$P^* = 21.671\times 10^6\ \text{Pa}. \tag{3.3}$$

Again these reference constants are close to but not identical with the critical parameters.[24]

As in the case of H_2O, the fundamental equation adopted by IAPS for D_2O is an equation for the dimensionless Helmholtz function $\overline{A} = A\rho^*/P^*$ in terms of the reduced temperature $\overline{T} = T/T^*$ and the reduced density $\overline{\rho} = \rho/\rho^*$.

The fundamental equation has the form

$$\overline{A}(\overline{T},\overline{\rho}) = \overline{A}_0 + \overline{A}_1, \tag{3.4}$$

where the functions $\overline{A}_0$ and $\overline{A}_1$ are given by

$$\overline{A}_0 = (A_{00} + A_{01}\overline{T})\ln\overline{T} + \sum_{j=2}^{7} A_{0j}\overline{T}^{\,j-2} + A_{08}\overline{T}\ln\overline{\rho}, \tag{3.4a}$$

$$\overline{A}_1 = \overline{T}\overline{\rho}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2} X_i(\overline{\rho}), \tag{3.4b}$$

with

$$X_i(\overline{\rho}) = \sum_{j=1}^{8} A_{ij}(\overline{\rho}-\overline{\rho}_i)^{j-1} + e^{-z_0\overline{\rho}}(A_{i,9} + A_{i,10}\overline{\rho}). \tag{3.4c}$$

The coefficients A_{ij} and the constants $\overline{T}_i$ and $\overline{\rho}_i$ are given in Tables II.1–II.3 in Appendix II, while z_0 is

$$z_0 = 1.5394. \tag{3.4d}$$

The use of this formulation for fluid D_2O has been endorsed by IAPS for temperatures up to 800 K and for pressures up to 1000 bar, except for a region around the critical point bounded by

$$|T - T^*| \leqslant 10\ \text{K}, \quad |\overline{\rho} - 1| \leqslant 0.3. \tag{3.5}$$

A comparison between values of thermodynamic properties calculated from this fundamental equation with selected experimental data can be found in the article of Hill *et al.*[18] The estimated uncertainty of this equation is indicated by the tolerances included in Table II.4 of Appendix II.

3.2. Thermodynamic Derivatives

Again, all thermodynamic properties can be expressed in terms of the function $\overline{A}(\overline{T},\overline{\rho})$ and its first and second derivatives with respect to $\overline{T}$ and $\overline{\rho}$, as indicated in Secs. 1.3 and 2.3 of Appendix II. These derivatives can be written

$$\left(\frac{\partial\overline{A}}{\partial\overline{T}}\right)_{\overline{\rho}} = \overline{A}_{T,0} + \overline{A}_{T,1}, \tag{3.6}$$

$$\left(\frac{\partial^2\overline{A}}{\partial\overline{T}^2}\right)_{\overline{\rho}} = \overline{A}_{TT,0} + \overline{A}_{TT,1}, \tag{3.7}$$

$$\left(\frac{\partial\overline{A}}{\partial\overline{\rho}}\right)_{\overline{T}} = \overline{A}_{\rho,0} + \overline{A}_{\rho,1}, \tag{3.8}$$

$$\left(\frac{\partial^2\overline{A}}{\partial\overline{\rho}^2}\right)_{\overline{T}} = \overline{A}_{\rho\rho,0} + \overline{A}_{\rho\rho,1}, \tag{3.9}$$

$$\frac{\partial^2\overline{A}}{\partial\overline{T}\,\partial\overline{\rho}} = \overline{A}_{T\rho,0} + \overline{A}_{T\rho,1}. \tag{3.10}$$

For the convenience of the user we present in Tables 3.1–3.5 the explicit expressions for the functions $\overline{A}_{T,j}$, $\overline{A}_{TT,j}$, $\overline{A}_{\rho,j}$, $\overline{A}_{\rho\rho,j}$, and $\overline{A}_{T\rho,j}$.

In analogy to Eqs. (2.11) and (2.12), we obtain for the

b) By heavy water substance is meant heavy water whose molar mass (Refs. 22 and 23) is equal to 0.020 027 5 kg/mol.

