The International Association for the Properties of Water and Steam

Doorwerth, The Netherlands
September 2009

Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use

President:
Dr. Daniel G. Friend
Thermophysical Properties Division
National Institute of Standards and Technology
325 Broadway
Boulder, CO, 80305, USA

Executive Secretary:
Dr. R. B. Dooley
Structural Integrity Associates, Inc.
2616 Chelsea Drive
Charlotte, NC 28209, USA
email: bdooley@structint.com

This release contains 9 pages, including this cover page.

This release has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Doorwerth, The Netherlands, 6-11 September, 2009, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Japan, Russia, the United States of America, and associate members Argentina and Brazil, Italy, and Switzerland.

The equation of state provided in this release is a fundamental equation for the Gibbs energy as a function of temperature and pressure; details can be found in the articles "A new extended Gibbs thermodynamic potential of seawater" and "A Gibbs function for seawater thermodynamics for −6 to 80 °C and salinity up to 120 g kg^{-1}" by R. Feistel [1, 2]. This equation can be used instead of the IAPWS-95 formulation [3, 4] for thermodynamic properties of liquid water required for calculating properties of seawater according to the IAPWS seawater formulation [5]. It is restricted to the oceanographic standard range of temperature and pressure, within which its deviations from IAPWS-95 are well within the uncertainties of IAPWS-95.

Further information about this supplementary release and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from http://www.iapws.org.

Contents

1 Nomenclature

Symbol	Physical quantity	Unit
c_p	Specific isobaric heat capacity	$\mathrm{J\ kg^{-1}\ K^{-1}}$
h	Specific Helmholtz energy	$\mathrm{J\ kg^{-1}}$
g	Specific Gibbs energy	$\mathrm{J\ kg^{-1}}$
g^*	Reducing specific Gibbs energy, $g^* = 1\ \mathrm{J\ kg^{-1}}$	$\mathrm{J\ kg^{-1}}$
$g_{00}\ldots g_{76}$	Coefficients of the Gibbs potential function, Table 2	
h	Specific enthalpy	$\mathrm{J\ kg^{-1}}$
k	Uncertainty coverage factor	
p	Absolute pressure	Pa
p_0	Normal pressure, $p_0 = 101\ 325$ Pa	Pa
p_t	IAPWS-95 calculated triple-point pressure, $p_\mathrm{t} = 611.654\ 771\ 007\ 894$ Pa	Pa
p^*	Reducing pressure, $p^* = 10^8$ Pa	Pa
s	Specific entropy	$\mathrm{J\ kg^{-1}\ K^{-1}}$
T	Absolute temperature (ITS-90)	K
T_0	Celsius zero point, $T_0 = 273.15$ K	K
T_t	Triple-point temperature, $T_\mathrm{t} = 273.16$ K	K
T^*	Reducing temperature, $T^* = 40$ K	K
t	Celsius temperature	°C
t_min	Lower temperature bound	°C
u	Specific internal energy	$\mathrm{J\ kg^{-1}}$
U	Expanded uncertainty	
u_c	Combined standard uncertainty	

Symbol	**Physical quantity**	**Unit**
v	Specific volume	$\mathrm{m^3\ kg^{-1}}$
w	Speed of sound	$\mathrm{m\ s^{-1}}$
α	Thermal expansion coefficient	$\mathrm{K^{-1}}$
β_s	Isentropic temperature-pressure coefficient	$\mathrm{K\ Pa^{-1}}$
κ_s	Isentropic compressibility	$\mathrm{Pa^{-1}}$
κ_T	Isothermal compressibility	$\mathrm{Pa^{-1}}$
π	Reduced pressure, $\pi = (p - p_0)/p^*$	
ρ	Density	$\mathrm{kg\ m^{-3}}$
τ	Reduced temperature, $\tau = (T - T_0)/T^*$	

