

# Calculating density of water in geochemical lake stratification models

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## Web Appendix A

### A.1. Converting molar units into molal units

Mixing conserves molal units, whereas molar units are not strictly conserved when two volumes are mixed. Hence using molal units would be more advisable, though some numerical models may use molar units to include field data of chemical concentrations in a convenient way. For these models, a conversion of molar units into molal units may be required, especially when simulating salt lakes:

Starting from a solution of several components indexed  $i$ , we find the concentration  $c_n$  of one particular solute  $n$  of  $b_n$  [mol kg<sup>-1</sup>] in a solution of the volume  $V$ :

$$c_n = \frac{b_n \cdot m_w}{V} = \frac{b_n \cdot m_w}{m_w / \rho_w + m_w \sum b_i V_i} = \frac{b_n}{1 / \rho_w + \sum b_i V_i} \quad (A1)$$

where  $V_i$  represents partial molal volumes in [L mol<sup>-1</sup>] We solve the equation for  $b_n$ :

$$b_n = c_n \cdot (1 / \rho_w + \sum b_i V_i) \quad (A2)$$

and use an iterative approach. In the first step, all  $b_i$  on the right side are approximated by  $c_i / \rho_w$ . In most cases, e.g. for freshwater lakes, the first iteration provides very accurate values for molal concentrations:

$$b_n \approx \frac{c_n}{\rho_w} (1 + \sum c_i V_i).$$

Only for extremely high concentrations, more than one iteration may be required.

### A.2. Evaluating conventional molal volumes for separate ion species

We start from partial molal volumes of salts published in Millero's book (2001; Table 3.19). We select all chlorides (Table A1). For better legibility, we replace the index  $i$  at molal volumes with an explicit inclusion of the respective solute as a mathematical argument. Under the assumption of separable contributions of cation and anion, we find for hydrochloric acid:

$$V(HCl) = V(H^+) + V(Cl^-) \quad (A3)$$

A corresponding relation is valid for any other salt listed in Table A1. Hence the difference

$$V(NaCl) - V(HCl) = V(Na^+) - V(H^+) \quad (A4)$$

For practical reasons, we define this result as the conventional partial molal volume of the sodium ion  $\bar{V}(Na^+)$ , which is included in Table A1. In general, the conventional molal volume of an ion X of charge Z is defined as

$$\bar{V}(X^Z) = V(X^Z) - ZV(H^+) \quad (A5)$$

For example, for Mg<sup>2+</sup>, a cation of double charge  $Z = 2$ , we find

$$V(MgCl_2) - 2V(HCl) = V(Mg^{2+}) - 2V(H^+) = \bar{V}(Mg^{2+}) \quad (A6)$$

Anions are approached in a similar way: We make an excerpt of Millero's table (2001; Table 3.19) of all sodium salts (Table A2). Also here, we assume that the contribution of cation and anion can be separated:

$$\bar{V}(F^-) = V(F^-) + V(H^+) = V(NaF) - V(Na^+) + V(H^+) = V(NaF) - \bar{V}(Na^+) \quad (A7)$$

For an anion X of charge Z ( $Z < 0$ ), the conventional partial molal volume can be calculated.

$$\begin{aligned} \bar{V}(X^Z) &= V(X^Z) - ZV(H^+) = V(Na_{-Z}X) + ZV(Na^+) - ZV(H^+) \\ &= V(Na_{-Z}X) + Z\bar{V}(Na^+) \end{aligned} \quad (A8)$$

The results for the anions most relevant in limnic waters are listed in Table A2.

This evaluation of conventional partial molal volumes can be done for any ionic strength. Therefore, also the higher order coefficients can be transferred in the same way. As a consequence, we find a value  $\bar{V}$  at infinite dilution, and the coefficients  $\bar{A}$  and  $\bar{B}$  for higher ionic strengths. The numbers we find for  $I = 0$  differ slightly from the values tabled by Millero (1969), generally in the order of 1%. Hence this is not really a concern for the accuracy of the approach.

Not necessarily do sodium salts or chlorides need to be used to evaluate the conventional molal volumes. Also other salts could be used, just starting the calculation from a common

acid. Interestingly, the results are not very sensitive to the chosen path. However, it must be stated that some pairs of ions show a particular interaction (as known for  $\text{MgSO}_4$ ). The accuracy for determining partial molal volumes can be limited by such effects.

### A.3. Converting partial molal volumes into conventional partial molal volumes

Partial molal volumes at 25°C have been published by Millero (1969; Table 4). As they do not follow the convention of referring all partial volumes to  $\text{H}^+$ , they cannot directly be used for the volume calculation. However, subtracting the  $\text{H}^+$  values as in Eq. A3, we find conventional partial molal volumes as listed in Table A3. Coefficients for temperature dependence and ionic strength dependence were not given. However, the table complements the substances listed in Table 1. Therefore substances already listed in Table 1 are not included in Table A3.