TABLE 3.1. The functions $\overline{A}_{T,j}$ for D_2O

$$\overline{A}_{T,0} = \frac{A_{00}}{\overline{T}} + A_{01}\ln\overline{T} + A_{01} + \sum_{i=2}^{7}(i-2)A_{0i}\overline{T}^{i-3} + A_{08}\ln\bar{\rho} \tag{3.1.1}$$

$$\overline{A}_{T,1} = -\frac{\bar{\rho}}{\overline{T}_1}\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2}X_i(\bar{\rho}) - \frac{\bar{\rho}}{\overline{T}}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}(i-2)\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-3}X_i(\bar{\rho}) \tag{3.1.2}$$

TABLE 3.2. The functions $\overline{A}_{TT,j}$ for D_2O

$$\overline{A}_{TT,0} = -\frac{A_{00}}{\overline{T}^2} + \frac{A_{01}}{\overline{T}} + \sum_{i=2}^{7}(i-2)(i-3)A_{0i}\overline{T}^{i-4} \tag{3.2.1}$$

$$\overline{A}_{TT,1} = \frac{2\bar{\rho}}{\overline{T}^3}\sum_{i=1}^{7}(i-2)\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-3}X_i(\bar{\rho}) + \frac{\bar{\rho}}{\overline{T}^3}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}(i-2)(i-3)\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-4}X_i(\bar{\rho}) \tag{3.2.2}$$

TABLE 3.3. The functions $\overline{A}_{\rho,j}$ for D_2O

$$\overline{A}_{\rho,0} = \frac{A_{08}\overline{T}}{\bar{\rho}} \tag{3.3.1}$$

$$\overline{A}_{\rho,1} = \frac{\overline{A}_1}{\bar{\rho}} + \overline{T}\bar{\rho}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2}\frac{dX_i}{d\bar{\rho}} \tag{3.3.2}$$

Note: $$\frac{dX_i}{d\bar{\rho}} = \sum_{j=1}^{8}(j-1)A_{ij}(\bar{\rho}-\bar{\rho}_i)^{j-2} - z_0e^{-z_0\bar{\rho}}(A_{i,9} + A_{i,10}\bar{\rho}) + A_{i,10}e^{-z_0\bar{\rho}} \tag{3.3.3}$$

TABLE 3.4. The functions $\overline{A}_{\rho\rho,j}$ for D_2O

$$\overline{A}_{\rho\rho,0} = -\frac{A_{08}\overline{T}}{\bar{\rho}^2} \tag{3.4.1}$$

$$\overline{A}_{\rho\rho,1} = 2\overline{T}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2}\frac{dX_i}{d\bar{\rho}} + \overline{T}\bar{\rho}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2}\frac{d^2X_i}{d\bar{\rho}^2} \tag{3.4.2}$$

Note: $$\frac{d^2X_i}{d\bar{\rho}^2} = \sum_{j=1}^{8}(j-1)(j-2)A_{ij}(\bar{\rho}-\bar{\rho}_i)^{j-3} + z_0^2e^{-z_0\bar{\rho}}(A_{i,9} + A_{i,10}\bar{\rho}) - 2A_{i,10}z_0e^{-z_0\bar{\rho}} \tag{3.4.3}$$

TABLE 3.5. The functions $\overline{A}_{T\rho,j}$ for D_2O

$$\overline{A}_{T\rho,0} = \frac{A_{08}}{\bar{\rho}} \tag{3.5.1}$$

$$\overline{A}_{T\rho,1} = \frac{\overline{A}_{T,1}}{\bar{\rho}} - \frac{\bar{\rho}}{\overline{T}_1}\sum_{i=1}^{7}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-2}\frac{dX_i}{d\bar{\rho}} - \frac{\bar{\rho}}{\overline{T}}\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_1}\right)\sum_{i=1}^{7}(i-2)\left(\frac{1}{\overline{T}} - \frac{1}{\overline{T}_i}\right)^{i-3}\frac{dX_i}{d\bar{\rho}} \tag{3.5.2}$$

dimensionless specific entropy $\overline{S} = \rho^*T^*S/P^*$ and dimensionless specific energy $\overline{U} = \rho^*U/P^*$,

$$\overline{S} = -(\overline{A}_{T,0} + \overline{A}_{T,1}), \tag{3.11}$$

$$\overline{U} = \overline{A}_0 + \overline{A}_1 - \overline{T}(\overline{A}_{T,0} + \overline{A}_{T,1}). \tag{3.12}$$

In this case the coefficients A_{02} and A_{03} appear as additive constants in $\overline{U}$ and $\overline{S}$ and, therefore, depend on the choice of the reference state where energy and entropy are taken to be zero. In the case of H_2O the reference state was the liquid at the triple point whose temperature is known exactly by virtue of the definition of the international temperature scale. In the case of D_2O the temperature of the triple point is not known exactly. In the IAPS 1984 Formulation the reference state of zero energy and entropy was taken to be the liquid state in coexistence with the vapor at 276.95 K. This reference state is close to (but not necessarily identical with) the liquid state at the triple point of D_2O. For a given computer code it is recommended that the coefficients A_{02} and A_{03} be

adjusted so as to guarantee that the calculated energy and entropy vanish at the reference state within the desired accuracy.

