

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

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# 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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . 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.<sup>1-3</sup>

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.<sup>4-6</sup> 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.<sup>7</sup> 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 programmed into a computer. The IFC arrived at two such formulations, namely, the 1967 IFC Formulation for Industrial Use<sup>8</sup> and the 1968 *IFC Formulation for Scientific and General Use*.<sup>9</sup> These formulations agree with the 1963 skeleton tables within the stated tolerances. The 1967 IFC Formulation for Industrial Use serves as the

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 formulations 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.<sup>10,11</sup> 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.*<sup>12</sup> and subsequently by Pollak.<sup>13</sup> 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.<sup>14</sup> 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.<sup>15</sup> 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

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 <sup>a</sup>	(FRG)
M. Uematsu	(Japan)
W. Wagner	(FRG)
K. Watanabe	(Japan)
A. Nagashima <sup>b</sup>	(Japan)

<sup>a</sup> Chairman.

<sup>b</sup> Co-opted expert.

was originally published by Haar *et al.* in the *Proceedings of the 8th Symposium on Thermophysical Properties*,<sup>16</sup> and subsequently issued as the *NBS/NRC Steam Tables*.<sup>17</sup> 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<sup>18</sup>; it was also issued as *Tables of Thermodynamic Properties of Heavy Water in S.I. Units*.<sup>19</sup> 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*.<sup>20</sup> 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.*<sup>21,22</sup>

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<sup>5</sup> 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<sup>a)</sup> 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  $\rho$  developed by Messrs. Haar, Gallagher, and by the late Dr. Kell.<sup>16,17</sup> 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.<sup>21</sup>

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

$$T^* = 647.27 \text{ K}, \quad (2.1)$$

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

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

These reference constants are close to but not identical with the critical parameters<sup>24</sup> of  $H_2O$ .

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

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

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

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

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

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

with

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

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

with

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

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

with

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

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

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

$$|T - T^*| \leq 1 \text{ K}, \quad |\bar{\rho} - 1| \leq 0.3, \quad (2.5)$$

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*.<sup>17</sup> 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  $\bar{A}(\bar{T}, \bar{\rho})$  and its first and second derivatives with respect to  $\bar{T}$  and  $\bar{\rho}$  as indicated in Secs. 1.3 and 2.3 of Appendix I. These derivatives can be written in the form

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

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

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

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

$$\frac{\partial^2 \bar{A}}{\partial \bar{T} \partial \bar{\rho}} = \sum_{j=0}^4 \bar{A}_{T\rho,j}. \quad (2.10)$$

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

$$\bar{S} = - \sum_{j=0}^4 \bar{A}_{T,j}, \quad (2.11)$$

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

When the expressions for  $\bar{A}_0$  and  $\bar{A}_{T,0}$  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  $\bar{U}$  and  $\bar{S}$ , 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.

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

TABLE 2.1. The functions  $\bar{A}_{T,j}$  for H<sub>2</sub>O

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

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

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

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

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

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

TABLE 2.2. The functions  $\bar{A}_{TT,j}$  for H<sub>2</sub>O

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

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

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

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

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

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

TABLE 2.3. The functions  $\bar{A}_{\rho,j}$  for H<sub>2</sub>O

$$\bar{A}_{\rho,0} = 0 \quad (2.3.1)$$

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

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

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

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

TABLE 2.4. The functions  $\bar{A}_{\rho\rho,j}$  for H<sub>2</sub>O

$$\bar{A}_{\rho\rho,0} = 0 \quad (2.4.1)$$

$$\bar{A}_{\rho\rho,1} = 0 \quad (2.4.2)$$

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

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

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

TABLE 2.5. The functions  $\bar{A}_{T,p,j}$  for H<sub>2</sub>O

$\bar{A}_{T,p,0} = 0$	(2.5.1)
$\bar{A}_{T,p,1} = \frac{\bar{A}_{T,1}}{\bar{\rho}}$	(2.5.2)
$\bar{A}_{T,p,2} = \frac{\bar{A}_{p,2}}{\bar{T}} + \frac{A_{20}\bar{T}}{\bar{\rho}} \left[ -\frac{127}{3(1-y)^2} + \frac{169-260y}{3(1-y)^3} + \frac{169y}{(1-y)^4} - 14 \right] \left( \frac{\partial y}{\partial \bar{T}} \right)_{\bar{\rho}}$	(2.5.3)
$\bar{A}_{T,p,3} = -z_0(1-z) \sum_{i=0}^{35} A_{3i} l(i) k(i) (1/\bar{T})^{l(i)+1} z^{k(i)-1}$	(2.5.4)
$\bar{A}_{T,p,4} = -2 \sum_{i=0}^3 \frac{A_{4i} \delta_i^{n(i)-1} \beta_i \tau_i}{\bar{T}_i \bar{\rho}_i} [n(i) - \alpha_i m(i) \delta_i^{m(i)}] \exp[-\alpha_i \delta_i^{m(i)} - \beta_i \tau_i^2]$	(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*<sup>b)</sup> is attached as Appendix II to this article. The formulation is based on a fundamental equation developed by Hill, MacMillan, and Lee.<sup>18,19</sup> 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.<sup>22</sup>

For D<sub>2</sub>O, the reference temperature  $T^*$ , the reference density  $\rho^*$ , and the reference pressure  $P^*$  are defined as

$$T^* = 643.89 \text{ K}, \quad (3.1)$$

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

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

Again these reference constants are close to but not identical with the critical parameters.<sup>24</sup>

As in the case of H<sub>2</sub>O, the fundamental equation adopted by IAPS for D<sub>2</sub>O is an equation for the dimensionless Helmholtz function  $\bar{A} = A\rho^*/P^*$  in terms of the reduced temperature  $\bar{T} = T/T^*$  and the reduced density  $\bar{\rho} = \rho/\rho^*$ .