2 Introductory Remarks and Special Constants

The "Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" [5] describes the difference between the specific Gibbs energies of seawater and water. At given temperature and pressure, the water part must separately be computed from the Helmholtz function provided by the IAPWS-95 formulation [3, 4], determining the pure-water density by numerical iteration. As a function of temperature and pressure, the Gibbs function for liquid water provided in this Supplementary Release eliminates the need for iteration. It is restricted in its validity to the range 100 Pa to 100 MPa and $t_{\min}(p) = -(2.65 + p \times 0.0743\ \mathrm{MPa}^{-1})\ ^\circ\mathrm{C}$ to 40 °C, only slightly exceeding the oceanographic standard range to include the triple point and the lowest oceanic freezing point. This Gibbs function significantly simplifies the implementation and reduces the computing time for oceanographic applications such as numerical circulation models or real-time processing of in-situ data, while still giving values for properties whose agreement with IAPWS-95 is well within the uncertainties associated with IAPWS-95.

TABLE 1 Special constants and values used in this release

Quantity	Symbol	Value	Unit	Reference
Triple-point pressure[a]	p_t	611.654 771 007 894	Pa	[3]
Normal pressure	p_0	101 325	Pa	[7]
Reducing pressure	p^*	10^8	Pa	[2]
Triple-point temperature	T_t	273.16	K	[8]
Celsius zero point	T_0	273.15	K	[8]
Reducing temperature	T^*	40	K	[2]

[a] Numerical triple-point pressure value computed from IAPWS-95 [3], being well within the uncertainty of the experimental value of 611.657(10) Pa [6]

3 The Equation of State

The equation of state presented here is in the form of the specific Gibbs energy as a function of temperature and pressure, $g(T,\ p)$, corresponding to a Gibbs potential. The temperatures are based on the temperature scale ITS-90 [8]. Reduced by $g^* = 1\ \mathrm{J\ kg^{-1}}$, the Gibbs function is the dimensionless polynomial given by Eq. (1)

$$g(T,p)/g^* = \sum_{j=0}^{7}\sum_{k=0}^{6} g_{jk}\tau^j\pi^k \ , \tag{1}$$

with the reduced temperature $\tau = (T - T_0)/T^*$ and the reduced pressure $\pi = (p - p_0)/p^*$. The reduced quantities τ and π vary from 0 to 1 in the oceanographic standard range. The constants T_0, p_0, T^*, and p^* are given in Table 1.

The coefficients of Eq. (1) are given in Table 2. Two of these 41 parameters (g_{00} and g_{10}) are arbitrary and are computed from the reference-state conditions of vanishing specific entropy, s, and specific internal energy, u, of liquid water at the triple point,

$$s(T_\mathrm{t}, p_\mathrm{t}) = 0, \tag{2}$$

$$u(T_\mathrm{t}, p_\mathrm{t}) = 0. \tag{3}$$

TABLE 2 Coefficients of the Gibbs function, as given by Eq. (1). Coefficients not contained in this table have the value $g_{jk} = 0$.

