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Numerical implementation and oceanographic application of the Gibbs thermodynamic potential of seawater

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Abstract. The 2003 Gibbs thermodynamic potential function represents a very accurate, compact, consistent and comprehensive formulation of equilibrium properties of seawater. It is expressed in the International Temperature Scale ITS-90 and is fully consistent with the current scientific pure water standard, IAPWS-95. Source code examples in FORTRAN, C++ and Visual Basic are presented for the numerical implementation of the potential function and its partial derivatives, as well as for potential temperature. A collection of thermodynamic formulas and relations is given for possible applications in oceanography, from density and chemical potential over entropy and potential density to mixing heat and entropy production. For colligative properties like vapour pressure, freezing points, and for a Gibbs potential of sea ice, the equations relating the Gibbs function of seawater to those of vapour and ice are presented.

1 Introduction

Thermodynamic potential functions (also called fundamental equations of state) offer a very compact and consistent way of representing equilibrium properties of a given substance, both theoretically and numerically (Alberty, 2001). This was very successfully demonstrated by subsequent standard formulations for water and steam (Wagner and Pruß, 2002). For seawater, this method was first studied by Fofonoff (1962) and later applied numerically in three subsequently improved versions by Feistel (1993), Feistel and Hagen (1995), and Feistel (2003), expressing free enthalpy (also called Gibbs energy) as a function of pressure, temperature and practical salinity. Their mathematical structures are polynomial-like and have remained identical throughout these versions with only slight modifications of their sets of coefficients. The

structure was chosen for its simplicity in analytical partial derivatives and its numerical implementation, as discussed in Feistel (1993).

This paper provides code examples for the numerical computation in FORTRAN, C++ and Visual Basic 6, and describes their algorithms for the latter case. This code is neither very compact, nor very fast, nor definitely error-free; it is just intended as functioning example and guide for the development of individual implementations into custom program environments. Users are free to use, modify and distribute the code at their own responsibility.

The recent Gibbs potential formulation of seawater thermodynamics has a number of advantages compared to the classical “EOS80”, the 1980 Equation of State (Fofonoff and Millard, 1983), as explained in detail by Feistel (2003). One important reason is that it is fully consistent with the current international scientific standard formulation of liquid and gaseous pure water, IAPWS-95 (Wagner and Pruß, 2002), and with a new comprehensive description of ice (Feistel and Wagner, 2005). It is valid for pressures from the triple point to 100 MPa (10 000 dbar), temperatures from -2°C to 40°C , for practical salinities up to 42 psu and up to 50 psu at normal pressure.

For faster computation, as e.g. required in circulation models, modified equations of state derived from the 1995 and 2003 Gibbs potential functions have recently been constructed by McDougall et al. (2003) and Jackett et al. (2005), available from the numerical supplement of this paper.

A significant advantage compared to the usual EOS80 formulation of seawater properties is the new availability of quantities like energy, enthalpy, entropy, or chemical potential. We present in Sect. 3 a collection of important thermodynamic and oceanographic relations with brief explanations, for which the new potential function can be applied. Such formulas are often only found scattered over various articles and textbooks. In Sect. 4, the Gibbs function of seawater is used in conjunction with numerically available thermo-

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dynamic formulations for water vapour and water ice, consistent with the current one (Tillner-Roth, 1998; Wagner and Pruß, 2002; Feistel, 2003; Feistel and Wagner, 2005; Feistel et al., 2005). This way colligative properties like vapour pressure or freezing points can be computed, as well as various properties of sea ice.

2 Gibbs potential and its derivatives

Specific free enthalpy (also called Gibbs function, Gibbs energy, Gibbs free energy, or free energy in the literature) of seawater, $g(S, t, p)$, is assumed to be a polynomial-like function of the independent variables practical salinity, $S=x^2 \cdot S_U$, temperature, $t=y \cdot t_U$, and applied pressure, $p=z \cdot p_U$, as,

$$\frac{g(S, t, p)}{g_U} = (g_{100} + g_{110}y) x^2 \ln x + \sum_{j,k} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) y^j z^k \quad (1)$$