Millero's work (1969; Table 4) also includes values for ionic strength of seawater. These values lie  $1.4 \pm 0.8 \text{ mL mol}^{-1}$  lower for each charge of the ion than the values for freshwater, and may serve as a rough idea for molal volumes in salt lake conditions. Only in very few cases, values listed in Table A3 contribute a decisive part to density. In most cases, the constant values  $\bar{\Phi}$  should suffice.

### A.4. Converting mass permille (mass parts per thousand) into molal units

The composition of sea water was inferred from Millero's book (2001; Table 4.2), where the contribution of the major components are listed relative to chlorinity. Requiring the concentration at a practical salinity of  $S = 35$ , the corresponding chlorinity is calculated from

$$Cl = (S - 0.030) / 1.8050 \quad (\text{A9})$$

Hence for given salinity, the mass  $g_n$  [g] of dissolved substances  $n$  is known from Millero (2001; Table 4.2). Then the amount of substance in moles is calculated by division through molar mass  $M_n$ . Molal concentrations are yielded by referring to the mass of water ( $\text{H}_2\text{O}$ ) contained in a 1 kg sample of lake water. In addition (converting g of solutes into kg)

$$b_n = \frac{g_n / M_n}{(1000 \text{ g} - \sum_i g_i) / 1000} = \frac{1000 \cdot g_n}{M_n (1000 \text{ g} - \sum_i g_i)} \quad (\text{A10})$$

where  $\sum_i g_i$  is the sum of the masses of all solutes and  $M_n$  is the molar mass of one particular ion  $n$ .

**Table A1.** Coefficients for calculating partial molal volumes of chlorides (from Millero 2001; Table 3.19) and conventional molal volumes of the corresponding cations.

Salt	$\Phi_i$	$A_i$	$B_i$	cation	$\bar{\Phi}_i$	$\bar{A}_i$	$\bar{B}_i$
Symbol	$I = 0, T = 25^\circ\text{C}$	coeff.	coeff.	symbol	$I = 0, T = 25^\circ\text{C}$	coeff.	coeff.
	mL/mol	mL kg <sup>1/2</sup> /mol <sup>3/2</sup>	mL · kg/mol <sup>2</sup>		mL/mol	mL kg <sup>1/2</sup> /mol <sup>3/2</sup>	mL · kg/mol <sup>2</sup>
HCl	17.854	1.460	-0.307	$\text{H}^+$	0	0	0
LiCl	16.961	1.700	-0.198	$\text{Li}^+$	-0.893	0.240	0.109
NaCl	16.613	1.811	0.094	$\text{Na}^+$	-1.241	0.351	0.401
KCl	26.850	1.839	0.087	$\text{K}^+$	8.996	0.379	0.394
RbCl	31.940	1.818	0.191	$\text{Rb}^+$	14.086	0.358	0.498
CsCl	39.166	1.843	0.162	$\text{Cs}^+$	21.312	0.383	0.469
$\text{NH}_4\text{Cl}$	35.815	1.717	-0.147	$\text{NH}_4^+$	17.961	0.257	0.160
$\text{MgCl}_2$	14.522	3.155	0.106	$\text{Mg}^{2+}$	-21.186	0.235	0.720
$\text{CaCl}_2$	17.858	3.611	-0.117	$\text{Ca}^{2+}$	-17.850	0.691	0.497
$\text{SrCl}_2$	17.975	3.941	-0.038	$\text{Sr}^{2+}$	-17.733	1.021	0.576
$\text{BaCl}_2$	23.208	4.576	-0.360	$\text{Ba}^{2+}$	-12.500	1.656	0.254

Values in this table are given in the usual units as they appear in the literature for easier reading and better comparison with the scientific literature. For the use in equations, they need to be multiplied by the unity factor 1000 mL/L, respectively, so that units cancel each other properly.

**Table A2.** Partial molal volumes of sodium salts (from Millero 2001; Table 3.19) and conventional molal volumes of the corresponding anions.

Salt symbol	$\Phi$	A	B	anion symbol	$\bar{\Phi}$	$\bar{A}$	$\bar{B}$
	I = 0, T = 25°C mL/mol	coeff. mL kg <sup>1/2</sup> /mol <sup>3/2</sup>	coeff. mL · kg/mol <sup>2</sup>		I = 0, T = 25°C mL/mol	coeff. mL kg <sup>1/2</sup> /mol <sup>3/2</sup>	coeff. mL · kg/mol <sup>2</sup>
NaF	-2.371	1.839	0.561	F <sup>-</sup>	-1.130	1.488	0.160
NaCl	16.613	1.811	0.094	Cl <sup>-</sup>	17.854	1.460	-0.307
NaBr	23.504	1.689	0.076	Br <sup>-</sup>	24.745	1.338	-0.325
NaI	35.018	1.593	-0.126	I <sup>-</sup>	36.259	1.242	-0.527
NaOH	-5.246	2.048	0.984	OH <sup>-</sup>	-4.005	1.697	0.583
NaNO <sub>3</sub>	27.805	2.586	-0.292	NO <sub>3</sub> <sup>-</sup>	29.046	2.235	-0.693
NaHCO <sub>3</sub>	23.118	3.662	-0.115	HCO <sub>3</sub> <sup>-</sup>	24.359	3.311	-0.516
Na <sub>2</sub> CO <sub>3</sub>	-6.195	7.710	-0.383	CO <sub>3</sub> <sup>2-</sup>	-3.713	7.008	-1.185
Na <sub>2</sub> SO <sub>4</sub>	11.559	6.750	0.087	SO <sub>4</sub> <sup>2-</sup>	14.041	6.048	-0.715