The fundamental equation has the form

$$\bar{A}(\bar{T}, \bar{\rho}) = \bar{A}_0 + \bar{A}_1, \quad (3.4)$$

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

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

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

with

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

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

$$z_0 = 1.5394. \quad (3.4d)$$

The use of this formulation for fluid D<sub>2</sub>O 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

$$|T - T^*| \leq 10 \text{ K}, \quad |\bar{\rho} - 1| \leq 0.3. \quad (3.5)$$

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.*<sup>18</sup> 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  $\bar{A}(\bar{T}, \bar{\rho})$  and its first and second derivatives with respect to  $\bar{T}$  and  $\bar{\rho}$ , as indicated in Secs. 1.3 and 2.3 of Appendix II. These derivatives can be written

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

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

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

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

$$\frac{\partial^2 \bar{A}}{\partial \bar{T} \partial \bar{\rho}} = \bar{A}_{T\rho,0} + \bar{A}_{T\rho,1}. \quad (3.10)$$

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

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

<sup>b)</sup> 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  $\bar{A}_{T,j}$  for D<sub>2</sub>O

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

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

TABLE 3.2. The functions  $\bar{A}_{TT,j}$  for D<sub>2</sub>O

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

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

TABLE 3.3. The functions  $\bar{A}_{\rho,j}$  for D<sub>2</sub>O

$$\bar{A}_{\rho,0} = \frac{A_{08} \bar{T}}{\bar{\rho}} \quad (3.3.1)$$

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

$$\text{Note: } \frac{dX_i}{d\bar{\rho}} = \sum_{j=1}^8 (j-1) A_{ij} (\bar{\rho} - \bar{\rho}_1)^{j-2} - z_0 e^{-z_0 \bar{\rho}} (A_{i,9} + A_{i,10} \bar{\rho}) + A_{i,10} e^{-z_0 \bar{\rho}} \quad (3.3.3)$$

TABLE 3.4. The functions  $\bar{A}_{\rho\rho,j}$  for D<sub>2</sub>O

$$\bar{A}_{\rho\rho,0} = -\frac{A_{08} \bar{T}}{\bar{\rho}^2} \quad (3.4.1)$$

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

$$\text{Note: } \frac{d^2 X_i}{d\bar{\rho}^2} = \sum_{j=1}^8 (j-1)(j-2) A_{ij} (\bar{\rho} - \bar{\rho}_1)^{j-3} + z_0^2 e^{-z_0 \bar{\rho}} (A_{i,9} + A_{i,10} \bar{\rho}) - 2A_{i,10} z_0 e^{-z_0 \bar{\rho}} \quad (3.4.3)$$

TABLE 3.5. The functions  $\bar{A}_{Tp,j}$  for D<sub>2</sub>O

$$\bar{A}_{Tp,0} = \frac{A_{08}}{\bar{\rho}} \quad (3.5.1)$$

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

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

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

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

In this case the coefficients  $A_{02}$  and  $A_{03}$  appear as additive constants in  $\bar{U}$  and  $\bar{S}$  and, therefore, depend on the choice of the reference state where energy and entropy are taken to be zero. In the case of H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O. 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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  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.<sup>25</sup> 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<sup>21,26</sup> as well as for heavy steam.<sup>22,27</sup> The problem remains how smoothly to connect the scaled equation in the critical region with a global analytic thermodynamic surface.<sup>28-30</sup> Recent work of Hill has indicated that a practical solution to this problem for steam is now within reach.<sup>31</sup> Secondly, while the IAPS formulations yield for both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . 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  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  at all concentrations is one of the goals of future research coordinated by IAPS.

#### 5. Acknowledgments

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## Appendix I

### The Tenth International Conference on The Properties of Steam

Moscow, USSR, September 1984

*Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use*

Unrestricted publication allowed in all countries.

Issued by the International Association for the Properties of Steam.

President, Professor V. V. Sytchev  
SOVMEK GNTK  
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103009 Moscow, USSR

Executive Secretary, Dr. Howard J. White, Jr.  
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This release is issued by the International Association for the Properties of Steam (IAPS) on the authority of the Tenth International Conference on the Properties of Steam, held in Moscow, USSR, September 2-7, 1984. The members of IAPS are: Canada, the Czechoslovak Socialist Republic, the Federal Republic of Germany, France, Japan, the Union of Soviet Socialist Republics, the United Kingdom, and the United States of America.

The formulation provided in this release is recommended for scientific and general use; it is a dimensionless version of the formulation issued on January 20, 1984 as the "Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use." This formulation provides the most accurate representation of the thermodynamic properties of the fluid phases of water substance over a wide range of conditions currently attainable.

The 1967 IFC Formulation for Industrial Use retains its status and remains intact.

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### The IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use

#### 1. Dimensionless Variables and Reference Constants

All equations in this release 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: three 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.

#### 1.1. Primary Reference Constants

Reference temperature:  $T^* = 647.27 \text{ K}$  (1)

Reference density:  $\rho^* = 317.763 \text{ kg/m}^3$  (2)

Reference pressure:  $P^* = 22.115 \times 10^6 \text{ Pa}$  (3)

The three reference constants  $T^*$ ,  $\rho^*$ ,  $P^*$ , are close to but not identical with the critical constants.