The unit specific free enthalpy is $g_U=1 \text{ J kg}^{-1}$. The reference values are defined arbitrarily as $S_U=40$ psu for salinity (PSS-78) (Lewis and Perkin, 1981; Unesco, 1981), $t_U=40^\circ\text{C}$ for temperature (ITS-90) (Blanke, 1989; Preston-Thomas, 1990), and $p_U=100 \text{ MPa}=10\,000 \text{ dbar}$ for pressure. The dimensionless variables x , y , z for salinity, temperature and pressure are not to be confused with spatial coordinates. We follow Fofonoff's (1992) proposal here and write for clarity "psu" as the unit expressing practical salinity, even though this notion is formally not recommended (Siedler, 1998). We shall use capital symbols $T=T_0+t$ for absolute temperatures, with Celsius zero point $T_0=273.15 \text{ K}$, and $P=P_0+p$ for absolute pressures, with normal atmospheric pressure $P_0=0.101325 \text{ MPa}$, in the following. The polynomial coefficients g_{ijk} are listed in Table 1. The specific dependence on salinity results from Planck's theory of ideal solutions and the Debye-Hückel theory of electrolytes (Landau and Lifschitz, 1966; Falkenhagen et al., 1971), providing a thermodynamically correct low-salinity limit of the formula.

Any Gibbs function of seawater contains four freely adjustable constants (Fofonoff, 1962), not available from measurements, which can be specified by suitable definitions of reference states. For the actual potential function, internal energy and entropy are set to zero at the pure water triple point ($S=0$ psu, $T=273.16 \text{ K}$, $P=611.657 \text{ Pa}$), and enthalpy and entropy are set to zero at the standard ocean state ($S=35$ psu, $T=273.15 \text{ K}$, $P=101325 \text{ Pa}$). This definition is consistent with the IAPWS-95 formulation for liquid water and vapour (Wagner and Pruß, 2002), and with the latest Gibbs potential of ice (Feistel and Wagner, 2005; Feistel et al., 2005). It differs, however, from the reference states used in earlier versions of the Gibbs function of seawater (Feistel, 1993; Feistel and Hagen, 1995).

There are three first derivatives of g with respect to its independent variables p , t , and S .

Density, ρ , and specific volume, v :

$$\frac{1}{\rho} = v = \left(\frac{\partial g}{\partial p} \right)_{S,t} \quad (2)$$

$$\text{with } \left(\frac{\partial g}{\partial p} \right)_{S,t} = \frac{g_U}{p_U} \sum_{j,k>0} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) \cdot k \cdot y^j z^{k-1}.$$

Specific entropy, σ :

$$\sigma = - \left(\frac{\partial g}{\partial t} \right)_{S,p} \quad (3)$$

$$\text{with } \left(\frac{\partial g}{\partial t} \right)_{S,p} =$$

$$\frac{g_U}{t_U} \left[g_{110} x^2 \ln x + \sum_{j>0,k} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) \cdot j \cdot y^{j-1} z^k \right].$$

Relative chemical potential, μ :

$$\mu = \left(\frac{\partial g}{\partial S} \right)_{t,p} \quad (4)$$

$$\text{with } \left(\frac{\partial g}{\partial S} \right)_{t,p} =$$

$$\frac{g_U}{2S_U} \left[(g_{100} + g_{110}y) (2 \ln x + 1) + \sum_{i>1,j,k} g_{ijk} \cdot i \cdot x^{i-2} y^j z^k \right].$$

Several thermodynamic coefficients require second derivatives of g .

Isothermal compressibility, K :

$$K = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_{S,t} = -\frac{(\partial^2 g / \partial p^2)_{S,t}}{(\partial g / \partial p)_{S,t}} \quad (5)$$

$$\text{with } \left(\frac{\partial^2 g}{\partial p^2} \right)_{S,t} =$$

$$\frac{g_U}{p_U^2} \sum_{j,k>1} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) \cdot k(k-1) \cdot y^j z^{k-2}.$$

Isobaric thermal expansion coefficient, α :

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial t} \right)_{S,p} = \frac{(\partial^2 g / \partial t \partial p)_S}{(\partial g / \partial p)_{S,t}} \quad (6)$$

$$\text{with } \left(\frac{\partial^2 g}{\partial p \partial t} \right)_S =$$

$$\frac{g_U}{p_U t_U} \sum_{j>0,k>0} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) \cdot j \cdot k \cdot y^{j-1} z^{k-1}.$$

Isobaric specific heat capacity, c_P :

$$c_P = T \left(\frac{\partial \sigma}{\partial t} \right)_{S,p} = \left(\frac{\partial h}{\partial t} \right)_{S,p} = -T \left(\frac{\partial^2 g}{\partial t^2} \right)_{S,p} \quad (7)$$

$$\text{with } \left(\frac{\partial^2 g}{\partial t^2} \right)_{S,p} =$$

$$\frac{g_U}{t_U^2} \sum_{j>1,k} \left(g_{0jk} + \sum_{i>1} g_{ijk} x^i \right) \cdot j(j-1) \cdot y^{j-2} z^k.$$

h is specific enthalpy, as defined below in Eq. (10).