j	k	g_{jk}	j	k	g_{jk}
0	0	$0.101\,342\,743\,139\,674 \times 10^3$	3	2	$0.499\,360\,390\,819\,152 \times 10^3$
0	1	$0.100\,015\,695\,367\,145 \times 10^6$	3	3	$-0.239\,545\,330\,654\,412 \times 10^3$
0	2	$-0.254\,457\,654\,203\,630 \times 10^4$	3	4	$0.488\,012\,518\,593\,872 \times 10^2$
0	3	$0.284\,517\,778\,446\,287 \times 10^3$	3	5	$-0.166\,307\,106\,208\,905 \times 10$
0	4	$-0.333\,146\,754\,253\,611 \times 10^2$	4	0	$-0.148\,185\,936\,433\,658 \times 10^3$
0	5	$0.420\,263\,108\,803\,084 \times 10$	4	1	$0.397\,968\,445\,406\,972 \times 10^3$
0	6	$-0.546\,428\,511\,471\,039$	4	2	$-0.301\,815\,380\,621\,876 \times 10^3$
1	0	$0.590\,578\,347\,909\,402 \times 10$	4	3	$0.152\,196\,371\,733\,841 \times 10^3$
1	1	$-0.270\,983\,805\,184\,062 \times 10^3$	4	4	$-0.263\,748\,377\,232\,802 \times 10^2$
1	2	$0.776\,153\,611\,613\,101 \times 10^3$	5	0	$0.580\,259\,125\,842\,571 \times 10^2$
1	3	$-0.196\,512\,550\,881\,220 \times 10^3$	5	1	$-0.194\,618\,310\,617\,595 \times 10^3$
1	4	$0.289\,796\,526\,294\,175 \times 10^2$	5	2	$0.120\,520\,654\,902\,025 \times 10^3$
1	5	$-0.213\,290\,083\,518\,327 \times 10$	5	3	$-0.552\,723\,052\,340\,152 \times 10^2$
2	0	$-0.123\,577\,859\,330\,390 \times 10^5$	5	4	$0.648\,190\,668\,077\,221 \times 10$
2	1	$0.145\,503\,645\,404\,680 \times 10^4$	6	0	$-0.189\,843\,846\,514\,172 \times 10^2$
2	2	$-0.756\,558\,385\,769\,359 \times 10^3$	6	1	$0.635\,113\,936\,641\,785 \times 10^2$
2	3	$0.273\,479\,662\,323\,528 \times 10^3$	6	2	$-0.222\,897\,317\,140\,459 \times 10^2$
2	4	$-0.555\,604\,063\,817\,218 \times 10^2$	6	3	$0.817\,060\,541\,818\,112 \times 10$
2	5	$0.434\,420\,671\,917\,197 \times 10$	7	0	$0.305\,081\,646\,487\,967 \times 10$
3	0	$0.736\,741\,204\,151\,612 \times 10^3$	7	1	$-0.963\,108\,119\,393\,062 \times 10$
3	1	$-0.672\,507\,783\,145\,070 \times 10^3$			

TABLE 3 Relations of the thermodynamic properties to the equation for the Gibbs energy of liquid water, Eq. (1), and its *T*-*p* derivatives[a]

Property	Relation	Unit	Eq.
Density			
$\rho(T,p)=v^{-1}=(\partial g/\partial p)_T^{-1}$	$\rho(T,p)=g_p^{-1}$	$\frac{\mathrm{kg}}{\mathrm{m}^3}$	(4)
Specific entropy			
$s(T,p)=-(\partial g/\partial T)_p$	$s(T,p)=-g_T$	$\frac{\mathrm{J}}{\mathrm{kg\,K}}$	(5)
Specific isobaric heat capacity			
$c_p(T,p)=T(\partial s/\partial T)_p$	$c_p(T,p)=-Tg_{TT}$	$\frac{\mathrm{J}}{\mathrm{kg\,K}}$	(6)
Specific enthalpy			
$h(T,p)=g+Ts$	$h(T,p)=g-Tg_T$	$\frac{\mathrm{J}}{\mathrm{kg}}$	(7)
Specific internal energy			
$u(T,p)=g+Ts-pv$	$u(T,p)=g-Tg_T-pg_p$	$\frac{\mathrm{J}}{\mathrm{kg}}$	(8)
Specific Helmholtz energy			
$f(T,p)=g-pv$	$f(T,p)=g-pg_p$	$\frac{\mathrm{J}}{\mathrm{kg}}$	(9)
Thermal expansion coefficient			
$\alpha(T,p)=v^{-1}(\partial v/\partial T)_p$	$\alpha(T,p)=g_{Tp}/g_p$	$\frac{1}{\mathrm{K}}$	(10)
Isentropic temperature-pressure coefficient, adiabatic lapse rate			
$\beta_s(T,p)=(\partial T/\partial p)_s$	$\beta_s(T,p)=-g_{Tp}/g_{TT}$	$\frac{\mathrm{K}}{\mathrm{Pa}}$	(11)
Isothermal compressibility			
$\kappa_T(T,p)=-v^{-1}(\partial v/\partial p)_T$	$\kappa_T(T,p)=-g_{pp}/g_p$	$\frac{1}{\mathrm{Pa}}$	(12)
Isentropic compressibility			
$\kappa_s(T,p)=-v^{-1}(\partial v/\partial p)_s$	$\kappa_s(T,p)=\left(g_{Tp}^2-g_{TT}g_{pp}\right)/\left(g_pg_{TT}\right)$	$\frac{1}{\mathrm{Pa}}$	(13)
Speed of sound			
$w(t,p)=\sqrt{(\partial p/\partial \rho)_s}$	$w(T,p)=g_p\sqrt{g_{TT}/\left(g_{Tp}^2-g_{TT}g_{pp}\right)}$	$\frac{\mathrm{m}}{\mathrm{s}}$	(14)

