

## Notes on the function gsw\_gibbs

Notes made 21<sup>st</sup> September 2010 and updated on 20<sup>th</sup> May 2015

This function, `gsw_gibbs`, calculates the Gibbs function of seawater and its various partial derivatives. The Gibbs function of seawater  $g(S_A, t, p)$  is naturally a function of Absolute Salinity, in situ temperature and pressure, and it is defined as the sum of the Gibbs function for pure water  $g^W(t, p)$  and the saline part of the Gibbs function  $g^S(S_A, t, p)$  so that

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p). \quad (\text{A.6.1})$$

The pure water part is the Gibbs function of Feistel (2003) (which is the IAPWS Release IAPWS-09) and the saline part is the Gibbs function of Feistel (2008) (which is the IAPWS Release IAPWS-08).

This function, `gsw_gibbs`, can calculate the Gibbs function of seawater and all its first and second order derivatives and some third order derivatives, namely  $g, g_{S_A}, g_T, g_P$  as well as  $g_{S_A S_A}, g_{TT}, g_{PP}, g_{P S_A}, g_{PT}, g_{S_A T}, g_{S_A S_A S_A}, g_{TTP}, g_{S_A TP}, g_{S_A S_A P}, g_{S_A TT}, g_{S_A S_A T}, g_{S_A PP}$  and  $g_{TTP}$ . The Gibbs function has units of  $\text{J kg}^{-1}$  and the derivatives are returned from `gsw_gibbs` consistently with  $S_A$  being in  $\text{g kg}^{-1}$ , in situ temperature being in  $^\circ\text{C}$  and pressure being in Pa (even though the pressure input to  $g(S_A, t, p)$  is in dbar).

Given the definition of Absolute Salinity, it is clear that for a real sample of pure water or of seawater, Absolute Salinity cannot be negative. Since salinity enters the TEOS-10 Gibbs function as powers of the square root of Absolute Salinity, even a slightly negative value of Absolute Salinity means that the outputs of many of the GSW functions become complex numbers. Hence it is convenient to ensure that the inputs to these functions do not contain negative values of Absolute Salinity. In all the functions in the GSW toolbox which rely on the Gibbs function or on the computationally efficient expression for specific volume (Roquet *et al.*, 2015), any negative input value of  $S_A$  are set to zero.

### References

- Feistel, R., 2003: A new extended Gibbs thermodynamic potential of seawater. *Progr. Oceanogr.*, **58**, 43-114.
- Feistel, R., 2008: A Gibbs function for seawater thermodynamics for  $-6$  to  $80$   $^\circ\text{C}$  and salinity up to  $120$   $\text{g kg}^{-1}$ . *Deep-Sea Res. I*, **55**, 1639-1671.
- IAPWS, 2008: Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater. The International Association for the Properties of Water and Steam. Berlin, Germany, September 2008, available from <http://www.iapws.org>. This Release is referred to in the text as IAPWS-08.
- IAPWS, 2009: Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use. The International Association for the Properties of Water and Steam. Doorwerth, The Netherlands, September 2009, available from <http://www.iapws.org>. This Release is referred to in the text as IAPWS-09.
- IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp. Available from <http://www.TEOS-10.org>
- Roquet, F., G. Madec, T. J. McDougall and P. M. Barker, 2015: Accurate polynomial expressions for the density and specific volume of seawater using the TEOS-10 standard. *Ocean Modelling*, **90**, pp. 29-43. <http://dx.doi.org/10.1016/j.ocemod.2015.04.002>

Here follows appendix A.6 of the TEOS-10 Manual (IOC et al. (2010)), followed by appendices G and H of this TEOS-10 Manual.

## A.6 Gibbs function of seawater

The Gibbs function of seawater  $g(S_A, t, p)$  is defined as the sum of the Gibbs function for pure water  $g^W(t, p)$  and the saline part of the Gibbs function  $g^S(S_A, t, p)$  so that

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p). \quad (\text{A.6.1})$$

In this way at zero Absolute Salinity, the thermodynamic properties of seawater are equal to those of pure water. This consistency is also maintained with respect to the Gibbs function for ice so that the properties along the equilibrium curve can be accurately determined (such as the freezing temperature as a function of Absolute Salinity and pressure). The careful alignment of the thermodynamic potentials of pure water, ice Ih and seawater is described in Feistel *et al.* (2008a).

