The International Association for the Properties of Water and Steam

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

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This release replaces the corresponding release of 1984
and contains 11 pages, including this cover page.

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The material contained in this release is identical to that contained in the Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance, issued by IAPS in September 1984, except for some minor amendments including those resulting from the change of temperature scale from the International Practical Temperature Scale of 1968 (IPTS-68) to the International Temperature Scale of 1990 (ITS-90). The critical point temperature (ITS-90) used for the reference temperature in the formulation has been taken from the IAPWS Release on the Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at their Respective Critical Points (1992).

The formulation provided in this release is a dimensionless version of "A Fundamental Equation of State for Heavy Water," P. G. Hill, R. D. Chris MacMillan and V. Lee, *Journal of Physical and Chemical Reference Data*, **11** (1982), pp. 1-14 and **12** (1983) p.1065; See also, J. Cooper "Revised Release for Equation of State for Heavy Water Accounting for Change in Temperature Scale," (in preparation).

The IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance[‡]

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: $T^* = 643.847$ K (1)

reference density: $\rho^* = 358$ kg/m^3 (2)

reference pressure: $p^* = 21.671$ MPa (3)

1.2 Secondary reference constants

Reference constant for specific Helmholtz function, specific internal energy, specific enthalpy and specific Gibbs function: $f^{**} = p^*/\rho^*$ (4)

reference constant for specific entropy and specific heat capacity: $s^{**} = p^*/(\rho^* T^*)$ (5)

reference constant for speed of sound: $w^{**} = (p^*/\rho^*)^{1/2}$ (6)

[‡]Ordinary water substance, "H_2O", has normal naturally occurring isotopic abundances. Heavy water substance, "D_2O", is ^2H_2O with the oxygen isotopes in the same abundances as in H_2O.

†The three primary reference constants agree with the critical parameters presented in the IAPWS Release: Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at their Respective Critical Points, (1992).

1.3 Thermophysical Properties in dimensionless form

Temperature[†]:	$\overline{T} = T / T^*$	(7)
pressure:	$\overline{p} = p / p^*$	(8)
density:	$\overline{\rho} = \rho / \rho^*$	(9)
specific volume:	$\overline{v} = v \rho^*$	(10)
specific Helmholtz function:	$\overline{f} = f / f^{**}$	(11)
specific internal energy:	$\overline{u} = u / f^{**}$	(12)
specific enthalpy:	$\overline{h} = h / f^{**}$	(13)
specific Gibbs function:	$\overline{g} = g / f^{**}$	(14)
specific entropy:	$\overline{s} = s / s^{**}$	(15)
specific isochoric heat capacity:	$\overline{c_v} = c_v / s^{**}$	(16)
specific isobaric heat capacity:	$\overline{c_p} = c_p / s^{**}$	(17)
isothermal compressibility:	$\overline{\kappa_T} = \kappa_T p^*$	(18)
speed of sound:	$\overline{w} = w / w^{**}$	(19)

[†] Note: T denotes absolute temperature on the International Temperature Scale of 1990. No distinction is made between this temperature scale and thermodynamic temperature.

2. Equations for thermodynamic properties

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

2.1 Fundamental equation in canonical form

The fundamental equation is defined as

$$\bar{f}(\overline{T}, \overline{\rho}) = \bar{f}_0(\overline{T}, \overline{\rho}) + \bar{f}_1(\overline{T}, \overline{\rho}), \tag{20}$$

with

$$\bar{f}_0(\overline{T}, \overline{\rho}) = \left(A_{00} + A_{01}\overline{T}\right)\ln \overline{T} + \sum_{j=2}^{7} A_{0j}\overline{T}^{\,j-2} + A_{08}\overline{T}\ln\overline{\rho}, \qquad \text{and} \tag{21}$$

$$\bar{f}_1(\overline{T}, \overline{\rho}) = \overline{T}\overline{\rho}\left(1/\overline{T} - 1/\overline{T}_1\right)\times \sum_{i=1}^{7}\left[\left(1/\overline{T} - 1/\overline{T}_i\right)^{i-2}\left(\sum_{j=1}^{8} A_{ij}\left(\overline{\rho} - \overline{\rho}_i\right)^{j-1} + \exp\left(-1.5394\overline{\rho}\right)\sum_{j=9}^{10} A_{ij}\overline{\rho}^{\,j-9}\right)\right]. \tag{22}$$

2.2 Coefficients in the equations for the Helmholtz function $\bar{f}(\bar{T},\bar{\rho})$

The values of the parameters A_{ij}, $\bar{T}_i$ and $\bar{\rho}_i$ in the equations for $\bar{f}_0(\bar{T},\bar{\rho})$ and $\bar{f}_1(\bar{T},\bar{\rho})$ are listed in Tables 1, 2 and 3.