4. Future Research

Having reached a milestone in the development of international standards for the properties of H_2O and D_2O in the two formulations discussed in this article, the General Assembly at the Tenth International Conference in Moscow authorized IAPS to reorganize its working groups, to put more emphasis on the study of the properties of aqueous mixtures and solutions in the future. Accordingly, while retaining its Subcommittee on Industrial Calculations, IAPS created two working groups: Working Group A will be concerned with the thermophysical properties of normal and heavy water substance and aqueous systems; Working Group B will be concerned with the chemical thermodynamics of power cycles.

As part of its task, Working Group A will continue to monitor and coordinate research on the thermodynamic properties of ordinary and heavy water. Specifically two topics will require further research. First, the thermodynamic properties of fluids are known to satisfy nonanalytic scaling laws near the critical point. These cannot be accommodated by the present IAPS formulations, which are analytic at the critical point.[25] As a consequence the IAPS formulations cease to be valid close to the critical point. Fundamental equations for the thermodynamic properties in the critical region that incorporate the nonanalytic scaling laws have been developed for normal steam[21,26] as well as for heavy steam.[22,27] The problem remains how smoothly to connect the scaled equation in the critical region with a global analytic thermodynamic surface.[28–30] Recent work of Hill has indicated that a practical solution to this problem for steam is now within reach.[31] Secondly, while the IAPS formulations yield for both H_2O and D_2O a fundamental equation for the Helmholtz free energy in terms of temperature and density, the two fundamental equations do not have the same mathematical form. As a consequence the present IAPS formulations do not provide a suitable basis for a generalization to include a representation of the thermodynamic properties of mixtures of fluid H_2O and D_2O. The development of a unified global equation that incorporates the correct singular asymptotic critical behavior and that will represent the thermodynamic properties of mixtures of H_2O and D_2O at all concentrations is one of the goals of future research coordinated by IAPS.

5. Acknowledgments

The authors express their appreciation to the members of Working Group I of IAPS listed in Table 1.1 for their extensive research towards agreed-upon formulations for the thermodynamic properties of H_2O and D_2O. The authors are indebted to J. S. Gallagher, L. Haar, B. Kamgar-Parsi, and J. C. Nieuwoudt for valuable assistance in the preparation of this article. The work of P. G. Hill, E. J. Le Fèvre, A. Nagashima, and W. Wagner also had a significant impact on the final form of the releases adopted by IAPS. The research was supported by the Office of Standard Reference Data at the National Bureau of Standards. The Computer Science Center of the University of Maryland supplied computer time consumed for this project.

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TABLE I.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	20 000	0.100 389 28 E + 1	0.988 768 21 E + 0	− 0.323 294 94 E − 2
1	2	2	40	20 000	0.100 389 28 E + 1	0.988 768 21 E + 0	− 0.241 393 55 E − 1
2	2	0	30	40 000	0.100 389 28 E + 1	0.991 240 13 E + 0	0.790 276 51 E − 3
3	4	0	1050	25	0.487 784 92 E + 1	0.417 136 59 E + 0	− 0.133 628 57 E + 1

in this release the "E-notation" has been adopted. That is, the integer which follows E indicates the power of ten by which the listed coefficient should be multiplied. Thus E + 2 represents the factor $10^2 = 100$, etc.

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

$$T_{tr} = 273.16\ \text{K}, \quad P_{tr} = 611.73\ \text{Pa}, \tag{26}$$

$$U_{tr} = 0, \quad S_{tr} = 0, \tag{27}$$

$$H_{tr} = 0.611\ 87\ \text{J/kg}. \tag{28}$$

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 in Eq. (27) 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. (21) by imposing the condition of Eq. (27) with the desired accuracy.

