# **APPENDIX 5. PROPERTIES OF SEA WATER**

#### **A5.1. The Equation of State**

It is necessary to know the equation of state for the ocean very accurately to determine stability properties, particularly in the deep ocean. The equation of state defined by the Joint Panel on Oceanographic Tables and Standards (UNESCO, 1981) fits available measurements with a standard error of 3.5 ppm for pressure up to 1000 bar, for temperatures between freezing and  $40^{\circ}$ C, and for salinities between 0 and 42 (Millero *et al.*, 1980; Millero and Poisson, 1981). The density  $\rho$  (kg m<sup>-3</sup>) is expressed in terms of pressure  $p$  (bar), temperature  $t$  ( $\degree$ C), and practical salinity *S*. The last quantity is defined in such a way (Dauphinee, 1980) that its value (in practical salinity units or psu) is very close to the old value expressed in parts per thousand  $\binom{0}{00}$  or ppt). Its relation to previously defined measures of salinity is given by Lewis and Perkin (1981).

The equation for  $\rho$  is obtained in a sequence of steps. First, the density  $\rho_w$  of pure water (*S* = 0) is given by

$$
\rho_{\rm w} = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2 + 1.001685 \times 10^{-4}t^3
$$
  
- 1.120083 × 10<sup>-6</sup>t<sup>4</sup> + 6.536332 × 10<sup>-9</sup>t<sup>5</sup> [A5.1]

Second, the density at one standard atmosphere (effectively  $p = 0$ ) is given by

$$
\rho(S, t, 0) = \rho_w + S(0.824493 - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4) + S^{3/2}(-5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2) + 4.8314 \times 10^{-4}S^2
$$
 [A5.2]

Finally, the density at pressure *p* is given by

$$
\rho(S, t, p) = \frac{\rho(S, t, 0)}{1 - p/K(S, t, p)}
$$
 [A5.3]

where *K* is the secant bulk modulus. The pure water value  $K_w$  is given by

$$
K_{\rm w} = 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 - 5.155288 \times 10^{-5}t^4 \quad [A5.4]
$$

The value at one standard atmosphere  $(p = 0)$  is given by

$$
K(S, t, 0) = K_{w} + S(54.6746 - 0.603459t + 1.09987 \times 10^{-2}t^{2} - 6.1670 \times 10^{-5}t^{3})
$$
  
+ 
$$
S^{3/2}(7.944 \times 10^{-2} + 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^{2})
$$
 [A5.5]

and the value at pressure *p* by

$$
K(S, t, p) = K(S, t, 0) + p(3.239908 + 1.43713 \times 10^{-3}t + 1.16092 \times 10^{-4}t^{2}
$$
  
- 5.77905 × 10<sup>-7</sup>t<sup>3</sup>) + pS(2.2838 × 10<sup>-3</sup> – 1.0981 × 10<sup>-5</sup>t – 1.6078 × 10<sup>-6</sup>t<sup>2</sup>)  
+ 1.91075 × 10<sup>-4</sup>pS<sup>3/2</sup> + p<sup>2</sup>(8.50935 × 10<sup>-5</sup> – 6.12293 × 10<sup>-6</sup>t + 5.2787 × 10<sup>-8</sup>t<sup>2</sup>)  
+ p<sup>2</sup>S( - 9.9348 × 10<sup>-7</sup> + 2.0816 × 10<sup>-8</sup>t + 9.1697 × 10<sup>-10</sup>t<sup>2</sup>) [A5.6]



**Figure A5.1** The ranges of temperature *t* (in °C) and salinity *S* for 98% of the ocean as a function of depth and the corresponding ranges of density  $\sigma$  and potential density  $\sigma_\theta$  (From Bryan and Cox (1972).)

Values for checking the formula are  $\rho(0, 5, 0) = 999.96675$ ,  $\rho(35, 5, 0) = 1027.67547$ , and  $\rho(35, 25, 1000) = 1062.53817.$ 

Since  $\rho$  is always close to 1000 kg m<sup>-3</sup>, values quoted are usually those of the difference ( $\rho$  – 1000) in kg m<sup>-3</sup> as is done in **Table A5.1**. The table is constructed so that values can be calculated for 98% of the ocean (see **Figure A5.1**). The maximum errors in density on straight linear interpolation are  $0.013 \text{ kg m}^{-3}$ for both temperature and pressure interpolation and only 0.006 for salinity interpolation in the range of salinities between 30 and 40. The error when combining all types of interpolation for the 98% range of values is less than  $0.03 \text{ kg m}^{-3}$ .