The choice of the coefficients A_{02} and A_{03} is related to the convention adopted for the zero points of energy and entropy. For ordinary water substance the values of the specific internal energy and the specific entropy of the liquid at the triple point are set equal to zero (5^{th} ICPS, London 1956). In the case of ordinary water substance the temperature is not measured since it defines the SI unit of temperature, the kelvin. In the case of heavy water the triple-point temperature is obtained from accurate measurements which are subject to improvement. In this release at the triple point the specific internal energy and entropy are set equal to zero. The triple-point temperature T_t is taken as 276.95 K. At this datum state

$$T_t = 276.95 \text{ K}, \tag{23}$$

$$u_t = 0, \qquad s_t = 0, \tag{24}$$

and from the equations:

$$p_t = 660.096 \text{ Pa}, \qquad h_t = 0.598 \text{ J/kg}. \tag{25}$$

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

2.3 Thermodynamic relations

Some thermodynamic properties of interest can be derived from the fundamental equation (20) using the following thermodynamic relations

$$\bar{v} = 1/\bar{\rho} \tag{26}$$

$$\bar{p} = \bar{\rho}^2 \left(\partial \bar{f} / \partial \bar{\rho}\right)_{\bar{T}} \tag{27}$$

$$\left(\partial \bar{p} / \partial \bar{\rho}\right)_{\bar{T}} = 2\,\bar{p}/\bar{\rho} + \bar{\rho}^2 \left(\partial^2 \bar{f} / \partial \bar{\rho}^2\right)_{\bar{T}} \tag{28}$$

$$1/\bar{\kappa}_T = \bar{\rho}\left(\partial \bar{p} / \partial \bar{\rho}\right)_{\bar{T}} \tag{29}$$

$$\left(\partial \bar{p} / \partial \bar{T}\right)_{\bar{\rho}} = \bar{\rho}^2 \left(\partial^2 \bar{f} / \partial \bar{\rho} \partial \bar{T}\right) \tag{30}$$

$$\bar{s} = -\left(\partial \bar{f} / \partial \bar{T}\right)_{\bar{\rho}} \tag{31}$$

$$\bar{u} = \bar{f} + \bar{T}\,\bar{s} \tag{32}$$

$$\bar{h} = \bar{u} + \bar{p}/\bar{\rho} \tag{33}$$

$$\bar{g} = \bar{f} + \bar{p}/\bar{\rho} \tag{34}$$

$$\bar{c}_v = -\bar{T}\left(\partial^2 \bar{f}/\partial \bar{T}^2\right)_{\bar{\rho}} \tag{35}$$

$$\bar{c}_p = \bar{c}_v + \frac{\bar{T}(\partial \bar{p}/\partial \bar{T})^2_{\bar{\rho}}}{\bar{\rho}^2(\partial \bar{p}/\partial \bar{\rho})_{\bar{T}}} \tag{36}$$

$$\bar{w} = \left[\frac{\bar{c}_p}{\bar{c}_v}(\partial \bar{p}/\partial \bar{\rho})_{\bar{T}}\right]^{1/2} \tag{37}$$

2.4 Idea1-gas properties

The ideal-gas properties of D_2O are obtained from Eq. (21) as a function of temperature and density. Or, as a function of temperature and pressure, they may be obtained from:

$$\bar{f}_{\rm id} = \left(A_{00} + A_{01}\bar{T} - A_{08}\bar{T}\right)\ln \bar{T} + \sum_{j=2}^{7} A_{0j}\bar{T}^{j-2} - A_{08}\bar{T}\ln A_{08} + A_{08}\bar{T}\ln \bar{p}\,. \tag{38}$$

3. Range of validity and estimated uncertainty

3.1 Range of validity

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

$$T_{\rm t} \le T \le 800\ {\rm K}\,, \qquad 0 \le p \le 100\ {\rm MPa}\,. \tag{39}$$

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

$$\left|T - T^*\right| \le 10\ {\rm K}\,, \qquad \left|\bar{\rho} - 1\right| \le 0.3\,. \tag{40}$$

3.2 Estimates of uncertainty

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

4. Computer-program verification

To assist the user in computer-program verification, Table 5 lists values for $\bar{f}$, $\bar{p}$ and $\bar{c}_v$ calculated at selected values of $\bar{T}$ and $\bar{\rho}$. The dimensionless fundamental equation presented in the Release of 1984 yielded thermodynamic property values identical to those calculated from the dimensional equation published by Hill *et al.*, *J. Phys. Chem. Ref. Data* **11**, 1 (1982); **12**, 1065 (1983). The equation with T^* changed to the ITS-90 value and re-evaluated values for A_{02} and A_{03} gives property values close to those of Hill *et al*.