2.3. Thermodynamic Relations

All thermodynamic properties of interest can be derived from the fundamental Eq. (20) by the use of the following thermodynamic relations:

$$\bar{V} = \bar{\rho}^{-1}, \tag{29}$$

$$\bar{P} = \bar{\rho}^2 \left(\frac{\partial \bar{A}}{\partial \bar{\rho}}\right)_{\bar{T}}, \tag{30}$$

$$\left(\frac{\partial \bar{P}}{\partial \bar{\rho}}\right)_{\bar{T}} = \frac{2\bar{P}}{\bar{\rho}} + \bar{\rho}^2 \left(\frac{\partial^2 \bar{A}}{\partial \bar{\rho}^2}\right)_{\bar{T}}, \tag{31}$$

$$\bar{K}_{\bar{T}}^{-1} = \bar{\rho} \left(\frac{\partial \bar{P}}{\partial \bar{\rho}}\right)_{\bar{T}}, \tag{32}$$

$$\left(\frac{\partial \bar{P}}{\partial \bar{T}}\right)_{\bar{\rho}} = \bar{\rho}^2 \frac{\partial^2 \bar{A}}{\partial \bar{\rho}\, \partial \bar{T}}, \tag{33}$$

$$\bar{S} = -\left(\frac{\partial \bar{A}}{\partial \bar{T}}\right)_{\bar{\rho}}, \tag{34}$$

$$\bar{U} = \bar{A} + \bar{T}\bar{S}, \tag{35}$$

$$\bar{H} = \bar{U} + \frac{\bar{P}}{\bar{\rho}}, \tag{36}$$

$$\bar{G} = \bar{A} + \frac{\bar{P}}{\bar{\rho}}, \tag{37}$$

$$\bar{C}_v = -\bar{T}\left(\frac{\partial^2 \bar{A}}{\partial \bar{T}^2}\right)_{\bar{\rho}}, \tag{38}$$

$$\bar{C}_p = \bar{C}_v + \frac{\bar{T}}{\bar{\rho}^2} \frac{(\partial \bar{P}/\partial \bar{T})_{\bar{\rho}}^2}{(\partial \bar{P}/\partial \bar{\rho})_{\bar{T}}}, \tag{39}$$

$$\bar{w} = \left[\frac{\bar{C}_p}{\bar{C}_v}\left(\frac{\partial \bar{P}}{\partial \bar{\rho}}\right)_{\bar{T}}\right]^{1/2}. \tag{40}$$

2.4. Ideal-Gas Properties

The ideal-gas properties of H_2O are obtained from

$$\bar{A}_{id} = \bar{A}_0(\bar{T}) + A_{20}\bar{T}\ln\bar{\rho}, \tag{41}$$

as a function of temperature and density, or

$$\bar{A}_{id} = \bar{A}_0(\bar{T}) - A_{20}\bar{T}\ln\bar{T} - A_{20}\bar{T}\ln A_{20} + A_{20}\bar{T}\ln\bar{P}, \tag{42}$$

as a function of temperature and pressure.

3. Range of Validity and Estimated Uncertainty

3.1. Range of Validity for Formulation

IAPS has tested the formulation and endorses its validity over the temperature range from 273.15 to 1273.15 K and in the range of pressures described by the conditions

$$P \leqslant 1500\ \text{MPa} \quad \text{for} \quad 423.15\ \text{K} \leqslant T \leqslant 1273.15\ \text{K}, \tag{43}$$

$$P \leqslant 100\left[5 + \frac{T - 273.15\ \text{K}}{15\ \text{K}}\right]\ \text{MPa}$$

$$\text{for } 273.15\ \text{K} \leqslant T < 423.15\ \text{K}.$$

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

$$|T - T^*| \leqslant 1\ \text{K}, \quad |\bar{\rho} - 1| \leqslant 0.3. \tag{44}$$

3.2. Estimates of Uncertainty

Estimates of the uncertainty for calculated values of density as a function of pressure and temperature are given in Fig. 1. The numerical values in the various regions indicate estimated relative uncertainty $\delta\rho/\rho$ in parts per 10 000. For instance, the number 10 indicates that the estimated relative error $\delta\rho/\rho$ in the density ρ is less than 10 parts in 10^4.

The estimated uncertainty of the formulation in the critical region is indicated in Fig. 2. In the near-critical region the error in density becomes a rapidly varying function of pressure and temperature and the accuracy of the formulation is better characterized by the estimated relative error $\delta P/P$ in the pressure P for a given ρ and T.