[a] $g_T\equiv\left[\frac{\partial g}{\partial T}\right]_p$, $g_p\equiv\left[\frac{\partial g}{\partial p}\right]_T$, $g_{TT}\equiv\left[\frac{\partial^2 g}{\partial T^2}\right]_p$, $g_{Tp}\equiv\frac{\partial^2 g}{\partial T\partial p}$, $g_{pp}\equiv\left[\frac{\partial^2 g}{\partial p^2}\right]_T$

4 Relations of the Thermodynamic Properties to the Specific Gibbs Energy

Thermodynamic properties can be derived from Eq. (1) by using the appropriate combinations of the specific Gibbs energy and its derivatives. Relations between thermodynamic properties and $g(T,\ p)$ and its derivatives with respect to T and p are summarized in Table 3. All required derivatives of the saline part of the specific Gibbs energy are explicitly given in Table 4.

TABLE 4 Equations for the Gibbs energy, Eq. (1), and its derivatives[a]

Equation	Unit
$g(T,p) = g^* \sum_{j=0}^{7}\sum_{k=0}^{6} g_{jk}\tau^j\pi^k$ with $g^* = 1\ \mathrm{J\ kg^{-1}}$, $\tau = (T - T_0)/T^*$, $T_0 = 273.15\,\mathrm{K}$, $T^* = 40\,\mathrm{K}$, $\pi = (p - p_0)/p^*$, $p_0 = 101\,325\,\mathrm{Pa}$, $p^* = 10^8\ \mathrm{Pa}$	$\frac{\mathrm{J}}{\mathrm{kg}}$
$g_T(T,p) = \frac{g^*}{T^*}\sum_{j=1}^{7}\sum_{k=0}^{6} j\, g_{jk}\, \tau^{j-1}\pi^k$	$\frac{\mathrm{J}}{\mathrm{kg\ K}}$
$g_p(T,p) = \frac{g^*}{p^*}\sum_{j=0}^{7}\sum_{k=1}^{6} k\, g_{jk}\tau^j\pi^{k-1}$	$\frac{\mathrm{m^3}}{\mathrm{kg}}$
$g_{TT}(T,p) = \frac{g^*}{(T^*)^2}\sum_{j=2}^{7}\sum_{k=0}^{6} j(j-1)g_{jk}\, \tau^{j-2}\pi^k$	$\frac{\mathrm{J}}{\mathrm{kg\ K^2}}$
$g_{Tp}(T,p) = \frac{g^*}{T^*\, p^*}\sum_{j=1}^{7}\sum_{k=1}^{6} jk\, g_{jk}\tau^{j-1}\pi^{k-1}$	$\frac{\mathrm{m^3}}{\mathrm{kg\ K}}$
$g_{pp}(T,p) = \frac{g^*}{(p^*)^2}\sum_{j=0}^{7}\sum_{k=2}^{6} k(k-1)g_{jk}\tau^j\pi^{k-2}$	$\frac{\mathrm{m^3}}{\mathrm{kg\ Pa}}$

[a] $g_T \equiv \left[\frac{\partial g}{\partial T}\right]_p$, $g_p \equiv \left[\frac{\partial g}{\partial p}\right]_T$, $g_{TT} \equiv \left[\frac{\partial^2 g}{\partial T^2}\right]_p$, $g_{Tp} \equiv \frac{\partial^2 g}{\partial T\,\partial p}$, $g_{pp} \equiv \left[\frac{\partial^2 g}{\partial p^2}\right]_T$