Table 1. Coefficients g_{ijk} of specific free enthalpy $g(S, t, p)$, Eq. (1).

i	j	k	g_{ijk}	i	j	k	g_{ijk}	i	j	k	g_{ijk}
0	0	0	101.342743139672	0	5	4	6.48190668077221	2	4	2	74.726141138756
0	0	1	100015.695367145	0	6	0	-18.9843846514172	2	4	3	-36.4872919001588
0	0	2	-2544.5765420363	0	6	1	63.5113936641785	2	5	0	-17.43743842213
0	0	3	284.517778446287	0	6	2	-22.2897317140459	3	0	0	-2432.0947227047
0	0	4	-33.3146754253611	0	6	3	8.17060541818112	3	0	1	199.459603073901
0	0	5	4.20263108803084	0	7	0	3.05081646487967	3	0	2	-52.2940909281335
0	0	6	-0.546428511471039	0	7	1	-9.63108119393062	3	0	3	68.0444942726459
0	1	0	5.90578348518236	1	0	0	5813.28667992895	3	0	4	-3.41251932441282
0	1	1	-270.983805184062	1	1	0	851.295871122672	3	1	0	-493.512590658728
0	1	2	776.153611613101	2	0	0	1376.28030233939	3	1	1	-175.292041186547
0	1	3	-196.51255088122	2	0	1	-3310.49154044839	3	1	2	83.1923927801819
0	1	4	28.9796526294175	2	0	2	384.794152978599	3	1	3	-29.483064349429
0	1	5	-2.13290083518327	2	0	3	-96.5324320107458	3	2	0	-158.720177628421
0	2	0	-12357.785933039	2	0	4	15.8408172766824	3	2	1	383.058066002476
0	2	1	1455.0364540468	2	0	5	-2.62480156590992	3	2	2	-54.1917262517112
0	2	2	-756.558385769359	2	1	0	140.576997717291	3	2	3	25.6398487389914
0	2	3	273.479662323528	2	1	1	729.116529735046	3	3	0	67.5232147262047
0	2	4	-55.5604063817218	2	1	2	-343.956902961561	3	3	1	-460.319931801257
0	2	5	4.34420671917197	2	1	3	124.687671116248	3	4	0	-16.8901274896506
0	3	0	736.741204151612	2	1	4	-31.656964386073	3	4	1	234.565187611355
0	3	1	-672.50778314507	2	1	5	7.04658803315449	4	0	0	2630.93863474177
0	3	2	499.360390819152	2	2	0	929.460016974089	4	0	1	-54.7919133532887
0	3	3	-239.545330654412	2	2	1	-860.764303783977	4	0	2	-4.08193978912261
0	3	4	48.8012518593872	2	2	2	337.409530269367	4	0	3	-30.1755111971161
0	3	5	-1.66307106208905	2	2	3	-178.314556207638	4	1	0	845.15825213234
0	4	0	-148.185936433658	2	2	4	44.2040358308	4	1	1	-22.6683558512829
0	4	1	397.968445406972	2	2	5	-7.92001547211682	5	0	0	-2559.89065469719
0	4	2	-301.815380621876	2	3	0	-260.427286048143	5	0	1	36.0284195611086
0	4	3	152.196371733841	2	3	1	694.244814133268	5	1	0	-810.552561548477
0	4	4	-26.3748377232802	2	3	2	-204.889641964903	6	0	0	1695.91780114244
0	5	0	58.0259125842571	2	3	3	113.561697840594	6	1	0	506.103588839417
0	5	1	-194.618310617595	2	3	4	-11.1282734326413	7	0	0	-466.680815621115
0	5	2	120.520654902025	2	4	0	97.1562727658403	7	1	0	-129.049444012372
0	5	3	-55.2723052340152	2	4	1	-297.728741987187				