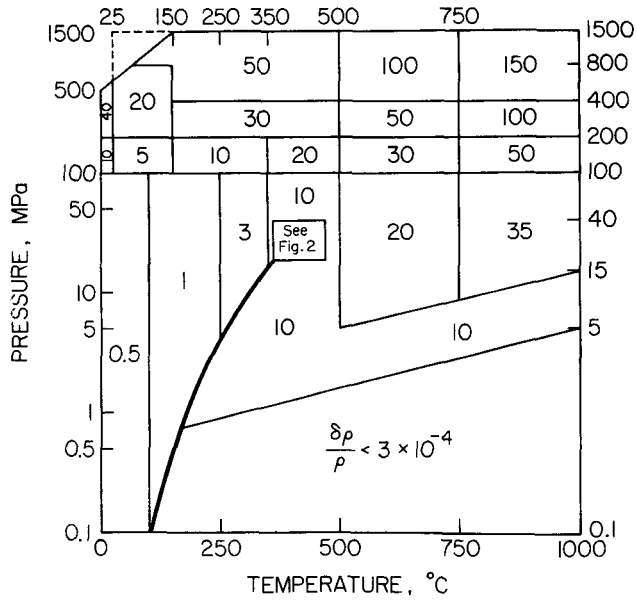

FIG. 1. Estimated relative uncertainty in calculated values of density as a function of pressure and temperature. The numerical values in the various regions indicate estimated relative density errors $\delta\rho/\rho$ in parts per 10 000.

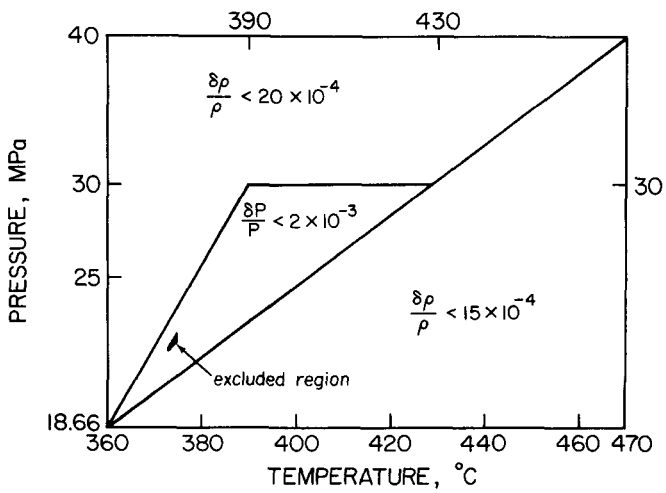

FIG. 2. Estimated uncertainty of the formulation in the critical region: $\delta\rho/\rho$ indicates estimated relative uncertainty in density; $\delta P/P$ indicates estimated relative uncertainty in pressure for given ρ and T.

Estimates of the uncertainty for calculated values of specific enthalpy as a function of pressure and temperature are given in Fig. 3. $H(T,P)$ is the specific enthalpy at temperature T and pressure P minus the specific enthalpy at the triple point. In the various regions in Fig. 3 the numerical values indicate the maximum error δH in units of kJ/kg, except for the liquid at pressures below 100 MPa and temperatures between 50 and 330 °C, where the maximum relative error $\delta H/H$ is 3 parts in 10^4. For pressures above 100 MPa, the estimates of uncertainty are given by the equations contained in Fig. 3, where $\delta H(T,P = 100\ \text{MPa})$ refers to the estimated uncertainty δH at 100 MPa at the same temperature T. In the region marked A the estimated uncertainty δH is twice the amount calculated from the equation applicable at the same pressure but at temperatures above 25 °C. Again in the near-critical region the error in the density, and hence in H, becomes sensitive to small changes in pressure and temperature. The error $\delta H < 3$ kJ/kg quoted for the triangle that includes the critical point refers to the estimated error in H for given ρ and T.

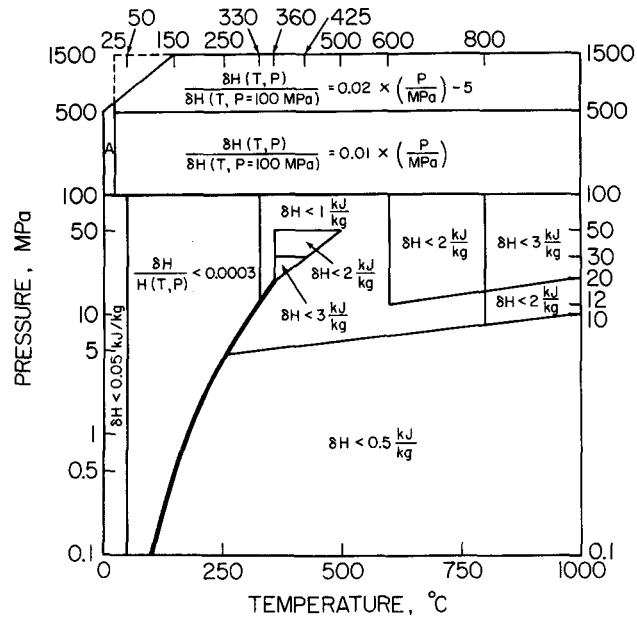

FIG. 3. Estimated uncertainty in calculated values of specific enthalpy $H(T,P)$ as function of temperature T and pressure P. (As noted in the text the reference state of zero specific energy and entropy is the liquid at the triple point.) In region A between 0 and 25 °C and at pressures above 100 MPa the estimated error is twice the estimate calculated from the equation for $\delta H(T,P)$ at the same pressure but at temperatures above 25 °C. In the small triangle that includes the critical point the error $\delta H < 3$ kJ/kg refers to the estimated error for a given density ρ and temperature T.