#### 1.2. Secondary Reference Constants

Reference constant for Helmholtz function, internal energy, enthalpy, Gibbs function:

$$A^{**} \equiv \frac{P^*}{\rho^*} = 69\,595.89 \text{ J/kg} \quad (4)$$

Reference constant for entropy, specific heats:

$$S^{**} \equiv \frac{P^*}{\rho^* T^*} = 107.5222 \text{ J/kg K} \quad (5)$$

Reference constant for sound velocity:

$$w^{**} \equiv \left( \frac{P^*}{\rho^*} \right)^{1/2} = 263.810 \text{ m/s} \quad (6)$$

#### 1.3. Thermodynamic Properties in Dimensionless Form

Temperature <sup>a)</sup> :	$\bar{T} = T/T^*$	(7)
Pressure:	$\bar{P} = P/P^*$	(8)
Density:	$\bar{\rho} = \rho/\rho^*$	(9)
Specific volume:	$\bar{V} = V/\rho^*$	(10)
Specific Helmholtz function:	$\bar{A} = A/A^{**}$	(11)
Specific energy:	$\bar{U} = U/A^{**}$	(12)
Specific enthalpy:	$\bar{H} = H/A^{**}$	(13)
Specific Gibbs function:	$\bar{G} = G/A^{**}$	(14)
Specific entropy:	$\bar{S} = S/S^{**}$	(15)
Specific heat at constant volume:	$\bar{C}_v = C_v/S^{**}$	(16)
Specific heat at constant pressure:	$\bar{C}_p = C_p/S^{**}$	(17)
Isothermal compressibility:	$\bar{K}_T = K_T/P^*$	(18)
Speed of sound:	$\bar{w} = w/w^{**}$	(19)

## 2. Equations for Thermodynamic Properties

The formulation is based on a fundamental equation for the Helmholtz function expressed in terms of temperature and density.

<sup>a)</sup>  $T$  denotes absolute temperature on the International Practical Temperature Scale of 1968. No distinction is made between this temperature scale and the thermodynamic temperature scale.

## 2.1. Fundamental Equation in Canonical Form

The fundamental equation is defined as

$$\bar{A}(\bar{T}, \bar{\rho}) = \bar{A}_0(\bar{T}) + \bar{A}_1(\bar{T}, \bar{\rho}) + \bar{A}_2(\bar{T}, \bar{\rho}) + \bar{A}_3(\bar{T}, \bar{\rho}) + \bar{A}_4(\bar{T}, \bar{\rho}), \quad (20)$$

with

$$\bar{A}_0(\bar{T}) = (A_{00} + A_{01}\bar{T})\ln \bar{T} + \sum_{i=2}^{17} A_{0i} \bar{T}^{i-4}, \quad (21)$$

$$\bar{A}_1(\bar{T}, \bar{\rho}) = \bar{\rho} \sum_{i=0}^4 A_{1i} \left( \frac{1}{\bar{T}} \right)^{i-1}, \quad (22)$$

$$\bar{A}_2(\bar{T}, \bar{\rho}) = A_{20}\bar{T} \left[ \ln \left( \frac{\bar{\rho}}{1-y} \right) - \frac{130}{3(1-y)} + \frac{169}{6(1-y)^2} - 14y \right], \quad (23)$$

with

$$y = \bar{\rho} \left[ y_0 + y_1 \ln \bar{T} + \frac{y_2}{\bar{T}^3} + \frac{y_3}{\bar{T}^5} \right],$$

$$\bar{A}_3(\bar{T}, \bar{\rho}) = \sum_{i=0}^{35} A_{3i} \left( \frac{1}{\bar{T}} \right)^{l(i)} z^{k(i)}, \quad (24)$$

with

$$z = 1 - e^{-z_0 \bar{\rho}},$$

$$\bar{A}_4(\bar{T}, \bar{\rho}) = \sum_{i=0}^3 A_{4i} \delta_i^{n(i)} \exp[ -\alpha_i \delta_i^{m(i)} - \beta_i \tau_i^2 ], \quad (25)$$

with

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

2.2. 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 I.1.–I.5. In all tables presented

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

<i>i</i>	<i>A<sub>0i</sub></i>
0	−0.130 840 393 653 E + 2
1	−0.857 020 420 940 E + 2
2	0.765 192 919 131 E − 2
3	−0.620 600 116 069 E + 0
4	−0.106 924 329 402 E + 2
5	−0.280 671 377 296 E + 1
6	0.119 843 634 845 E + 3
7	−0.823 907 389 256 E + 2
8	0.555 864 146 443 E + 2
9	−0.310 698 122 980 E + 2
10	0.136 200 239 305 E + 2
11	−0.457 116 129 409 E + 1
12	0.115 382 128 188 E + 1
13	−0.214 242 224 683 E + 0
14	0.282 800 597 384 E − 1
15	−0.250 384 152 737 E − 2
16	0.132 952 679 669 E − 3
17	−0.319 277 411 208 E − 5

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

<i>i</i>	<i>A<sub>1i</sub></i>
0	0.153 830 53 E + 1
1	−0.810 483 67 E + 0
2	−0.683 057 48 E + 1
3	0.000 000 00
4	0.867 562 71 E + 0

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

$$A_{20} = 0.429 234 15 E + 1$$

<i>i</i>	<i>y<sub>i</sub></i>
0	0.594 022 27 E − 1
1	−0.281 282 38 E − 1
2	0.568 266 74 E − 3
3	−0.279 874 51 E − 3