[†] A fundamental equation for D_2O in the critical region can be found in the paper "Thermodynamic Properties of H_2O and D_2O in the Critical Region," A. Kostrowicka Wyczalkowska, Kh.S. Abdulkadirova, M.A. Anisimov, and J.V. Sengers, *J. Chem. Phys.* **113** (2000), pp 4985-5002.

Table 1. Coefficients A_{0j}

j	A_{0j}
0	0.5399322597D-02
1	-.1288399716D+02
2	0.3087155964D+02
3	-.3827264031D+02
4	0.4424799189D+00
5	-.1256336874D+01
6	0.2843343470D+00
7	-.2401555088D-01
8	0.4415884023D+01

Table 2. Coefficients A_{ij} (omitted coefficients are zero identically)

i	j	A_{ij}	i	j	A_{ij}
1	1	0.115623643567D+03	4	1	0.157859762687D+02
1	2	-.161413392951D+03	4	2	-.194973173813D+02
1	3	0.108543003981D+03	4	3	0.114841391216D+02
1	4	-.471342021238D+02	4	4	-.196956103010D+01
1	5	0.149218685173D+02	4	9	-.277379051954D+03
1	6	-.360628259650D+01	4	10	-.481991835255D+03
1	7	0.686743026455D+00	5	1	-.619344658242D+02
1	8	-.951913721401D-01	5	2	0.791406411518D+02
1	9	-.157513472656D+04	5	3	-.484238027539D+02
1	10	-.433677787466D+03	5	4	0.191546335463D+02
2	1	0.607446060304D+02	5	9	0.128039793871D+04
2	2	-.927952190464D+02	5	10	0.186367898973D+04
2	3	0.632086750422D+02	6	1	-.749615505949D+02
2	4	-.264943219184D+02	6	2	0.947388734799D+02
2	5	0.905675051855D+01	6	3	-.575266970986D+02
2	6	-.578949005123D+00	6	4	0.173229892427D+02
2	7	0.665590447621D+00	6	9	0.137572687525D+04
2	8	-.525687146109D-01	6	10	0.231749018693D+04
2	9	-.341048601697D+04	7	1	-.260841561347D+02
2	10	-.146971631028D+04	7	2	0.328640711440D+02
3	1	0.444139703648D+02	7	3	-.186464444026D+02
3	2	-.580410482641D+02	7	4	0.484262639275D+01
3	3	0.354090438940D+02	7	9	0.430179479063D+03
3	4	-.144432210128D+02	7	10	0.822507844138D+03
3	9	-.102135518748D+04			
3	10	-.136324396122D+04			

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

i	$\bar{T}_i$	$\bar{\rho}_i$
1	0.1000038832D+01	0.1955307263D+01
2	0.6138578282D+00	0.3072625698D+01
3	0.6138578282D+00	0.3072625698D+01
4	0.6138578282D+00	0.3072625698D+01
5	0.6138578282D+00	0.3072625698D+01
6	0.6138578282D+00	0.3072625698D+01
7	0.6138578282D+00	0.3072625698D+01

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

Pressure	Temperature, °C						
MPa	3.8	20	50	100	150	200	250
0.1	0.9045	0.9047	0.9127	0.9404	1741.5	1953.9	2164.3
	0.0001	0.0001	0.0001	0.0001	0.2	0.1	0.1
0.5	0.9044	0.9045	0.9125	0.9403	0.9830	382.0	426.6
	0.0001	0.0001	0.0001	0.0001	0.0001	0.1	0.1
1.0	0.9041	0.9043	0.9123	0.9400	0.9827	185.0	209.2
	0.0001	0.0001	0.0001	0.0001	0.0001	0.1	0.1
2.5	0.9034	0.9036	0.9117	0.9393	0.9818	1.0428	78.1
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.1
5.0	0.9023	0.9026	0.9107	0.9382	0.9803	1.0404	1.1299
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
7.5	0.9011	0.9015	0.9097	0.9370	0.9788	1.0382	1.1258
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
10.0	0.9000	0.9005	0.9087	0.9359	0.9773	1.0360	1.1218
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
12.5	0.8989	0.8994	0.9077	0.9348	0.9759	1.0338	1.1179
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
15.0	0.8977	0.8984	0.9067	0.9337	0.9744	1.0317	1.1142
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
20.0	0.8955	0.8963	0.9047	0.9315	0.9716	1.0275	1.1071
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
22.5	0.8944	0.8953	0.9038	0.9305	0.9702	1.0255	1.1038
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
25.0	0.8933	0.8943	0.9028	0.9294	0.9688	1.0235	1.1005
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
30.0	0.8912	0.8924	0.9010	0.9273	0.9662	1.0197	1.0942
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
35.0	0.8890	0.8904	0.8991	0.9253	0.9635	1.0160	1.0882
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
40.0	0.8869	0.8885	0.8973	0.9233	0.9610	1.0124	1.0826
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
45.0	0.8849	0.8867	0.8955	0.9213	0.9585	1.0089	1.0771
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
50.0	0.8829	0.8848	0.8937	0.9193	0.9560	1.0055	1.0720
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
60.0	0.8789	0.8812	0.8903	0.9155	0.9513	0.9990	1.0622
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
70.0	0.8750	0.8776	0.8869	0.9118	0.9467	0.9928	1.0532
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
80.0	0.8713	0.8742	0.8835	0.9082	0.9423	0.9869	1.0448
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0003
90.0	0.8677	0.8708	0.8803	0.9047	0.9380	0.9813	1.0369
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004	0.0003
100.0	0.8643	0.8675	0.8771	0.9013	0.9339	0.9759	1.0294
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0005	0.0003