4. Computer-Program Verification

To assist the user in computer-program verification Table I.6 lists values for $\bar{A}$, $\bar{P}$, and $\bar{C}_v$ calculated at selected values of $\bar{T}$ and $\bar{\rho}$. The dimensionless formulation presented in this Release yields thermodynamic property values identical with those calculated from the provisional dimensional IAPS formulation 1982 up to the six digits displayed in Table I.6.

TABLE II.3. Parameters $\overline{T}_i$ and $\overline{\rho}_i$

	$\overline{T}_i$	$\overline{\rho}_i$
1	0.100 003 883 2 E + 1	0.195 530 726 3 E + 1
2	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1
3	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1
4	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1
5	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1
6	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1
7	0.613 857 828 2 E + 0	0.307 262 569 8 E + 1

equal to zero. In the case of H_2O the temperature of the triple point need not be measured, because it constitutes the (single) fixed point on the internationally accepted temperature scale. In the case of D_2O the triple-point temperature must be obtained from accurate measurements which are subject to improvement. In this release the specific energy and entropy are set equal to zero for the liquid state in equilibrium with the vapor at $T_R = 276.95$ K. At this reference state

$$T_R = 276.95 \text{ K}, \quad P_R = 660.066 \text{ Pa}, \tag{23}$$

$$U_R = 0, \quad S_R = 0, \tag{24}$$

$$H_R = 0.597 \text{ J/kg}. \tag{25}$$

This reference state is close to (but not necessarily equal to) the liquid state at the triple point.

In the liquid 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 in Eqs. (24) at the reference state. This problem can be solved by adjusting the constants A_{02} and A_{03} in Eq. (21) so that condition of Eq. (24) is satisfied with the desired accuracy.

2.3. Thermodynamic Relations

All thermodynamic properties of interest can be derived from the fundamental Eq. (20) by the use of the following thermodynamic relations:

$$\overline{V} = \overline{\rho}^{-1}, \tag{26}$$

$$\overline{P} = \overline{\rho}^2 \left(\frac{\partial \overline{A}}{\partial \overline{\rho}}\right)_{\overline{T}}, \tag{27}$$

$$\left(\frac{\partial \overline{P}}{\partial \overline{\rho}}\right)_{\overline{T}} = \frac{2\overline{P}}{\overline{\rho}} + \overline{\rho}^2 \left(\frac{\partial^2 \overline{A}}{\partial \overline{\rho}^2}\right)_{\overline{T}}, \tag{28}$$

$$\overline{K}_{\overline{T}}^{-1} = \overline{\rho} \left(\frac{\partial \overline{P}}{\partial \overline{\rho}}\right)_{\overline{T}}, \tag{29}$$

$$\left(\frac{\partial \overline{P}}{\partial \overline{T}}\right) = \overline{\rho}^2 \frac{\partial^2 \overline{A}}{\partial \overline{\rho}\, \partial \overline{T}}, \tag{30}$$

$$\overline{S} = -\left(\frac{\partial \overline{A}}{\partial \overline{T}}\right)_{\overline{\rho}}, \tag{31}$$

$$\overline{U} = \overline{A} + \overline{T}\,\overline{S}, \tag{32}$$

$$\overline{H} = \overline{U} + \frac{\overline{P}}{\overline{\rho}}, \tag{33}$$

$$\overline{G} = \overline{A} + \frac{\overline{P}}{\overline{\rho}}, \tag{34}$$

$$\overline{C}_v = -\overline{T}\left(\frac{\partial^2 \overline{A}}{\partial \overline{T}^2}\right)_{\overline{\rho}}, \tag{35}$$

$$\overline{C}_p = \overline{C}_v + \frac{\overline{T}}{\overline{\rho}^2} \frac{(\partial \overline{P}/\partial \overline{T})_{\overline{\rho}}^2}{(\partial \overline{P}/\partial \overline{\rho})_{\overline{T}}}, \tag{36}$$

$$\overline{w} = \left[\frac{\overline{C}_p}{\overline{C}_v}\left(\frac{\partial \overline{P}}{\partial \overline{\rho}}\right)_{\overline{T}}\right]^{1/2}. \tag{37}$$

