

## 2.9 Chemical potentials

As for any two-component thermodynamic system, the Gibbs energy,  $G$ , of a seawater sample containing mass of water  $m_W$  and mass of salt  $m_S$  at temperature  $t$  and pressure  $p$  can be written in the form (Landau and Lifshitz (1959), Alberty (2001), Feistel (2008))

$$G(m_W, m_S, t, p) = m_W \mu^W + m_S \mu^S \quad (2.9.1)$$

where the chemical potentials of water in seawater  $\mu^W$  and of salt in seawater  $\mu^S$  are defined by the partial derivatives

$$\mu^W = \left. \frac{\partial G}{\partial m_W} \right|_{m_S, T, p}, \quad \text{and} \quad \mu^S = \left. \frac{\partial G}{\partial m_S} \right|_{m_W, T, p}. \quad (2.9.2)$$

Identifying absolute salinity with the mass fraction of salt dissolved in seawater,  $S_A = m_S / (m_W + m_S)$  (Millero *et al.* (2008a)), the specific Gibbs energy  $g$  is given by

$$g(S_A, t, p) = \frac{G}{m_W + m_S} = (1 - S_A) \mu^W + S_A \mu^S = \mu^W + S_A (\mu^S - \mu^W). \quad (2.9.3)$$

Note that this expression for  $g$  as the sum of a water part and a saline part is not the same as the pure water and the saline split in Eqn. (2.6.1) ( $\mu^W$  is the chemical potential of water in seawater; it does not correspond to a pure water sample as  $g^W$  does in Eqn. (2.6.1)). This Gibbs energy  $g$  is used as the thermodynamic potential function (Gibbs function) for seawater. The above three equations can be used to write expressions for  $\mu^W$  and  $\mu^S$  in terms of the Gibbs function  $g$  of seawater as

$$\mu^W = \left. \frac{\partial [(m_W + m_S) g]}{\partial m_W} \right|_{m_S, T, p} = g + (m_W + m_S) \left. \frac{\partial g}{\partial S_A} \right|_{T, p} \frac{\partial S_A}{\partial m_W} \bigg|_{m_S} = g - S_A \left. \frac{\partial g}{\partial S_A} \right|_{T, p} \quad (2.9.4)$$

and for the chemical potential of salt in seawater,

$$\mu^S = \left. \frac{\partial [(m_W + m_S) g]}{\partial m_S} \right|_{m_W, T, p} = g + (m_W + m_S) \left. \frac{\partial g}{\partial S_A} \right|_{T, p} \frac{\partial S_A}{\partial m_S} \bigg|_{m_W} = g + (1 - S_A) \left. \frac{\partial g}{\partial S_A} \right|_{T, p} \quad (2.9.5)$$

The relative chemical potential  $\mu$  (commonly called the “chemical potential of seawater”) follows from (2.9.4) and (2.9.5) as

$$\mu = \mu^S - \mu^W = \left. \frac{\partial g}{\partial S_A} \right|_{T, p}, \quad (2.9.6)$$

and describes the change in the Gibbs energy of a parcel of seawater of fixed mass if a small amount of water is replaced by salt at constant temperature and pressure. Also, from the fundamental thermodynamic relation (Eqn. (A.7.1) in appendix A.7) it follows that the chemical potential of seawater  $\mu$  describes the change of enthalpy  $dh$  if at constant pressure and entropy, a small mass fraction of water is replaced by salt,  $dS_A$ . Equations (2.9.4) – (2.9.6) serve to define the three chemical potentials in terms of the Gibbs function  $g$  of seawater. Note that the weights of the sums that appear in Eqns. (2.9.1) – (2.9.5) are strictly the mass fractions of salt and of pure water in seawater, so that for a seawater sample of anomalous composition these mass fractions would be more accurately given in terms of  $S_A^{\text{soln}}$  than by  $S_A \equiv S_A^{\text{dens}}$ . In this regard, the Gibbs energy in Eqn. (2.9.1) should strictly be the weighted sum of the chemical potentials of all the constituents in seawater. However, practically speaking, the vapour pressure, the latent heat and the freezing temperature are all rather weakly dependent on salinity, and hence the use of  $S_A$  in this section is recommended.

Note that both  $\mu$  and  $\mu^S$  have singularities at  $S_A = 0 \text{ g kg}^{-1}$  while  $\mu^W$  is well-behaved there.

The SIA computer software library (appendix M) predominantly uses basic SI units, so that  $S_A$  has units of  $\text{kg kg}^{-1}$  and  $g, \mu, \mu^S$  and  $\mu^W$  all have units of  $\text{J kg}^{-1}$ . In the GSW Oceanographic Toolbox (appendix N)  $S_A$  has units of  $\text{g kg}^{-1}$  while  $\mu, \mu^S$  and  $\mu^W$  all have units of  $\text{J g}^{-1}$ . This adoption of oceanographic (i.e. non-basic-SI) units for  $S_A$  means that special care is needed in evaluating equations such as (2.9.3) and (2.9.5) where in the term  $(1 - S_A)$  it is clear that  $S_A$  must have units of  $\text{kg kg}^{-1}$ . The adoption of non-basic-SI units is common in oceanography, but often causes some difficulties such as this. To be specific, the use of oceanographic units for Absolute Salinity (such as in the GSW Oceanographic Toolbox) means that the above equations (2.9.4) – (2.9.5) are evaluated as

$$\mu^W = \frac{g}{R} - \frac{S_A}{R} \frac{\partial g}{\partial S_A} \bigg|_{T,p}, \quad \text{and} \quad \mu^S = \frac{g}{R} + \left(1 - \frac{S_A}{R}\right) \frac{\partial g}{\partial S_A} \bigg|_{T,p} \quad (2.9.7)$$

where the constant  $R$  is defined as  $R = 1000 \text{ g kg}^{-1}$ , while Eqn. (2.9.6) is unchanged.