5 Range of Validity and Brief Discussion

The equation of state, Eq. (1), is valid for liquid water only within the pressure and temperature range

$$100\ \text{Pa} \le p \le 10^8\ \text{Pa} \ \text{ and } \ (270.5 - p \times 7.43 \times 10^{-8}\ \text{Pa}^{-1})\ \text{K} \ \le T \le 313.15\ \text{K},$$

including the region of ambient ocean water. The lower temperature limit depends on the pressure proportional to the experimental Clausius-Clapeyron coefficient [9] and covers the lowest temperature found in the global ocean: the freezing temperature of about –4.25 °C off the Antarctic shelf at 3000 m depth. The deviations of properties derived from this Gibbs function from those calculated with IAPWS-95 are significantly less than the experimental uncertainty for each property (Table 5). Within its range of validity, it is intended to be used as a simpler substitute for IAPWS-95, providing the water part of the Gibbs function of seawater [5] without significant loss in accuracy.

This formulation for the thermodynamic properties of liquid water was developed in cooperation with the SCOR/IAPSO Working Group 127 on Thermodynamics and Equation of State of Seawater.

6 Estimates of Uncertainty

Here, estimated combined standard uncertainties u_c [10] are reported, from which expanded uncertainties $U = k\,u_c$ can be obtained by multiplying with the coverage factor $k = 2$, corresponding to a 95% confidence level. The term “uncertainty” used in the following refers to combined standard uncertainties or to relative combined standard uncertainties.

Deviations of selected properties of this supplementary release from IAPWS-95 are reported in Table 5. These deviations are well within the estimated uncertainties of IAPWS-95.

TABLE 5 Combined standard uncertainties from IAPWS-95 [3, 4] of selected quantities in certain regions of the *T*-*p* space, compared with the root-mean-square (r.m.s.) and the maximum deviation between IAPWS-95 and the formulation of this release. The pressure-dependent lower temperature bound is $t_{\min} = -\left(2.65 + p \times 0.0743\ \text{MPa}^{-1}\right)\,°\text{C}$. For ρ and w the uncertainties and deviations are relative and therefore dimensionless.

Quantity	T interval °C	p interval MPa	IAPWS-95 Uncertainty	r.m.s. Deviation	Maximum Deviation	Units
c_p	–2.7 - 40	0.1	10	0.04	0.25	$\text{J kg}^{-1}\ \text{K}^{-1}$
α	–2.7 - 40	0.1	0.6×10^{-6} [a]	0.03×10^{-6}	0.19×10^{-6}	K^{-1}
α	$t_{\min}(p)$ - 40	0.0001 - 100	0.6×10^{-6} [a]	0.02×10^{-6}	0.19×10^{-6}	K^{-1}
ρ	–2.7 - 40	0.1	1×10^{-6}	0.03×10^{-6}	0.23×10^{-6}	–
ρ	$t_{\min}(p)$ - 40	0.0001 - 10	10×10^{-6}	0.03×10^{-6}	0.23×10^{-6}	–
ρ	$t_{\min}(p)$ - 40	10 - 100	30×10^{-6}	0.04×10^{-6}	0.23×10^{-6}	–
w	$t_{\min}(p)$ - 40	0.0001 - 100	1000×10^{-6}	3×10^{-6}	39×10^{-6}	–

[a] Estimate adopted from seawater data [1]

7 Computer-Program Verification

To assist the user in computer-program verification, Table 6 with test values is given. It contains values for the specific Gibbs energy, $g(T, p)$, together with the corresponding derivatives and some thermodynamic properties.

8 References

[1] Feistel, R., *Progr. Oceanogr.* **58**, 43 (2003).

[2] Feistel, R., *Deep-Sea Res. I* **55**, 1639 (2008).

[3] IAPWS, *Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use* (2009). Available from http://www.iapws.org.

[4] Wagner, W., and Pruß, A., *J. Phys. Chem. Ref. Data* **31**, 387 (2002).

[5] IAPWS, *Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater* (2008). Available from http://www.iapws.org.