2.4. Ideal-Gas Properties

The ideal-gas properties of D_2O are obtained from

$$\overline{A}_{\text{id}} = \overline{A}_0(\overline{T}, \rho) = (A_{00} + A_{01}\overline{T}) \ln \overline{T} + \sum_{j=2}^{7} A_{0j} \overline{T}^{\,j-2} + A_{08} \overline{T} \ln \rho, \tag{38}$$

as a function of temperature and density, or from

$$\overline{A}_{\text{id}} = (A_{00} + A_{01}\overline{T} - A_{08}\overline{T}) \ln \overline{T} + \sum_{j=2}^{7} A_{0j} \overline{T}^{\,j-2} - A_{08}\overline{T} \ln A_{08} + A_{08}\overline{T} \ln \overline{P}, \tag{39}$$

as a function of temperature and pressure,

3. Range of Validity and Estimated Uncertainty

3.1. Range of Validity

IAPS has tested the formulation and endorses its validity in the range of temperatures and pressures defined by

$$T_R \leqslant T \leqslant 800 \text{ K}, \quad 0 \leqslant P \leqslant 100 \text{ MPa}. \tag{40}$$

The formulation is not recommended in a region around the critical point bounded by[c)]

$$|T - T^*| \leqslant 10 \text{ K}, \quad |\overline{\rho} - 1| \leqslant 0.3. \tag{41}$$

3.2. Estimates of Uncertainty

Table II.4 lists calculated values of the specific volume as a function of pressure and temperature together with the estimated uncertainties.

[c)] A fundamental equation for D_2O in the critical region can be found in a paper "Thermodynamic Properties of D_2O in the Critical Region," B. Kamgar-Parsi, J. M. H. Levelt Sengers, and J. V. Sengers, J. Phys. Chem. Ref. Data **12**, 513 (1983).

TABLE II.4. Specific volumes of heavy water and tolerances (cm^3/g)