### **A5.2 Other Quantities Related to Density**

Older versions of the equation of state usually gave formulas not for calculating the absolute density  $\rho$ , but for the *specific gravity*  $\rho/\rho_m$ , where  $\rho_m$  is the maximum density of pure water. Since this is always close to unity, a quantity called  $\sigma$  was defined by

$$
1000\left(\frac{\rho}{\rho_m} - 1\right) = \frac{1000}{\rho_m}(\rho - \rho_m)
$$
 [A5.7]

Since the value of  $\rho_m$  is

$$
\rho_{\rm m} = 999.975 \quad \text{kg m}^{-3} \tag{A5.8}
$$

it follows that  $\sigma$ , as defined above, is related to the ( $\rho - 1000$ ) values by

$$
\sigma = (\rho - 1000) + 0.025 \tag{A5.9}
$$

i.e., 0.025 must be added to the values of ( $\rho - 1000$ ) on the table to obtain the old  $\sigma$  value. The notation  $\sigma_{\tau}$  (sigma-tau) was used for the value of  $\sigma$  calculated at zero pressure, and  $\sigma_{\theta}$  (sigma theta) for the quantity corresponding to potential density. Another quantity commonly used in oceanography is the specific volume (or steric) *anomaly*  $\delta$  defined by

$$
\delta = \nu_{s}(S, t, p) - \nu_{s}(35, 0, p) \tag{A5.10}
$$

and usually reported in units of  $10^{-8}$  m<sup>3</sup> kg<sup>-1</sup>.

#### **A5.3. Expansion Coef**\**cients**

The thermal expansion coefficient  $\alpha$  is given in **Table A5.1** in units of  $10^{-7}K^{-1}$  along with its *S* derivative. The maximum error from pressure interpolation is two units, that from temperature interpolation is three units, and that for salinity interpolation  $(30 < S < 40)$  is two units plus a possible round-off error of two units. The salinity expansion coefficient  $\beta$  can be calculated by using the given values of  $\partial \rho / \partial S$ .

#### **A5.4. Speci**\**c Heat**

The specific heat at surface pressure is given by Millero *et al.* (1973) and can be calculated in two stages. First, the value in  $\lfloor \log^{-1} K^{-1} \rfloor$  for fresh water is given by

$$
c_p(0, t, 0) = 4217.4 - 3.720283t + 0.1412855t^2 - 2.654387 \times 10^{-3}t^3 + 2.093236 \times 10^{-5}t^4
$$
\n[A5.11]

Second,

$$
c_p(S, t, 0) = c_p(0, t, 0) + S(-7.6444 + 0.107276t - 1.3839 \times 10^{-3}t^2) + S^{3/2}(0.17709 - 4.0772 \times 10^{-3}t + 5.3539 \times 10^{-5}t^2)
$$
 [A5.12]

The formula can be checked against the result  $c_p(40, 40, 0) = 3981.050$ . The standard deviation of the algorithm fit is 0.074. Values at nonzero pressures can be calculated by using eqn  $[As.13]$  and the equation of state.

$$
\left(\frac{\partial c_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 v_s}{\partial T^2}\right)_p \tag{A5.13}
$$

The values in **Table A5.1** are based on the above formula and a polynomial fit for higher pressures derived from the equation of state by N. P. Fofonoff. The intrinsic interpolation errors in the table are 0.4, 0.1, and  $0.3$  J kg<sup>-1</sup> K<sup>-1</sup> for pressure, temperature, and salinity interpolation, respectively, and there are additional obvious round-off errors.