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

$$z_0 = 0.317 763 E + 0$$

<i>i</i>	<i>k(i)</i>	<i>l(i)</i>	<i>A<sub>3i</sub></i>
0	1	1	−0.762 211 901 380 79 E + 1
1	1	2	0.326 614 937 075 55 E + 2
2	1	4	0.113 057 631 568 21 E + 2
3	1	6	−0.100 154 047 677 12 E + 1
4	2	1	0.128 300 643 550 28 E + 3
5	2	2	−0.283 714 167 898 46 E + 3
6	2	4	0.242 562 798 391 82 E + 3
7	2	6	−0.993 576 456 267 25 E + 2
8	3	1	−0.122 754 530 131 71 E + 4
9	3	2	0.230 776 225 062 34 E + 4
10	3	4	−0.163 522 199 298 59 E + 4
11	3	6	0.584 366 482 977 64 E + 3
12	4	1	0.423 654 414 156 41 E + 4
13	4	2	−0.780 275 269 618 28 E + 4
14	4	4	0.388 556 457 395 89 E + 4
15	4	6	−0.912 251 125 293 81 E + 3
16	5	1	−0.901 438 957 036 66 E + 4
17	5	2	0.151 962 148 177 34 E + 5
18	5	4	−0.396 166 513 585 08 E + 4
19	5	6	−0.720 275 116 175 58 E + 3
20	6	1	0.111 471 267 059 90 E + 5
21	6	2	−0.174 120 652 522 10 E + 5
22	6	4	0.999 182 812 077 82 E + 3
23	6	6	0.335 048 071 538 54 E + 4
24	7	1	−0.647 526 449 226 31 E + 4
25	7	2	0.983 237 309 078 47 E + 4
26	7	4	0.838 778 541 084 22 E + 3
27	7	6	−0.279 193 499 031 03 E + 4
28	9	1	0.111 124 100 811 92 E + 4
29	9	2	−0.172 875 872 618 07 E + 4
30	9	4	−0.362 332 627 954 23 E + 3
31	9	6	0.611 394 290 101 44 E + 3
32	3	0	0.329 680 647 285 62 E + 2
33	3	3	0.104 112 396 050 66 E + 3
34	1	3	−0.382 258 747 125 90 E + 2
35	5	3	−0.203 074 786 075 99 E + 3

TABLE 1.5. Coefficients for  $\bar{A}_4(\bar{T}, \bar{\rho})$ 

<i>i</i>	<i>m</i> ( <i>i</i> )	<i>n</i> ( <i>i</i> )	$\alpha_i$	$\beta_i$	$\bar{\rho}_i$	$\bar{T}_i$	$A_{4i}$
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

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

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

$$H_{tr} = 0.611 \text{ 87 J/kg}. \quad (28)$$

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:

$$\bar{V} = \bar{\rho}^{-1}, \quad (29)$$

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

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

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

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

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

$$\bar{U} = \bar{A} + \bar{T} \bar{S}, \quad (35)$$

$$\bar{H} = \bar{U} + \frac{\bar{P}}{\bar{\rho}}, \quad (36)$$

$$\bar{G} = \bar{A} + \frac{\bar{P}}{\bar{\rho}}, \quad (37)$$

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

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

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

### 2.4. Ideal-Gas Properties

The ideal-gas properties of  $\text{H}_2\text{O}$  are obtained from

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

as a function of temperature and density, or

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

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

$$P \leq 1500 \text{ MPa} \quad \text{for} \quad 423.15 \text{ K} \leq T \leq 1273.15 \text{ K}, \quad (43)$$

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

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

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

$$|T - T^*| \leq 1 \text{ K}, \quad |\bar{\rho} - 1| \leq 0.3. \quad (44)$$

### 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  $\rho$  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  $\rho$  and  $T$ .

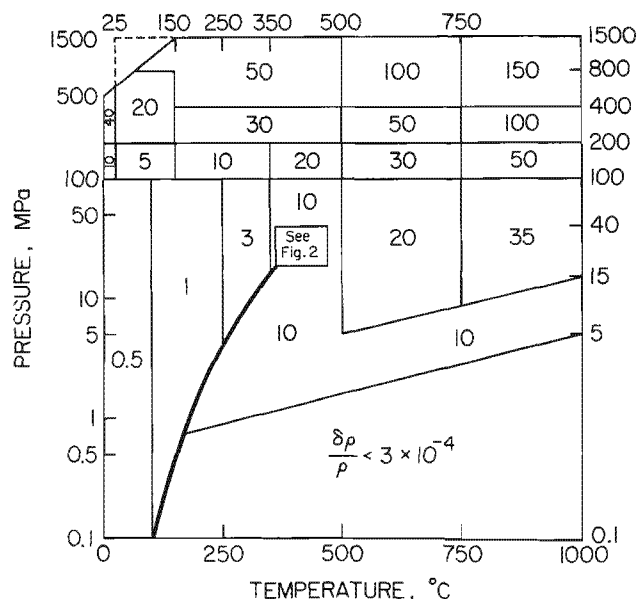


FIG. 1. Estimated relative uncertainty in calculated values of density as a function of pressure and temperature. The numerical values in the various regions indicate estimated relative density errors  $\delta\rho/\rho$  in parts per 10 000.