Isothermal haline contraction coefficient, β :

$$\beta = -\frac{1}{v} \left(\frac{\partial v}{\partial S} \right)_{t,p} = -\frac{(\partial^2 g / \partial p \partial S)_t}{(\partial g / \partial p)_{S,t}} \quad (8)$$

$$\text{with } \left(\frac{\partial^2 g}{\partial p \partial S} \right)_t = \frac{gU}{2p_{USU}} \sum_{i>1, j, k>0} g_{ijk} \cdot i \cdot k \cdot x^{i-2} y^j z^{k-1}.$$

The Gibbs potential and its partial derivatives as given by Eqs. (1)–(8) are available in the sample code by a function call of GSTP03(nS, nT, nP, S, Tabs, Pabs). Input parameters nS, nP and nT are the orders of partial derivatives to be carried out with respect to S , T and P . Input parameters S, Tabs, Pabs are the arguments for salinity S in psu, for absolute temperature T in K, and for absolute pressure P in Pa. Only lowest salinity derivatives are supported by the code, $nS \leq 2$ for $S > 0$ and $nS \leq 1$ for $S \geq 0$. Higher S -derivatives are hardly required in practical applications. A prior call of the procedure COEFFS03 is mandatory to initialise the array of coefficients g_{ijk} before calling GSTP03 the first time.

The function GSTP03 is a wrapper for the function Gxyz(nx, ny, nz, x, y, z) which represents the right-hand side of Eq. (1) without the leading logarithm term. Input parameters nx, ny and nz are the orders of derivatives with respect to the dimensionless variables x , y and z . A call of the pro-

cedure COEFFS03 is required to initialise the array of coefficients g_{ijk} before calling Gxyz the first time.

When the code is compiled and started, a procedure F03demo(psu, degC, dbar) is executed automatically. It creates a sample output with the input values psu=35, degC=20, dbar=2000. The corresponding piece of code in VB looks like,

```
Sub F03demo(ByVal S_psu As Double, _
            ByVal t_degC As Double, _
            ByVal p_dbar As Double)
```

```
Dim S As Double, T As Double, P As Double
```

```
Call COEFFS03
```

```
S = S_psu           'psu -> psu
T = t_degC + 273.15 'degC -> K
P = p_dbar * 10000# + 101325# 'dBar -> Pa
```

```
Debug.Print "S=", S_psu; "psu"
Debug.Print "T=", t_degC; "°C"
Debug.Print "P=", p_dbar; "dbar"
Debug.Print ""
```

```

Debug.Print "free enthalpy", GSTP03(0, 0, 0, S, T, P);
"J/kg"
Debug.Print "chem. pot.", GSTP03(1, 0, 0, S, T, P);
"J/kg psu"
Debug.Print "entropy", -GSTP03(0, 1, 0, S, T, P); "J/kgK"
Debug.Print "density", 1#/GSTP03(0, 0, 1, S, T, P);
"kg/m^3"
Debug.Print "heat capacity", -T * GSTP03(0, 2, 0, S, T,
P); "J/kgK"
Debug.Print "Ch. pot. H2O", GSTP03(0, 0, 0, S, T, P)-
S*GSTP03(1, 0, 0, S, T, P); "J/kg"
Debug.Print "therm. exp.", GSTP03(0, 1, 1, S, T,
P)/GSTP03(0, 0, 1, S, T, P); "1/K"
Debug.Print "compressib.", -GSTP03(0, 0, 2, S, T,
P)/GSTP03(0, 0, 1, S, T, P); "1/Pa"
Debug.Print "lapse rate", -GSTP03(0, 1, 1, S, T,
P)/GSTP03(0, 2, 0, S, T, P); "K/Pa"
Debug.Print "pot. temp.", PotTemp(S-psu, t.degC,
p_dbar); "°C"

End Sub

```

Only 8-byte floating points should be used ("Double"), indicated here by "#" in VB. The produced data should look like the following check value printout:

```

S=35 psu
T=20°C
P=2000 dbar

```

```

free enthalpy 16583.1806714797 J/kg
chem. pot. 60.0099366692805 J/kg psu
entropy 276.780886190056 J/kgK
density 1033.32930433584 kg/m^3
heat capacity 3951.77837149032 J/kgK
Ch. pot. H2O 14482.8328880549 J/kg
therm. exp. 2.78522499678412E-04 1/K
compressib. 4.06129773355324E-10 1/Pa
lapse rate 1.99948825300137E-08 K/Pa
pot. temp. 19.617987328589 °C

```

The reader may modify the input values as desired in the startup routine. In the case of Visual Basic, this procedure is Form.Load, and the output goes to the immediate (Debug) window of the VB developer environment.