The internationally accepted thermodynamic description of the properties of pure water (IAPWS-95) is the official pure-water basis upon which the Gibbs function of seawater is built according to (A.6.1). This  $g^W(t, p)$  Gibbs function of liquid water is valid over extended ranges of temperature and pressure from the freezing point to the critical point ( $-22\text{ }^\circ\text{C} < t < 374\text{ }^\circ\text{C}$  and  $600\text{ Pa} < p + P_0 < 1000\text{ MPa}$ ) however it is a computationally expensive algorithm. Part of the reason for this computational intensity is that the IAPWS-95 formulation is in terms of a Helmholtz function which has the pressure as a function of temperature and density, so that an iterative procedure is needed for the Gibbs function  $g^W(t, p)$  (see for example, Feistel *et al.* (2008a))

For practical oceanographic use in the oceanographic ranges of temperature and pressure, from less than the freezing temperature of seawater (at any pressure), up to  $40\text{ }^\circ\text{C}$  (specifically from  $-[2.65 + (p + P_0) \times 0.0743\text{ MPa}^{-1}]\text{ }^\circ\text{C}$  to  $40\text{ }^\circ\text{C}$ ), and in the pressure range  $0 < p < 10^4\text{ dbar}$  we also recommend the use of the pure water part of the Gibbs function of Feistel (2003) which has been approved by IAPWS as the Supplementary Release, IAPWS-09. The IAPWS-09 release discusses the accuracy to which the Feistel (2003) Gibbs function fits the underlying thermodynamic potential of IAPWS-95; in summary, for the variables density, thermal expansion coefficient and specific heat capacity, the rms misfit between IAPWS-09 and IAPWS-95, in the region of validity of IAPWS-09, are a factor of between 20 and 100 less than the corresponding error in the laboratory data to which IAPWS-95 was fitted. Hence, in the oceanographic range of parameters, IAPWS-09 and IAPWS-95 may be regarded as equally accurate thermodynamic descriptions of pure liquid water.

All of the thermodynamic properties of seawater that are described in this Manual are available as both FORTRAN and MATLAB implementations. These implementations are available for  $g^W(t, p)$  being IAPWS-95 and IAPWS-09, both being equally accurate relative to the laboratory-determined known properties, but with the computer code based on IAPWS-09 being approximately a factor of 65 faster than that based on IAPWS-95.

Most of the experimental seawater data that were already used for the construction of EOS-80 were exploited again for the IAPWS-08 formulation after their careful adjustment to the new temperature and salinity scales and the improved pure-water reference IAPWS-95. Additionally, IAPWS-08 was significantly improved (compared with EOS-80) by making use of theoretical relations such as the ideal-solution law and the Debye-Hückel limiting law, as well as by incorporating additional accurate measurements such as the temperatures of maximum density, vapour pressures and mixing heats, and implicitly by the enormous background data set which had entered the determination of

IAPWS-95 (Wagner and Pruß (2002), Feistel (2003, 2008)). For example, Millero and Li (1994) concluded that the pure-water part of the EOS-80 sound-speed formula of Chen and Millero (1977) was responsible for a deviation of  $0.5 \text{ m s}^{-1}$  from Del Grosso's (1974) formula for seawater at high pressures and temperature below  $5 \text{ }^\circ\text{C}$ . Chen and Millero (1977) only measured the differences in the sound speeds of seawater and pure water. The new Gibbs function in which we use IAPWS-95 for the pure-water part as well as sound speeds from Del Grosso (1974), is perfectly consistent with Chen and Millero's (1976) densities and Bradshaw and Schleicher's (1970) thermal expansion data at high pressures. The accuracy of high-pressure seawater densities has increased with the use of IAPWS-95, directly as the pure-water part, and indirectly by correcting earlier seawater measurements, making them "new" seawater data. In this manner the known sound-speed inconsistency of EOS-80 has been resolved in a natural manner.

## Appendix G: Coefficients of the pure liquid water Gibbs function of IAPWS-09

The pure liquid water part of the Gibbs function of Feistel (2003) has been approved by IAPWS (IAPWS (2009c)) as an alternative thermodynamic description of pure water to IAPWS-95 in the oceanographic ranges of temperature and pressure. The pure water specific Gibbs energy  $g^W(t, p)$  is the following function of the independent variables ITS-90 Celsius temperature,  $t = t_u \times y$ , and sea pressure,  $p = p_u \times z$

$$g^W(t, p) = g_u \sum_{j=0}^7 \sum_{k=0}^6 g_{jk} y^j z^k, \quad (\text{G.1})$$

with the reduced temperature  $y = t/t_u$  and the reduced (dimensionless) pressure  $z = p/p_u$ . The unit-related constants  $t_u$ ,  $p_u$  and  $g_u$  are given in Table D4 of appendix D (e. g.  $p_u = 10^8 \text{ Pa} = 10^4 \text{ dbar}$ ). Coefficients not contained in the table below have the value  $g_{jk} = 0$ . Two of these 41 parameters ( $g_{00}$  and  $g_{10}$ ) are arbitrary and are computed from the reference-state conditions of vanishing specific entropy,  $\eta$ , and specific internal energy,  $u$ , of liquid H<sub>2</sub>O at the triple point,

$$\eta(T_t, p_t) = 0, \quad \text{and} \quad u(T_t, p_t) = 0. \quad (\text{G.2})$$

