

Notes on the function gsw_gibbs

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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, namely g, g_{S_A}, g_T, g_P as well as $g_{S_A S_A}, g_{TT}, g_{PP}, g_{P S_A}, g_{PT}$ and $g_{S_A T}$. The Gibbs function has units of J kg^{-1} and the derivatives are returned from `gsw_gibbs` consistently with S_A being in 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 (McDougall *et al.* (2010)), 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 g kg^{-1} . *Deep-Sea Res. I*, **55**, 1639-1671.
- McDougall T. J., P. M. Barker, R. Feistel and D. R. Jackett, 2011: A computationally efficient 48-term expression for the density of seawater in terms of Conservative Temperature, and related properties of seawater. submitted to *Ocean Science Discussions*.
- 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.

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 ($-22\text{ °C} < t < 374\text{ °C}$ 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 °C (specifically from $-[2.65 + (p + P_0) \times 0.0743\text{ MPa}^{-1}]\text{ °C}$ to 40 °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 m s^{-1} from Del Grosso's (1974) formula for seawater at high pressures and temperature below 5 °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, η , and specific internal energy, u , of liquid H₂O 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				