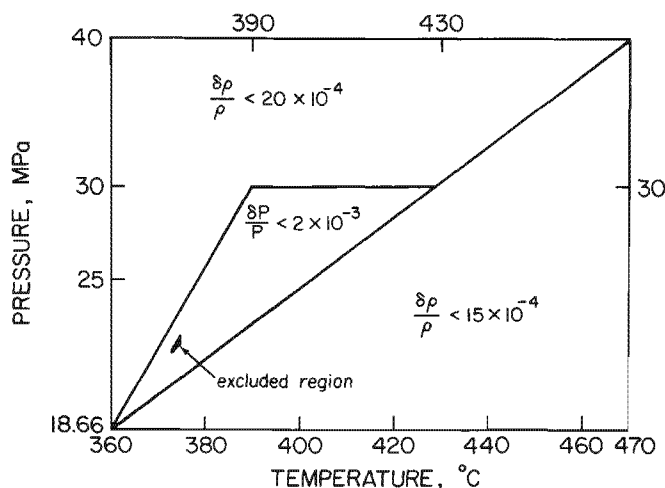


FIG. 2. Estimated uncertainty of the formulation in the critical region:  $\delta\rho/\rho$  indicates estimated relative uncertainty in density;  $\delta P/P$  indicates estimated relative uncertainty in pressure for given  $\rho$  and  $T$ .

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  $\delta H$  in units of kJ/kg, except for the liquid at pressures below 100 MPa and tem-

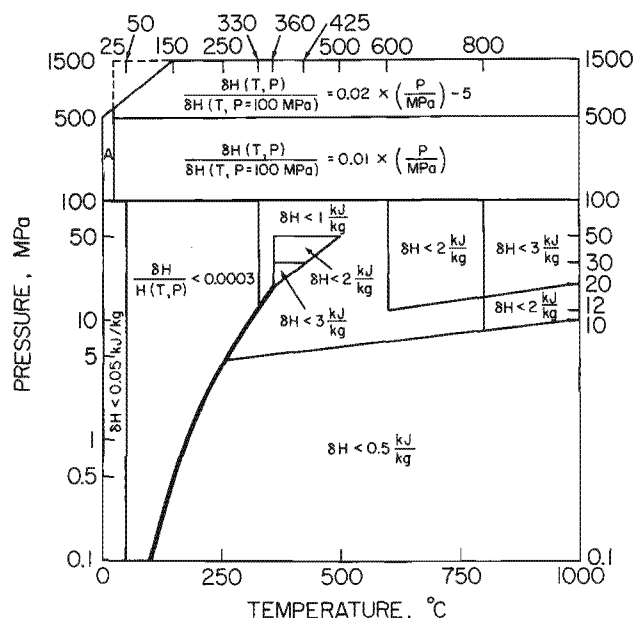


FIG. 3. Estimated uncertainty in calculated values of specific enthalpy  $H(T,P)$  as function of temperature  $T$  and pressure  $P$ . (As noted in the text the reference state of zero specific energy and entropy is the liquid at the triple point.) In region A between 0 and 25 °C and at pressures above 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  $\rho$  and temperature  $T$ .

peratures 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  $\delta H$  at 100 MPa at the same temperature  $T$ . In the region marked A the estimated uncertainty  $\delta H$  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  $\rho$  and  $T$ .

#### 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 I.6. Thermodynamic property values calculated for selected values of  $\bar{T}$  and  $\bar{p}$ 

$\bar{T}$	$\bar{p}$	$\bar{A}$	$\bar{P}$	$\bar{C}_v$
0.50	3.20	-0.250 554 E + 0	0.324 936 E + 1	0.359 788 E + 2
0.75	2.85	-0.400 493 E + 1	0.391 145 E + 1	0.299 897 E + 2
0.90	0.08	-0.127 371 E + 2	0.260 476 E + 0	0.196 868 E + 2
1.00	1.50	-0.116 979 E + 2	0.105 315 E + 1	0.306 178 E + 2
1.20	0.40	-0.237 304 E + 2	0.146 688 E + 1	0.214 850 E + 2
1.20	1.20	-0.203 908 E + 2	0.304 551 E + 1	0.248 417 E + 2
1.40	0.20	-0.383 216 E + 2	0.108 246 E + 1	0.182 170 E + 2
1.40	0.90	-0.309 982 E + 2	0.387 225 E + 1	0.218 535 E + 2
1.60	0.10	-0.551 985 E + 2	0.664 893 E + 0	0.178 744 E + 2
1.60	0.70	-0.429 449 E + 2	0.408 739 E + 1	0.206 189 E + 2

## Appendix II

### The Tenth International Conference on The Properties of Steam

Moscow, USSR, September 1984

*Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance*

Unrestricted publication allowed in all countries.

Issued by the International Association for the Properties of Steam.

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This release is issued by the International Association for the Properties of Steam (IAPS) on the authority of the Tenth International Conference on the Properties of Steam, held in Moscow, USSR, September 2-7, 1984. The members of IAPS are: Canada, the Czechoslovak Socialist Republic, the Federal Republic of Germany, France, Japan, the Union of Soviet Socialist Republics, the United Kingdom, and the United States of America.

The formulation provided in this release is a dimensionless version of "A Fundamental Equation of State for Heavy Water" by P. G. Hill, R. D. Chris MacMillan, and V. Lee, published in J. Phys. Chem. Ref. Data **11**, 1 (1982) and J. Phys. Chem. Ref. Data **12**, 1065 (1983).

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### The IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance<sup>a)</sup>

#### 1. Dimensionless Variables and Reference Constants

All equations in this release 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: three 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.