[6] Guildner, L. A., Johnson, D. P., and Jones, F. E., *J. Res. Natl. Bur. Stand.* **80A**, 505 (1976).

[7] ISO, *ISO Standards Handbook: Quantities and Units* (International Organization for Standardization, Geneva, 1993).

[8] Preston-Thomas, H., *Metrologia* **27**, 3 (1990).

[9] Feistel, R., and Wagner, W., *J. Phys. Chem. Ref. Data* **35**, 1021 (2006).

[10] ISO, *Guide to the Expression of Uncertainty in Measurement* (International Organization for Standardization, Geneva, 1993).

TABLE 6 Numerical check values for the Gibbs function g and its derivatives, Table 4, The numerical functions evaluated here at given points (T, p) are defined in Tables 3 and 4.

Quantity	Value	Value	Value	Unit
T	273.15	273.15	313.15	K
p	101 325	10^{8}	101 325	Pa
g	$0.101\,342\,743 \times 10^{3}$	$0.977\,303\,868 \times 10^{5}$	$-0.116\,198\,898 \times 10^{5}$	$\mathrm{J\,kg^{-1}}$
$(\partial g/\partial T)_p$	$0.147\,644\,587$	$0.851\,506\,346 \times 10$	$-0.572\,365\,181 \times 10^{3}$	$\mathrm{J\,kg^{-1}\,K^{-1}}$
$(\partial g/\partial p)_T$	$0.100\,015\,695 \times 10^{-2}$	$0.956\,683\,354 \times 10^{-3}$	$0.100\,784\,471 \times 10^{-2}$	$\mathrm{m^{3}\,kg^{-1}}$
$(\partial^2 g/\partial T^2)_p$	$-0.154\,472\,324 \times 10^{2}$	$-0.142\,970\,174 \times 10^{2}$	$-0.133\,463\,968 \times 10^{2}$	$\mathrm{J\,kg^{-1}\,K^{-2}}$
$\partial^2 g/\partial T \partial p$	$-0.677\,459\,513 \times 10^{-7}$	$0.199\,088\,060 \times 10^{-6}$	$0.388\,499\,694 \times 10^{-6}$	$\mathrm{m^{3}\,kg^{-1}\,K^{-1}}$
$(\partial^2 g/\partial p^2)_T$	$-0.508\,915\,308 \times 10^{-12}$	$-0.371\,527\,164 \times 10^{-12}$	$-0.445\,841\,077 \times 10^{-12}$	$\mathrm{m^{3}\,kg^{-1}\,Pa^{-1}}$
h	$0.610\,136\,242 \times 10^{2}$	$0.954\,044\,973 \times 10^{5}$	$0.167\,616\,267 \times 10^{6}$	$\mathrm{J\,kg^{-1}}$
f	$0.183\,980\,891 \times 10^{-2}$	$0.206\,205\,140 \times 10^{4}$	$-0.117\,220\,097 \times 10^{5}$	$\mathrm{J\,kg^{-1}}$
u	$-0.403\,272\,791 \times 10^{2}$	$-0.263\,838\,183 \times 10^{3}$	$0.167\,514\,147 \times 10^{6}$	$\mathrm{J\,kg^{-1}}$
s	$-0.147\,644\,587$	$-0.851\,506\,346 \times 10$	$0.572\,365\,181 \times 10^{3}$	$\mathrm{J\,kg^{-1}\,K^{-1}}$
ρ	$0.999\,843\,071 \times 10^{3}$	$0.104\,527\,793 \times 10^{4}$	$0.992\,216\,354 \times 10^{3}$	$\mathrm{kg\,m^{-3}}$
c_p	$0.421\,941\,153 \times 10^{4}$	$0.390\,523\,030 \times 10^{4}$	$0.417\,942\,416 \times 10^{4}$	$\mathrm{J\,kg^{-1}\,K^{-1}}$
w	$0.140\,240\,099 \times 10^{4}$	$0.157\,543\,089 \times 10^{4}$	$0.152\,891\,242 \times 10^{4}$	$\mathrm{m\,s^{-1}}$