#### **A5.5. Potential Temperature**

The *adiabatic lapse rate*  $\Gamma$  is given by

$$
\Gamma = \frac{g\alpha T}{c_p} \tag{A5.14}
$$

and therefore can be calculated from the above formulas. The definition of potential temperature

$$
\frac{\theta}{T} = \left(\frac{p_r}{p}\right)^{\kappa} \tag{A5.15}
$$

where  $p_r$  is a reference pressure level (usually 1 bar) and  $\kappa = (\gamma - 1)/\gamma$  where  $\gamma$  is the ratio of specific heats at constant pressure and at constant volume, can then be used to obtain  $\theta$ . The following algorithm, however, was derived by Bryden (1973), using experimental compressibility data, to give  $\theta$  ( $\degree$ C) as a function of salinity *S*, temperature  $t$ <sup>( $\degree$ </sup>C), and pressure *p* (bar) for 30 < *S* < 40, 2 < *t* < 30, and 0 < *p* < 1000:

$$
\theta(S, t, p) = t - p(3.6504 \times 10^{-4} + 8.3198 \times 10^{-5}t - 5.4065 \times 10^{-7}t^2 \n+ 4.0274 \times 10^{-9}t^3) - p(S - 35)(1.7439 \times 10^{-5} \n- 2.9778 \times 10^{-7}t) - p^2(8.9309 \times 10^{-7} - 3.1628 \times 10^{-8}t \n+ 2.1987 \times 10^{-10}t^2) + 4.1057 \times 10^{-9}(S - 35)p^2 \n- p^3(-1.6056 \times 10^{-10} + 5.0484 \times 10^{-12}t)
$$
\n(S. 16)



Figure A5.2 A profile of buoyancy frequency N in the ocean. [From the North Atlantic near 28°N, 70°W, courtesy of Dr. R. C. Millard.]

A check value is  $\theta$ (25, 10, 1000) = 8.4678516, and the standard deviation of Bryden's polynomial fit was 0.001 K. Values in **Table A5.1** are given millidegrees, the intrinsic interpolation errors being 2, 0.3, and 0 millidegrees for pressure, temperature, and salinity interpolation, respectively (**Figure A5.2**).

#### **A5.6. Speed of Sound**

The speed of sound  $c_s$  can be calculated from the equation of state, using eqn [A5.17]

$$
c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_{\theta, s} \tag{A5.17}
$$

Values given in **Table A5.1** use algorithms derived by Chen and Millero (1977) on the basis of direct measurements. The formula applies for  $0 < S < 40$ ,  $0 < t < 40$ ,  $0 < p < 1000$  with a standard deviation of  $0.19 \,\mathrm{m\,s^{-1}}$ . Values in the table are given in meters per second, the intrinsic interpolation errors being 0.05, 0.10, and  $0.04 \text{ m s}^{-1}$  for pressure, temperature, and salinity interpolation, respectively.

#### **A5.7. Freezing Point of Sea Water**

The freezing point  $t_f$  of sea water ( ${}^{\circ}$ C) is given (Millero, 1978) by

$$
t_{\rm f}(S,p) = -0.0575S + 1.710523 \times 10^{-3} S^{3/2} - 2.154996 \times 10^{-4} S^2 - 7.53 \times 10^{-3} p \qquad [A5.18]
$$

The formula fits measurements to an accuracy of  $\pm 0.004$ K.



**Table A5.1**

## **Further Reading**

- Bryan K and Cox MD (1972) An approximate equation of state for numerical models of ocean circulation. *Journal of Physical Oceanography* 2: 510-514.
- Bryden HL (1973) New polynomials for thermal expansion, adiabatic temperature gradient and potential temperature gradient of sea water. *Deep Sea Research* 20: 401-408.
- Chen C-T and Millero FJ (1977) Speed of sound in sea-water at high pressures. *Journal of the Acoustical Society of* America 62: 1129-1135.
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- Gill AE (1982) *Atmosphere*}*Ocean Dynamics*, International Geophysics Series Volume 30. San Diego: Academic Press.

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- Millero FJ, Chen C-T, Bradshaw A and Schleicher K (1980) A new high pressure equation of state for seawater. *Deep Sea Research 27A: 255-264.*
- Millero FJ, Perron G and Desnoyers JE (1973) Heat capacity of seawater solutions from 5 to 25 $\degree$ C and 0.5 to 22% chlorinity. *Journal of Geophysical Research* 78: 4499-4507.
- UNESCO (1981) *Tenth Report of the Joint Panel on Oceanographic Tables and Standards*, UNESCO Technical papers in Marine Science No. 36. Paris: UNESCO.