The FORTRAN and C++ program versions were obtained as later translations of the original VB code and have a quite analogous subroutine structure and functionality.

The numerical supplement further includes a MATLAB implementation by J. H. Reissmann of the Gibbs function and quantities derived from it, as described in the accompanying Ocean Science Discussion.

3 Related oceanographic quantities

Many additional properties of seawater can be computed by combinations of the derivatives given in the former section. A first group is that of thermodynamic functions available from g by mathematical so-called Legendre transforms (Alberty, 2001).

Specific free energy (also called Helmholtz energy or Helmholtz free energy), f :

$$f = g - Pv = g - P \cdot \left(\frac{\partial g}{\partial p} \right)_{S,t} \quad (9)$$

Specific enthalpy, h :

$$h = g + T\sigma = g - T \cdot \left(\frac{\partial g}{\partial t} \right)_{S,p} \quad (10)$$

Specific internal energy, e :

$$e = g + T\sigma - Pv = g - T \cdot \left(\frac{\partial g}{\partial t} \right)_{S,p} - P \cdot \left(\frac{\partial g}{\partial p} \right)_{S,t} \quad (11)$$

Chemical potential of water in seawater, μ^W :

$$\mu^W = g - S\mu = g - S \cdot \left(\frac{\partial g}{\partial S} \right)_{t,p} \quad (12)$$

A second group is that of adiabatic quantities, describing isentropic processes, i.e. without heat exchange.

Adiabatic lapse rate, Γ :

$$\Gamma = \left(\frac{\partial t}{\partial p} \right)_{S,\sigma} = - \frac{(\partial^2 g / \partial t \partial p)_S}{(\partial^2 g / \partial t^2)_{S,p}} = \frac{\alpha T v}{c_P} \quad (13)$$

Adiabatic compressibility, κ , and sound speed, U :

$$\kappa = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_{S,\sigma} = \frac{(\partial^2 g / \partial t \partial p)_S^2 - (\partial^2 g / \partial t^2)_{S,p} (\partial^2 g / \partial p^2)_{S,t}}{(\partial g / \partial p)_{S,t} (\partial^2 g / \partial t^2)_{S,p}} \quad (14)$$

$$\kappa = \frac{v}{U^2} = K - \frac{\alpha^2 T v}{c_P} = K - \alpha \Gamma$$

Adiabatic haline contraction coefficient, β_σ :

$$\beta_\sigma = - \frac{1}{v} \left(\frac{\partial v}{\partial S} \right)_{\sigma,p} = \frac{(\partial^2 g / \partial S \partial t)_p (\partial^2 g / \partial t \partial p)_S - (\partial^2 g / \partial t^2)_{S,p} (\partial^2 g / \partial S \partial p)_t}{(\partial g / \partial p)_{S,t} (\partial^2 g / \partial t^2)_{S,p}} \quad (15)$$

Closely related to the adiabatic quantities are the so-called “potential” ones, which can be directly computed from entropy (Bradshaw, 1978; Feistel, 1993; Feistel and Hagen, 1994; McDougall et al. 2003; McDougall and Feistel, 2003). They are obtained by formally replacing in-situ temperature t and in-situ pressure p by potential temperature θ and reference pressure p_r . They describe the property a water parcel would take if moved from in-situ pressure p to reference pressure p_r without exchange of matter and heat. By definition of θ , specific entropy is equal to “potential” specific entropy.

Potential temperature, $\theta(S, t, p, p_r)$, is implicitly given by

$$\sigma(S, t, p) = \sigma(S, \theta, p_r). \quad (16)$$

This equation can be solved numerically by Newton iteration and avoids Runge-Kutta integration (Fofonoff, 1985). An example for the algorithm is provided in the accompanying code by the function PotTemp(Spsu, tdegC, pdBar, prefdBar), which uses the input parameters S , t , p , p_r and returns potential temperature θ in °C as solution of Eq. (16). Once potential temperature $\theta(S, t, p, p_r)$ is known, other related “potential” quantities can be computed straight forward.