##### 1.1. Primary Reference Constants

Reference temperature:  $T^* = 643.89 \text{ K}$  (1)

Reference density:  $\rho^* = 358 \text{ kg/m}^3$  (2)

Reference pressure:  $P^* = 21.671 \times 10^6 \text{ Pa}$  (3)

##### 1.2. Secondary Reference Constants

Reference constant for Helmholtz function, internal energy, enthalpy, Gibbs function:

$$A^{**} \equiv \frac{P^*}{\rho^*} = 60\,533.52 \text{ J/kg} \quad (4)$$

Reference constant for entropy, specific heats:

$$S^{**} \equiv \frac{P^*}{\rho^* T^*} = 94.012\,21 \text{ J/kg K} \quad (5)$$

Reference constant for sound velocity:

$$w^{**} \equiv \left( \frac{P^*}{\rho^*} \right)^{1/2} = 246.036 \text{ m/s} \quad (6)$$

<sup>a)</sup> Ordinary water substance, "H<sub>2</sub>O," has normal naturally occurring isotopic abundances. Heavy water substance, "D<sub>2</sub>O," is <sup>2</sup>H<sub>2</sub>O with the oxygen isotopes in the same abundances as in H<sub>2</sub>O.

### 1.3. Thermophysical Properties in Dimensionless Form

Temperature <sup>b)</sup> :	$\bar{T} = T/T^*$	(7)
Pressure:	$\bar{P} = P/P^*$	(8)
Density:	$\bar{\rho} = \rho/\rho^*$	(9)
Specific volume:	$\bar{V} = V\rho^*$	(10)
Specific Helmholtz function:	$\bar{A} = A/A^{**}$	(11)
Specific energy	$\bar{U} = U/A^{**}$	(12)
Specific enthalpy:	$\bar{H} = H/A^{**}$	(13)
Specific Gibbs function:	$\bar{G} = G/A^{**}$	(14)
Specific entropy:	$\bar{S} = S/S^{**}$	(15)
Specific heat at constant volume:	$\bar{C}_v = C_v/S^{**}$	(16)
Specific heat at constant pressure:	$\bar{C}_p = C_p/S^{**}$	(17)
Isothermal compressibility:	$\bar{K}_T = K_T P^*$	(18)
Speed of sound:	$\bar{w} = w/w^{**}$	(19)

## 2. Equations for Thermodynamic Properties

The formulation is based on a fundamental equation for the Helmholtz function in terms of temperature and density.

### 2.1. Fundamental Equation in Canonical Form

The fundamental equation is defined as

$$\bar{A}(\bar{T}, \bar{\rho}) = \bar{A}_0(\bar{T}, \bar{\rho}) + \bar{A}_1(\bar{T}, \bar{\rho}), \quad (20)$$

with

$$\begin{aligned} \bar{A}_0(\bar{T}, \bar{\rho}) = & (A_{00} + A_{01}\bar{T})\ln \bar{T} \\ & + \sum_{j=2}^7 A_{0j}\bar{T}^{j-2} + A_{08}\bar{T}\ln \bar{\rho}, \end{aligned} \quad (21)$$

$$\begin{aligned} \bar{A}_1(\bar{T}, \bar{\rho}) = & \bar{T}\bar{\rho} \left( \frac{1}{\bar{T}} - \frac{1}{\bar{T}_1} \right) \sum_{i=1}^7 \left( \frac{1}{\bar{T}} - \frac{1}{\bar{T}_i} \right)^{i-2} \\ & \times \left[ \sum_{j=1}^8 A_{ij}(\bar{\rho} - \bar{\rho}_i)^{j-1} \right. \\ & \left. + e^{-1.5394\bar{\rho}} \sum_{j=9}^{10} A_{ij}\bar{\rho}^{j-9} \right]. \end{aligned} \quad (22)$$

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

The values of the parameters  $A_{ij}$ ,  $\bar{T}_i$ , and  $\rho_i$  in the equations for  $\bar{A}_0(\bar{T}, \bar{\rho})$  and  $\bar{A}_1(\bar{T}, \bar{\rho})$  are listed in Tables II.1–II.3. In all tables presented 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. The E + 2 represents the factor  $10^2 = 100$ , etc.

The choice of the coefficients  $A_{02}$  and  $A_{03}$  in Eq. (21) is related to the convention adopted for the zero points of energy and entropy. In the *IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use*, the values of the specific energy and the specific entropy of the liquid at the triple point are set

TABLE II.1. Coefficients  $A_{0j}$ 

$j$	$A_{0j}$
0	0.539 932 259 7 E – 2
1	– 0.128 839 971 6 E + 2
2	0.308 728 458 7 E + 2
3	– 0.382 756 305 9 E + 2
4	0.442 479 918 9 E + 0
5	– 0.125 633 687 4 E + 1
6	0.284 334 347 0 E + 0
7	– 0.240 155 508 8 E – 1
8	0.441 588 402 3 E + 1