Values in this table are given in the usual units as they appear in the literature for easier reading and better comparison with the scientific literature. For the use in equations, they need to be multiplied by the unity factor 1000 mL/L, respectively, so that units cancel each other properly.

**Table A3.** Conventional partial molal volumes at 25°C and dilute conditions of less abundant solutes in limnic waters (Enns et al. 1965\*, Tiepel and Gubbins 1972†, Kritchevsky and Ilinskaya 1945‡, Lo Surdo and Millero 1980§).

ion	$\bar{\Phi}$	ion	$\bar{\Phi}$	ion	$\bar{\Phi}$	gas	$\bar{\Phi}$	ion	$\bar{\Phi}$	ion	$\bar{\Phi}$
	mL/mol		mL/mol		mL/mol		mL/mol		mL/mol		mL/mol
Cr <sup>3+</sup>	-39.6	Be <sup>2+</sup>	-21.6	Li <sup>+</sup>	-0.87	He	29.7 <sup>a</sup>	Br <sup>-</sup>	24.71	S <sup>2-</sup>	-9.2
Yb <sup>3+</sup>	-43.9	Co <sup>2+</sup>	-25.8 <sup>e</sup>	Rb <sup>+</sup>	14.08	Ar	32.2 <sup>a</sup>	I <sup>-</sup>	36.03	SeO <sub>4</sub> <sup>2-</sup>	21.0
Er <sup>3+</sup>	-42.3	Ni <sup>2+</sup>	-29.5 <sup>e</sup>	Cs <sup>+</sup>	21.35	H <sub>2</sub>	25.2 <sup>b</sup>	B(OH) <sub>4</sub> <sup>-</sup>	21.84	PtCl <sub>6</sub> <sup>2-</sup>	145.4
Ho <sup>3+</sup>	-41.8	Cu <sup>2+</sup>	-25.5 <sup>e</sup>			CO	36 <sup>c</sup>	NO <sub>2</sub> <sup>-</sup>	25.0	HPO <sub>4</sub> <sup>2-</sup>	8.0
Dy <sup>3+</sup>	-40.8	Zn <sup>2+</sup>	-26.6 <sup>e</sup>			C <sub>2</sub> H <sub>6</sub>	53.3 <sup>b</sup>	MnO <sub>4</sub> <sup>-</sup>	42.7	AsO <sub>4</sub> <sup>2-</sup>	-11.2
Tb <sup>3+</sup>	-40.3	Sr <sup>2+</sup>	-17.86					ClO <sub>3</sub> <sup>-</sup>	36.5	CrO <sub>4</sub> <sup>2-</sup>	19.7
Gd <sup>3+</sup>	-40.4	Cd <sup>2+</sup>	-14.2 <sup>e</sup>					BrO <sub>3</sub> <sup>-</sup>	35.3	WO <sub>4</sub> <sup>2-</sup>	25.7
Sm <sup>3+</sup>	-42.3	Ba <sup>2+</sup>	-12.49					IO <sub>3</sub> <sup>-</sup>	24.4	MoO <sub>4</sub> <sup>2-</sup>	28.9
Nd <sup>3+</sup>	-43.3	Hg <sup>2+</sup>	-19.7					ClO <sub>4</sub> <sup>-</sup>	46.1		
Pr <sup>3+</sup>	-42.5	Pb <sup>2+</sup>	-15.5					HSO <sub>4</sub> <sup>-</sup>	28.5		
La <sup>3+</sup>	-39.1							VO <sub>3</sub> <sup>-</sup>	27.0		
								H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	29.1		
								HSeO <sub>4</sub> <sup>-</sup>	31.0		
								H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	39.4		
								HSO <sub>3</sub> <sup>-</sup>	108.9		
								SH <sup>-</sup>	19.2		
								CN <sup>-</sup>	20.9		
								N <sub>3</sub> <sup>-</sup>	25.0		
								SCN <sup>-</sup>	35.6		
								HCOO <sup>-</sup>	25.6		
								CH <sub>3</sub> COO <sup>-</sup>	40.4		

Values in this table are given in the usual units as they appear in the literature for easier reading and better comparison with the scientific literature. For the use in equations, they need to be multiplied by the unity factor 1000 g/kg or 1000 mL/L, respectively, so that units cancel each other properly.