Potential density, ρ_θ , is defined as

$$\rho_\theta(S, t, p, p_r) = \rho(S, \theta, p_r). \quad (17)$$

For a given profile at geographic position (x, y) , the vertical derivative of potential density provides the Brunt-Väisälä frequency, N , describing vertical stability of the water column (z pointing in opposite direction of gravity acceleration, grav)

$$N^2 = -\frac{\text{grav}}{\rho} \left(\frac{\partial \rho_\theta}{\partial z} \right)_{x,y} = -\frac{\text{grav}}{\rho} \left(\frac{\partial \rho}{\partial z} \right)_{x,y} - \frac{\text{grav}^2}{U^2} \quad (18)$$

Potential enthalpy, h_θ ,

$$h_\theta(S, t, p, p_r) = h(S, \theta, p_r) \quad (19)$$

is supposed to benefit from the combination of conservative behaviour of potential temperature during adiabatic excursions, Eq. (16), and conservation of enthalpy during isobaric mixing, Eq. (29). For a more detailed discussion of potential enthalpy, see McDougall (2003), McDougall and Feistel (2003).

The hydrostatic equilibrium pressure stratification in an external gravity field with acceleration grav in opposite z -direction is given by the solution of the differential equation

$$\frac{1}{\rho} \frac{\partial p}{\partial z} = -\text{grav} \quad (20)$$

If grav is a constant, and the vertical profiles $S(p)$ of salinity and $t(p)$ of temperature are known e.g. from a CTD cast,

the solution of Eq. (20) is usually obtained by separation of variables and numerical integration over p , as,

$$\int_{p_0}^p v \{S(p), t(p), p\} dp = -\text{grav} \cdot (z - z_0). \quad (21)$$

In numerical models with fixed spatial grids, however, $S(z)$ and $t(z)$ may be known and $p(z)$ wanted (Dewar et al., 1998). Then, the variables p and z of the nonlinear differential Eq. (20) for $p(z)$ can no longer be analytically separated, and standard numerical procedures must be employed for its solution, like Runge-Kutta, or successive iteration. The latter one then reads for the iteration step $(i+1)$,

$$p_{i+1}(z) = -\text{grav} \int_{z_0}^z \rho \{S(z), t(z), p_i(z)\} dz, \quad (22)$$

starting from some trivial initial pressure profile, say, $p_0(z) = -\rho_0 \cdot \text{grav} \cdot (z - z_0)$. Error estimates of such procedures are essentially numerical rather than physical questions. But, in case of Eq. (22), the first iterate can often be considered an already sufficient approximation due to the small compressibility of seawater. Taking as usual the size of the next iteration step as an estimate for the residual error, $\Delta p(z)$, we have

$$\Delta p(z) \approx p_2 - p_1 \approx -\text{grav} \int_{z_0}^z \left(\frac{\partial \rho}{\partial p} \right)_{S,t} [p_1(z') - p_0(z')] dz'. \quad (23)$$

The compressibility term depends only weakly on depth and can be taken in front of the integral for the estimate. For standard seawater, its value is $(\partial \rho / \partial p)_{S,t} \approx 0.476 \times 10^{-6} \text{ s}^2 / \text{m}^2$.

For important special cases, however, Eq. (20) can be solved analytically in compact form, namely if vertical stratification is ruled by proper thermodynamic conditions instead of arbitrary ones coined by its particular oceanographic history. If both temperature t and salinity S are constant over the water column, as in thermodynamic equilibrium, we can use Eq. (2) and obtain upon integration

$$g \{S, t, p(z)\} - g \{S, t, p_0\} = -\text{grav} \cdot (z - z_0) \quad (24)$$

i.e. free enthalpy g is a linear function of depth.

If, however, salinity S and entropy σ (or potential temperature) are constant over the water column, as e.g. in the cases of winter convection or wind mixing, we can use the relation $v = (\partial h / \partial p)_{S,\sigma}$ to find

$$h \{S, \sigma, p(z)\} - h \{S, \sigma, p_0\} = -\text{grav} \cdot (z - z_0). \quad (25)$$

In this case, enthalpy h grows linear with depth, Eq. (10). These equations implicitly define pressure as function of

depth, $p(z)$, and can be solved numerically by Newton iteration at any given z without integrating over the entire column as in case of Eq. (21). As an alternative method to Eq. (21), for more realistic oceanic situations, Eqs. (24) or (25) may serve as first approximations which can be improved by perturbation calculations with respect to the profile's vertical property fluctuations.