p	t,°C													
bar	3.8	20.0	50.0	100.0	150.0	200.0	250.0	300.0	350.0	375.0	400.0	450.0	500.0	550.0
1	0.9045	0.9047	0.9127	0.9404	1741.4	1953.8	2164.2	2373.6	2582.4	2686.7	2790.9	2999.1	3207.2	3415.1
	.0001	.0001	.0001	.0001	.2	.1	.1	.2	.4	.8	1.0	1.0	1.0	1.0
5	0.9044	0.9045	0.9125	0.9402	0.9830	381.9	426.6	470.0	512.8	534.0	555.2	597.4	639.4	681.3
	.0001	.0001	.0001	.0001	.0001	.1	.1	.2	.2	.3	.3	.3	.3	.4
10	0.9041	0.9043	0.9123	0.9400	0.9827	184.9	209.2	232.0	254.0	264.9	275.7	297.1	318.4	339.6
	.0001	.0001	.0001	.0001	.0001	.1	.1	.1	.1	.2	.2	.2	.2	.2
25	0.9034	0.9036	0.9117	0.9393	0.9818	1.0427	78.1	88.9	98.7	103.4	108.0	117.0	125.0	134.6
	.0001	.0001	.0001	.0001	.0001	.0001	.1	.1	.1	.1	.1	.1	.1	.1
50	0.9023	0.9026	0.9107	0.9382	0.9803	1.0404	1.1298	40.68	46.68	49.375	51.958	56.886	61.612	66.210
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.1	.1	.05	.05	.05	.06	.06
75	0.9011	0.9015	0.9096	0.9370	0.9788	1.0381	1.1257	23.9401	29.125	31.239	33.195	36.812	40.189	43.422
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.1	.05	.03	.03	.04	.05	.04
100	0.9000	0.9005	0.9086	0.9359	0.9773	1.0359	1.1217	1.2685	20.135	22.047	23.737	26.742	29.464	32.025
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.03	.03	.03	.04	.05	.04
125	0.8989	0.8994	0.9077	0.9348	0.9758	1.0337	1.1179	1.2586	14.486	16.406	17.990	20.673	23.017	25.183
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.02	.02	.02	.03	.05	.02
150	0.8977	0.8984	0.9067	0.9337	0.9744	1.0316	1.1142	1.2495	10.332	12.502	14.088	16.602	18.711	20.618
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.01	.01	.01	.02	.05	.02
200	0.8955	0.8963	0.9047	0.9315	0.9716	1.0275	1.1071	1.2332	1.5286	6.982	8.987	11.452	13.305	14.905
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.01	.01	.01	.02	.02
225	0.8944	0.8953	0.9038	0.9305	0.9702	1.0255	1.1037	1.2258	1.4902	3.765	7.135	9.705	11.493	12.997
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.2	.02	.01	.02	.02
250	0.8933	0.8943	0.9028	0.9294	0.9688	1.0235	1.1004	1.2188	1.4603	1.8639	5.494	8.287	10.038	11.469
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.01	.01	.01	.02
300	0.8912	0.8924	0.9010	0.9273	0.9661	1.0196	1.0941	1.2060	1.4147	1.6489	2.705	6.110	7.842	9.174
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.03	.01	.01	.02
350	0.8890	0.8904	0.8991	0.9253	0.9635	1.0159	1.0882	1.1944	1.3802	1.5569	1.959	4.517	6.265	7.533
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.01	.005	.01	.02
400	0.8869	0.8885	0.8973	0.9232	0.9610	1.0123	1.0825	1.1837	1.3524	1.4976	1.7569	3.3901	5.090	6.307
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.002	.002	.01	.02
450	0.8849	0.8866	0.8955	0.9213	0.9585	1.0088	1.0771	1.1739	1.3289	1.4538	1.6510	2.6928	4.204	5.364
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
500	0.8829	0.8848	0.8937	0.9193	0.9560	1.0054	1.0719	1.1648	1.3087	1.4190	1.5806	2.2954	3.544	4.629
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
600	0.8789	0.8812	0.8902	0.9155	0.9512	0.9989	1.0622	1.1483	1.2750	1.3655	1.4871	1.9115	2.711	3.597
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
700	0.8750	0.8776	0.8868	0.9118	0.9467	0.9927	1.0531	1.1337	1.2475	1.3250	1.4240	1.7286	2.263	2.951
	.0001	.0001	.0001	.0001	.0001	.0001	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
800	0.8713	0.8742	0.8835	0.[illegible]82	0.9423	0.9869	1.0447	1.1205	1.2242	1.2925	1.3767	1.6171	2.005	2.536
	.0001	.0001	.0001	.0001	.0001	.0002	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
900	0.8677	0.8708	0.8803	0.9047	0.9380	0.9812	1.0368	1.1085	1.2041	1.2653	1.3390	1.5392	1.841	2.257
	.0001	.0001	.0001	.0001	.0001	.0004	.0003	.0002	.0008	.0008	.0006	.002	.01	.02
1000	0.8643	0.8675	0.8771	0.9013	0.9339	0.9759	1.0294	1.0975	1.1864	1.2420	1.3078	1.4802	1.727	2.063
	.0001	.0001	.0001	.0001	.0001	.0005	.0003	.0002	.0008	.0008	.0006	.002	.01	.02

TABLE II.5. Thermophysical property values calculated for selected values of $\overline{T}$ and $\overline{\rho}$

$\overline{T}$	$\overline{\rho}$	$\overline{A}$	$\overline{P}$	$\overline{C}_v$
0.50	0.0002	− 0.264 519 E + 1	0.440 215 E − 3	0.142 768 E + 2
0.50	3.1800	− 0.217 597 E + 0	0.435 497 E + 1	0.414 463 E + 2
0.75	0.0295	− 0.727 350 E + 1	0.870 308 E − 1	0.201 586 E + 2
0.75	2.8300	− 0.429 366 E + 1	0.447 530 E + 1	0.334 367 E + 2
1.00	0.3000	− 0.151 650 E + 2	0.801 404 E + 0	0.308 587 E + 2
1.00	1.5500	− 0.126 455 E + 2	0.109 763 E + 1	0.330 103 E + 2
1.20	0.4000	− 0.254 738 E + 2	0.149 910 E + 1	0.236 594 E + 2
1.20	1.6100	− 0.212 805 E + 2	0.456 438 E + 1	0.254 800 E + 2

4. Computer-Program Verification

To assist the user in computer-program verification, Table II.5 lists values for $\overline{A}$, $\overline{P}$, and $\overline{C}_v$ calculated at selected values of $\overline{T}$ and $\overline{\rho}$. The dimensionless fundamental equation presented in this Release yields thermodynamic property values identical to those calculated from the dimensional equation by Hill *et al.*, J. Phys. Chem Ref. Data **11**, 1 (1982); **12**, 1065 (1983), up to the six digits displayed in Table II.5.