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

Pressure MPa	Temperature, °C 300	350	375	400	450	500	550
0.1	2373.8	2582.6	2686.9	2791.1	2999.3	3207.4	3415.4
	0.2	0.4	0.8	1.0	1.0	1.0	1.0
0.5	470.0	512.8	534.1	555.2	597.4	639.4	681.4
	0.2	0.2	0.3	0.3	0.3	0.3	0.4
1.0	232.0	254.1	264.9	275.7	297.2	318.5	339.6
	0.1	0.1	0.2	0.2	0.2	0.2	0.2
2.5	88.9	98.7	103.4	108.0	117.0	125.8	134.6
	0.1	0.1	0.1	0.1	0.1	0.1	0.1
5.0	40.68	46.68	49.38	51.96	56.89	61.62	66.21
	0.10	0.10	0.05	0.05	0.05	0.06	0.06
7.5	23.94	29.128	31.243	33.198	36.815	40.192	43.426
	0.10	0.050	0.030	0.030	0.040	0.050	0.040
10.0	1.2687	20.138	22.050	23.740	26.744	29.466	32.028
	0.0002	0.030	0.030	0.030	0.040	0.050	0.040
12.5	1.2588	14.490	16.409	17.993	20.675	23.020	25.185
	0.0002	0.020	0.020	0.020	0.030	0.050	0.020
15.0	1.2497	10.337	12.505	14.090	16.604	18.713	20.620
	0.0002	0.010	0.010	0.010	0.020	0.050	0.020
20.0	1.2333	1.5291	6.987	8.990	11.454	13.307	14.907
	0.0002	0.0008	0.010	0.010	0.010	0.020	0.020
22.5	1.2259	1.4906	3.788	7.138	9.707	11.495	12.999
	0.0002	0.0008	0.200	0.020	0.010	0.020	0.020
25.0	1.2190	1.4606	1.8657	5.498	8.289	10.039	11.471
	0.0002	0.0008	0.0008	0.010	0.010	0.010	0.020
30.0	1.2061	1.4150	1.6495	2.709	6.112	7.843	9.175
	0.0002	0.0008	0.0008	0.030	0.010	0.010	0.020
35.0	1.1945	1.3805	1.5573	1.961	4.520	6.267	7.534
	0.0002	0.0008	0.0008	0.010	0.005	0.010	0.020
40.0	1.1838	1.3526	1.4979	1.7576	3.3921	5.091	6.308
	0.0002	0.0008	0.0008	0.0020	0.0020	0.010	0.020
45.0	1.1740	1.3291	1.4540	1.6514	2.6943	4.205	5.365
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
50.0	1.1649	1.3089	1.4192	1.5810	2.2965	3.545	4.630
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
60.0	1.1484	1.2751	1.3657	1.4874	1.9121	2.712	3.598
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
70.0	1.1337	1.2476	1.3252	1.4242	1.7290	2.264	2.952
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
80.0	1.1206	1.2243	1.2926	1.3769	1.6174	2.005	2.537
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
90.0	1.1086	1.2042	1.2654	1.3392	1.5395	1.841	2.258
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020
100.0	1.0976	1.1865	1.2421	1.3079	1.4804	1.727	2.063
	0.0002	0.0008	0.0008	0.0006	0.0020	0.010	0.020

Table 5. Property values calculated for selected values of $\bar{T}$ and $\bar{\rho}$

$\bar{T}$	$\bar{\rho}$	$\bar{f}$	$\bar{p}$	$\bar{c}_v$
0.5000	0.0002	-2.644979	0.0004402	14.2768
0.5000	3.1800	-0.217388	4.3549719	41.4463
0.7500	0.0295	-7.272543	0.0870308	20.1586
0.7500	2.8300	-4.292707	4.4752958	33.4367
1.0000	0.3000	-15.163326	0.8014044	30.8587
1.0000	1.5500	-12.643811	1.0976283	33.0103
1.2000	0.4000	-25.471535	1.4990994	23.6594
1.2000	1.6100	-21.278164	4.5643798	25.4800