The total energy per mass of a water parcel moving with advection speed \mathbf{u} is specific internal energy e , Eq. (11), plus kinetic plus potential energy in the gravity field:

$$e_{tot} = e + u^2/2 + \text{grav} \cdot z \quad (26)$$

If dissipative processes are neglected, energy conservation in the ocean is expressed locally by the continuity equation (τ is used for time here)

$$\frac{\partial}{\partial \tau} (\rho e_{tot}) + \text{div} \left\{ \rho \mathbf{u} \left(h + u^2/2 + \text{grav} \cdot z \right) \right\} = 0 \quad (27)$$

In a stationary ocean, using mass conservation as $\text{div}(\rho \mathbf{u}) = 0$, this equation reduces to

$$\mathbf{u} \nabla b = 0 \quad (28)$$

i.e. the Bernoulli function $b \equiv h + u^2/2 + \text{grav} \cdot z = e_{tot} + pv$ is always conserved along the advection trajectories in time-independent flows (Landau and Lifschitz, 1974; Gill, 1982; Feistel, 1993; Saunders, 1995).

In the practically interesting f -plane approximation of geostrophic currents, this equation is expressed as

$$\frac{\partial p}{\partial x} \cdot \frac{\partial b}{\partial y} - \frac{\partial p}{\partial y} \cdot \frac{\partial b}{\partial x} = \frac{\partial (p, b)}{\partial (x, y)} = 0 \quad (29)$$

This vanishing Jacobian implies that the Bernoulli function b is a function of pressure alone on any given depth horizon z , i.e. $b(x, y, z) = b(p, z)$. In other words, in this geostrophic special case b is conserved along the horizontal isobars, which of course are identical with the trajectories.

If a given parcel of seawater is initially inhomogeneous in salinity and/or temperature, and during the progressing mixing process it remains at constant pressure p and without exchange of heat or salt with its surroundings, then its total enthalpy is conserved (Fofonoff, 1962, 1992). Denoting by brackets (...) the average over the parcel's mass elements, we thus find, comparing the inhomogeneous initial with the final homogeneous state,

$$h(\langle S \rangle, \langle t \rangle + \Delta t, p) = \langle h(S, t, p) \rangle \quad (30)$$

This equation permits the numerical calculation of excess temperature Δt upon isobaric mixing, e.g. by Newton iteration. The corresponding excess of specific volume, Δv , is then given by

$$v(\langle S \rangle, \langle t \rangle + \Delta t, p) + \Delta v = \langle v(S, t, p) \rangle \quad (31)$$

If heat is assumed to be exchanged as necessary to keep the parcel's average temperature constant, we can get released mixing heat Δh from

$$h(\langle S \rangle, \langle t \rangle, p) + \Delta h = \langle h(S, t, p) \rangle \quad (32)$$

This formula is commonly applied to mixing processes with isothermal initial state, $t = \langle t \rangle$. The values of Δt and Δh do not have definite signs for seawater mixing, i.e. either cooling or warming can occur depending on the values of S, t, p .

Internal energy is conserved due to the First Law if the mixing process is conducted isochorically (isopycnally), and without exchange of heat and salt. The corresponding balance

$$e(\langle S \rangle, \langle t \rangle + \Delta t, p + \Delta p) = \langle e(S, t, p) \rangle \quad (33)$$

together with supposed constant specific volume

$$v(\langle S \rangle, \langle t \rangle + \Delta t, p + \Delta p) = \langle v(S, t, p) \rangle \quad (34)$$

represent the two equations required to determine the changes caused in both pressure and temperature, Δp and Δt . From these, nonnegative entropy production $\Delta \sigma$ of the isopycnal mixing process can be computed, obeying the Second Law,

$$\Delta \sigma = \sigma(\langle S \rangle, \langle t \rangle + \Delta t, p + \Delta p) - \langle \sigma(S, t, p) \rangle \geq 0. \quad (35)$$

For easier thermodynamic treatment, isopycnal mixing is formally thought here to be a two-step process, first mixing at constant volume without exchange of heat and work, and then compression for pressure adjustment without exchange of heat. The increased entropy value (Eq. 35) remains unaltered in the second step when the mixed parcel is displaced adiabatically to its neutral buoyancy position, i.e. another depth level where its new density and pressure equals that of the ambient water column (cabbeling).

4 Phase equilibria

Equilibria between seawater and other aqueous phases are controlled by equal chemical potentials of water in both. It is important to use for these computations only formulae with mutually consistent reference points, which for the IAPWS-95 pure water standard is zero entropy and zero internal energy of liquid water at the triple point (Wagner and Pruß, 2002). The same reference point is valid for the 2003 seawater formulation, but not for the earlier ones.