Note that the values of  $g_{00}$  and  $g_{10}$  in the table below are taken from Feistel *et al.* (2008a) and IAPWS (2009), and are not identical to the values in Feistel (2003). The modified values have been chosen to most accurately achieve the triple-point conditions (G.2) (see Feistel *et al.* (2008a) for a discussion of this point).

$j$	$k$	$g_{jk}$	$j$	$k$	$g_{jk}$
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	$-0.672\ 507\ 783\ 145\ 070 \times 10^3$			

## Appendix H: Coefficients of the saline Gibbs function for seawater of IAPWS-08

Non-zero coefficients  $g_{ijk}$  of the saline specific Gibbs energy  $g^S(S_A, t, p)$  as a function of the independent variables absolute salinity,  $S_A = S_u \times x^2$ , ITS-90 Celsius temperature,  $t = t_u \times y$ , and sea pressure,  $p = p_u \times z$ :

$$g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ g_{1,jk} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j z^k . \quad (\text{H.1})$$

The unit-related constants  $S_u$ ,  $t_u$ ,  $p_u$  and  $g_u$  are given in Table D4 of appendix D (e. g.  $p_u = 10^8 \text{ Pa} = 10^4 \text{ dbar}$ ). Coefficients with  $k > 0$  are adopted from Feistel (2003). Pure-water coefficients with  $i = 0$  do not occur in the saline contribution. The coefficients  $g_{200}$  and  $g_{210}$  were determined to exactly achieve Eqns. (2.6.7) and (2.6.8) when the pure water Gibbs function was that of IAPWS-95.

$i$	$j$	$k$	$g_{ijk}$	$i$	$j$	$k$	$g_{ijk}$	$i$	$j$	$k$	$g_{ijk}$
1	0	0	5812.81456626732	2	5	0	-21.6603240875311	3	2	2	-54.1917262517112
1	1	0	851.226734946706	4	5	0	2.49697009569508	2	3	2	-204.889641964903
2	0	0	1416.27648484197	2	6	0	2.13016970847183	2	4	2	74.7261411387560
3	0	0	-2432.14662381794	2	0	1	-3310.49154044839	2	0	3	-96.5324320107458
4	0	0	2025.80115603697	3	0	1	199.459603073901	3	0	3	68.0444942726459
5	0	0	-1091.66841042967	4	0	1	-54.7919133532887	4	0	3	-30.1755111971161
6	0	0	374.601237877840	5	0	1	36.0284195611086	2	1	3	124.687671116248
7	0	0	-48.5891069025409	2	1	1	729.116529735046	3	1	3	-29.4830643494290
2	1	0	168.072408311545	3	1	1	-175.292041186547	2	2	3	-178.314556207638
3	1	0	-493.407510141682	4	1	1	-22.6683558512829	3	2	3	25.6398487389914
4	1	0	543.835333000098	2	2	1	-860.764303783977	2	3	3	113.561697840594
5	1	0	-196.028306689776	3	2	1	383.058066002476	2	4	3	-36.4872919001588
6	1	0	36.7571622995805	2	3	1	694.244814133268	2	0	4	15.8408172766824
2	2	0	880.031352997204	3	3	1	-460.319931801257	3	0	4	-3.41251932441282
3	2	0	-43.0664675978042	2	4	1	-297.728741987187	2	1	4	-31.6569643860730
4	2	0	-68.5572509204491	3	4	1	234.565187611355	2	2	4	44.2040358308000
2	3	0	-225.267649263401	2	0	2	384.794152978599	2	3	4	-11.1282734326413
3	3	0	-10.0227370861875	3	0	2	-52.2940909281335	2	0	5	-2.62480156590992
4	3	0	49.3667694856254	4	0	2	-4.08193978912261	2	1	5	7.04658803315449
2	4	0	91.4260447751259	2	1	2	-343.956902961561	2	2	5	-7.92001547211682
3	4	0	0.875600661808945	3	1	2	83.1923927801819				
4	4	0	-17.1397577419788	2	2	2	337.409530269367				