TABLE II.2. Coefficients<sup>a</sup>  $A_{ij}$ 

$i$	$j$	$A_{ij}$
1	1	0.115 623 643 567 E + 3
1	2	– 0.161 413 392 951 E + 3
1	3	0.108 543 003 981 E + 3
1	4	– 0.471 342 021 238 E + 2
1	5	0.149 218 685 173 E + 2
1	6	– 0.360 628 259 650 E + 1
1	7	0.686 743 026 455 E + 0
1	8	– 0.951 913 721 401 E – 1
1	9	– 0.157 513 472 656 E + 4
1	10	– 0.433 677 787 466 E + 3
2	1	0.607 446 060 304 E + 2
2	2	– 0.927 952 190 464 E + 2
2	3	0.632 086 750 422 E + 2
2	4	– 0.264 943 219 184 E + 2
2	5	0.905 675 051 855 E + 1
2	6	– 0.578 949 005 123 E + 0
2	7	0.665 590 447 621 E + 0
2	8	– 0.525 687 146 109 E – 1
2	9	– 0.341 048 601 697 E + 4
2	10	– 0.146 971 631 028 E + 4
3	1	0.444 139 703 648 E + 2
3	2	– 0.580 410 482 641 E + 2
3	3	0.354 090 438 940 E + 2
3	4	– 0.144 432 210 128 E + 2
3	9	– 0.102 135 518 748 E + 4
3	10	– 0.136 324 396 122 E + 4
4	1	0.157 859 762 687 E + 2
4	2	– 0.194 973 173 813 E + 2
4	3	0.114 841 391 216 E + 2
4	4	– 0.196 956 103 010 E + 1
4	9	– 0.277 379 051 954 E + 3
4	10	– 0.481 991 835 255 E + 3
5	1	– 0.619 344 658 242 E + 2
5	2	0.791 406 411 518 E + 2
5	3	– 0.484 238 027 539 E + 2
5	4	0.191 546 335 463 E + 2
5	9	0.128 039 793 871 E + 4
5	10	0.186 367 898 973 E + 4
6	1	– 0.749 615 505 949 E + 2
6	2	0.947 388 734 799 E + 2
6	3	– 0.575 266 970 986 E + 2
6	4	0.173 229 892 427 E + 2
6	9	0.137 572 687 525 E + 4
6	10	0.231 749 018 693 E + 4
7	1	– 0.260 841 561 347 E + 2
7	2	0.328 640 711 440 E + 2
7	3	– 0.186 464 444 026 E + 2
7	4	0.484 262 639 275 E + 1
7	9	0.430 179 479 063 E + 3
7	10	0.822 507 844 138 E + 3

<sup>a</sup>Note: Coefficients  $A_{ij}$  omitted from table are zero identically.

<sup>b)</sup>  $T$  denotes absolute temperature on the International Practical Temperature Scale of 1968. No distinction is made between this temperature scale and the thermodynamic temperature.

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

	$\bar{T}_i$	$\bar{\rho}_i$
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  $\text{H}_2\text{O}$  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  $\text{D}_2\text{O}$  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

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

$$U_R = 0, \quad S_R = 0, \quad (24)$$

$$H_R = 0.597 \text{ J/kg}. \quad (25)$$

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:

$$\bar{V} = \bar{\rho}^{-1}, \quad (26)$$

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

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

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

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

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

$$\bar{U} = \bar{A} + \bar{T}\bar{S}, \quad (32)$$

$$\bar{H} = \bar{U} + \frac{\bar{P}}{\bar{\rho}}, \quad (33)$$

$$\bar{G} = \bar{A} + \frac{\bar{P}}{\bar{\rho}}, \quad (34)$$

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

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

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

### 2.4. Ideal-Gas Properties

The ideal-gas properties of  $\text{D}_2\text{O}$  are obtained from

$$\begin{aligned} \bar{A}_{\text{id}} = \bar{A}_0(\bar{T}, \rho) = & (A_{00} + A_{01}\bar{T}) \ln \bar{T} \\ & + \sum_{j=2}^7 A_{0j} \bar{T}^{j-2} + A_{08} \bar{T} \ln \rho, \end{aligned} \quad (38)$$

as a function of temperature and density, or from

$$\begin{aligned} \bar{A}_{\text{id}} = & (A_{00} + A_{01}\bar{T} - A_{08}\bar{T}) \ln \bar{T} \\ & + \sum_{j=2}^7 A_{0j} \bar{T}^{j-2} - A_{08} \bar{T} \ln A_{08} + A_{08} \bar{T} \ln \bar{P}, \end{aligned} \quad (39)$$

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

$$T_R \leq T \leq 800 \text{ K}, \quad 0 \leq P \leq 100 \text{ MPa}. \quad (40)$$

The formulation is not recommended in a region around the critical point bounded by<sup>c)</sup>

$$|T - T^*| \leq 10 \text{ K}, \quad |\bar{\rho} - 1| \leq 0.3. \quad (41)$$

### 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.

<sup>c)</sup> A fundamental equation for  $\text{D}_2\text{O}$  in the critical region can be found in a paper "Thermodynamic Properties of  $\text{D}_2\text{O}$  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<sup>3</sup>/g)