Osmotic pressure of seawater, $\pi(S, t, p)$ is the excess pressure of seawater in equilibrium with pure water behind a membrane impenetrable for salt. It is implicitly given by

$$\mu^W(S, t, p + \pi) = \mu^W(0, t, p) \quad (36)$$

Vapour pressure, $p_V(S, t, p)$, above seawater under pressure p , is implicitly given by

$$\mu^W(S, t, p) = \mu^{Vapour}(t, p_V) \equiv g^{Vapour}(t, p_V) \quad (37)$$

Additionally to the chemical potential of water in seawater, μ^W , Eq. (12), the chemical potential of water vapour, $\mu^{Vapour} = g^{Vapour}$, is required here. It is available from the IAPWS-95 formulation for the fluid water phases (Wagner and Pruß, 2002).

Freezing point temperature of seawater, $t_f(S, p)$, is implicitly given by

$$\mu^W(S, t_f, p) = \mu^{Ice}(t_f, p) \equiv g^{Ice}(t_f, p). \quad (38)$$

The chemical potential of ice, $\mu^{Ice} = g^{Ice}$, is required here additionally. A low-pressure Gibbs potential of ice is given by Feistel (2003), and a high-pressure formulation by Tillner-Roth (1998). However, the new and significantly improved high-pressure version by Feistel and Wagner (2005) is recommended for use here instead, which is available as source code from a later issue of this journal (Feistel et al., 2005).

Sea ice is considered a mixture of ice and seawater, which is usually called brine then, at thermodynamic equilibrium. Its Gibbs potential function, g^{SI} , is given as a function of temperature t , pressure p , and bulk salinity s by,

$$g^{SI}(s, t, p) = w \cdot g(S, t, p) + (1 - w) \cdot g^{Ice}(T, P) \quad (39)$$

(Feistel and Hagen, 1998). The salt of sea ice is entirely contained in the liquid brine phase, so bulk salinity s is related to brine salinity S by the mass fraction w of brine, $s = w \cdot S$. Brine salinity, and therefore the mass ratio of the liquid and solid fractions, follows from the equilibrium condition that the chemical potentials of water in brine, μ^W , and of ice, μ^{Ice} , must be equal,

$$\begin{aligned} \mu^{Ice}(T, P) &\equiv g^{Ice}(T, P) = \\ \mu^W(S, t, p) &= g(S, t, p) - S \cdot \left(\frac{\partial g}{\partial S} \right)_{t,p}. \end{aligned} \quad (40)$$

Depending on the pair of independent variables chosen, this equation implicitly defines either brine salinity $S_B(t, p)$ of sea ice, or its melting pressure $P_m(S, t)$, or freezing temperature of seawater $t_f(S, p)$. Assuming brine salinity to be known this way, we can express Eq. (39) in the form

$$g^{SI}(s, t, p) = g^{Ice}(T, P) + s \cdot \mu^B(t, p), \quad (41)$$

where the relative chemical potential of brine, $\mu^B = \left(\frac{\partial g}{\partial S} \right)_{t,p}$ has to be taken at brine salinity $S = S_B(t, p)$. Thus, the Gibbs function of sea ice is linear in bulk salinity with coefficients being functions of pressure and temperature, describing both its separate components, ice and brine.

Thermodynamic properties of sea ice can be obtained from Eq. (41) by partial derivatives in the usual way, e.g. specific entropy $\sigma^{SI} = - \left(\frac{\partial g^{SI}}{\partial t} \right)_{s,p}$, specific enthalpy $h^{SI} = g^{SI} + T \sigma^{SI}$, or specific volume $v^{SI} = \left(\frac{\partial g^{SI}}{\partial p} \right)_{s,t}$. While density, enthalpy or entropy are strictly additive in the contributions of ice and brine, coefficients like heat capacity

or compressibility include significant additional parts due to phase equilibrium shifts, like latent heat, dilution heat, or haline contraction, which make the properties of sea ice so distinct from those of either ice or seawater alone. Vapour pressure over sea ice equals the one over pure ice at same temperature and pressure, as follows from Eq. (41). Thermodynamic functions for sea ice obtained by the Gibbs function formalism are discussed in more detail by Feistel and Hagen (1998).

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