P bar	t, °C														
	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 .0001	0.9047 .0001	0.9127 .0001	0.9404 .0001	1741.4 .2	1953.8 .1	2164.2 .1	2373.6 .2	2582.4 .4	2686.7 .8	2790.9 1.0	2999.1 1.0	3207.2 1.0	3415.1 1.0	
5	0.9044 .0001	0.9045 .0001	0.9125 .0001	0.9402 .0001	0.9830 .0001	381.9 .1	426.6 .1	470.0 .2	512.8 .2	534.0 .3	555.2 .3	597.4 .3	639.4 .3	681.3 .4	
10	0.9041 .0001	0.9043 .0001	0.9123 .0001	0.9400 .0001	0.9827 .0001	184.9 .1	209.2 .1	232.0 .1	254.0 .1	264.9 .2	275.7 .2	297.1 .2	318.4 .2	339.6 .2	
25	0.9034 .0001	0.9036 .0001	0.9117 .0001	0.9393 .0001	0.9818 .0001	1.0427 .0001	78.1 .1	88.9 .1	98.7 .1	103.4 .1	108.0 .1	117.0 .1	125.0 .1	134.6 .1	
50	0.9023 .0001	0.9026 .0001	0.9107 .0001	0.9382 .0001	0.9803 .0001	1.0404 .0001	1.1298 .0003	40.68 .1	46.68 .1	49.375 .05	51.958 .05	56.886 .05	61.612 .06	66.210 .06	
75	0.9011 .0001	0.9015 .0001	0.9096 .0001	0.9370 .0001	0.9788 .0001	1.0381 .0001	1.1257 .0003	23.9401 .1	29.125 .05	31.239 .03	33.195 .03	36.812 .04	40.189 .05	43.422 .04	
100	0.9000 .0001	0.9005 .0001	0.9086 .0001	0.9359 .0001	0.9773 .0001	1.0359 .0001	1.1217 .0003	1.2685 .0002	20.135 .03	22.047 .03	23.737 .03	26.742 .04	29.464 .05	32.025 .04	
125	0.8989 .0001	0.8994 .0001	0.9077 .0001	0.9348 .0001	0.9758 .0001	1.0337 .0001	1.1179 .0003	1.2586 .0002	14.486 .02	16.406 .02	17.990 .02	20.673 .03	23.017 .05	25.183 .02	
150	0.8977 .0001	0.8984 .0001	0.9067 .0001	0.9337 .0001	0.9744 .0001	1.0316 .0001	1.1142 .0003	1.2495 .0002	10.332 .01	12.502 .01	14.088 .01	16.602 .02	18.711 .05	20.618 .02	
200	0.8955 .0001	0.8963 .0001	0.9047 .0001	0.9315 .0001	0.9716 .0001	1.0275 .0001	1.1071 .0003	1.2332 .0002	1.5286 .0008	6.982 .01	8.987 .01	11.452 .01	13.305 .02	14.905 .02	
225	0.8944 .0001	0.8953 .0001	0.9038 .0001	0.9305 .0001	0.9702 .0001	1.0255 .0001	1.1037 .0003	1.2258 .0002	1.4902 .0008	3.765 .2	7.135 .02	9.705 .01	11.493 .02	12.997 .02	
250	0.8933 .0001	0.8943 .0001	0.9028 .0001	0.9294 .0001	0.9688 .0001	1.0235 .0001	1.1004 .0003	1.2188 .0002	1.4603 .0008	1.8639 .0008	5.494 .01	8.287 .01	10.038 .01	11.469 .02	
300	0.8912 .0001	0.8924 .0001	0.9010 .0001	0.9273 .0001	0.9661 .0001	1.0196 .0001	1.0941 .0003	1.2060 .0002	1.4147 .0008	1.6489 .0008	2.705 .03	6.110 .01	7.842 .01	9.174 .02	
350	0.8890 .0001	0.8904 .0001	0.8991 .0001	0.9253 .0001	0.9635 .0001	1.0159 .0001	1.0882 .0003	1.1944 .0002	1.3802 .0008	1.5569 .0008	1.959 .01	4.517 .005	6.265 .01	7.533 .02	
400	0.8869 .0001	0.8885 .0001	0.8973 .0001	0.9232 .0001	0.9610 .0001	1.0123 .0001	1.0825 .0003	1.1837 .0002	1.3524 .0008	1.4976 .0008	1.7569 .002	3.3901 .002	5.090 .01	6.307 .02	
450	0.8849 .0001	0.8866 .0001	0.8955 .0001	0.9213 .0001	0.9585 .0001	1.0088 .0001	1.0771 .0003	1.1739 .0002	1.3289 .0008	1.4538 .0008	1.6510 .0006	2.6928 .002	4.204 .01	5.364 .02	
500	0.8829 .0001	0.8848 .0001	0.8937 .0001	0.9193 .0001	0.9560 .0001	1.0054 .0001	1.0719 .0003	1.1648 .0002	1.3087 .0008	1.4190 .0008	1.5806 .0006	2.2954 .002	3.544 .01	4.629 .02	
600	0.8789 .0001	0.8812 .0001	0.8902 .0001	0.9155 .0001	0.9512 .0001	0.9989 .0001	1.0622 .0003	1.1483 .0002	1.2750 .0008	1.3655 .0008	1.4871 .0006	1.9115 .002	2.711 .01	3.597 .02	
700	0.8750 .0001	0.8776 .0001	0.8868 .0001	0.9118 .0001	0.9467 .0001	0.9927 .0001	1.0531 .0003	1.1337 .0002	1.2475 .0008	1.3250 .0008	1.4240 .0006	1.7286 .002	2.263 .01	2.951 .02	
800	0.8713 .0001	0.8742 .0001	0.8835 .0001	0.9082 .0001	0.9423 .0001	0.9869 .0002	1.0447 .0003	1.1205 .0002	1.2242 .0008	1.2925 .0008	1.3767 .0006	1.6171 .002	2.005 .01	2.536 .02	
900	0.8677 .0001	0.8708 .0001	0.8803 .0001	0.9047 .0001	0.9380 .0001	0.9812 .0004	1.0368 .0003	1.1085 .0002	1.2041 .0008	1.2653 .0008	1.3390 .0006	1.5392 .002	1.841 .01	2.257 .02	
1000	0.8643 .0001	0.8675 .0001	0.8771 .0001	0.9013 .0001	0.9339 .0001	0.9759 .0005	1.0294 .0003	1.0975 .0002	1.1864 .0008	1.2420 .0008	1.3078 .0006	1.4802 .002	1.727 .01	2.063 .02	



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

$\bar{T}$	$\bar{\rho}$	$\bar{A}$	$\bar{P}$	$\bar{C}_v$
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  $\bar{A}$ ,  $\bar{P}$ , and  $\bar{C}_v$  calculated at selected

values of  $\bar{T}$  and  $\bar{\rho}$ . 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.