



## The Equation of State of Lakes

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**Abstract.** In recent years, a number of workers have studied the stability of deep lakes such as Lake Tanganyika, Lake Baikal and Lake Malawi. In this paper, the methods that can be used to determine the effect that the components of lakes have on the equation of state are examined. The PVT properties of Lakes have been determined by using apparent molal volume data for the major ionic components of the lake. The estimated PVT properties (densities, expansibility and compressibilities) of the lakes are found to be in good agreement with the PVT properties (P) of seawater diluted to the same salinity. This is similar to earlier work that showed that the PVT properties of rivers and estuarine waters could also be estimated from the properties of seawater.

The measured densities of Lake Tanganyika were found to be in good agreement ( $\pm 2 \times 10^{-6}$  g cm<sup>-3</sup>) with the values estimated from partial molal properties and the values of seawater at the same total salinity ( $S_T = 0.568\text{‰}$ ). The increase in the densities of Lake Tanganyika waters increased due to changes in the composition of the waters. The measured increase in the measured density ( $45 \times 10^{-6}$  g cm<sup>-3</sup>) is in good agreement ( $46 \times 10^{-6}$  g cm<sup>-3</sup>) with the values calculated for the increase in Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Si(OH)<sub>4</sub>.

Methods are described that can be used to determine the conductivity salinity of lakes using the equations developed for seawater. By combining these relationships with apparent molal volume data, one can relate the PVT properties of the lake to those of seawater.

**Key words:** lakes, density, compressibility, expansibility, conductivity, stability, pvt properties

### Introduction

Recently a number of workers have examined the properties of Lakes (Edmond, 1974; Chen and Millero, 1977; Effler et al., 1986; Falkner et al., 1991; Mcmanus et al., 1992; Wüest, 1996; Callender and Granina, 1997). Much of the interest has been in determining the stability of the lakes (Chen and Millero, 1977; Mcmanus et al., 1992; Wüest, 1996). To determine the stability of these lakes, it is necessary to know the density of the waters as a function of temperature, pressure, and salinity or composition. The salinity of the lakes can be determined from the known composition of the lake or from measurements of some physical property like conductivity or density. The physical properties of a natural water are related to the ionic interactions of the major components (Lepple and Millero, 1971; Millero, 1973a,b, 1974; Millero and Lepple, 1973; Millero et al., 1973a,b). In our earlier studies, it has been shown that the physical chemical properties of seawater and other natural waters at low ionic strength could be estimated by accounting for

these ionic interactions using a simple additivity relationship (Young and Smith, 1954). The estimated properties have been shown to be in good agreement with the measured values. We have also demonstrated that the PVT properties of rivers and estuarine waters (Millero, 1975; Millero et al., 1976a) can be estimated from the values of seawater (Millero and Poisson, 1981; Millero et al., 1980) diluted to the same total salinity ( $S_T$ ).<sup>\*</sup> This is because the changes in the properties of dilute solutions are independent of the specific salt added.

The purpose of the present paper is to use these same methods to estimate the PVT properties of Lake Malawi, Lake Baikal and Lake Tanganyika. We will demonstrate that the physical chemical properties of most lakes can be determined from equations for seawater at the same total salinity. Methods that can be used to relate the conductivity of seawater to the lake are also discussed. This allows one to use the equation of state of seawater at the same total salinity to examine the stability of lakes. One also can determine other physical chemical properties of the lakes in a similar manner.

### 1. Methods of Estimating the Properties of Multi-component Electrolyte Solutions

A thorough description of the methods of estimating the properties of multi component electrolyte solutions has been given elsewhere (Millero, 1974), and will only be outlined here. The basic quantity used to examine the physical properties of a solution is the apparent equivalent quantity ( $\Phi$ ) defined by

$$\Phi = (P - P^0)/e_T, \quad (1)$$

where  $P$  is the property of the solution,  $P^0$  is the property of pure water and  $e_T$  is the total equivalents (eq  $L^{-1}$ ) in the solution ( $e_T = \frac{1}{2} \sum Z_i M_i$ , where  $Z_i$  is the charge and  $M_i$  is the molarity (mol  $L^{-1}$ ) of ion  $i$ ). By rearranging this equation, we have

$$P = P^0 + \Phi e_T, \quad (2)$$

and the property of the solution is equal to the property of pure water plus a contribution related to the product of the apparent molal property and the number

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<sup>\*</sup> The true or absolute salinity ( $S_T$ ) is defined as the grams of inorganic salts in a kilogram of solution. It is a unitless quantity and is reported in parts per thousand (‰, or ppt) or g/kg. The value of  $S_T$  can be estimated from composition data for a natural water. The values can also be estimated (Millero, 1984) from density measurements using the equation of state for seawater (Millero and Poisson, 1981). For seawater,  $S_T$  can be determined from the Practical Salinity Scale ( $S_T = 1.005 S$ ; Millero, 1984; Millero, 1996) where the factor 1.005 is estimated from the composition of average seawater (Millero, 1996). The Practical Salinity Scale (UNESCO, 1981) is also a unitless quantity and has been defined so that the symbol ‰, or ppt is not needed. The Practical Salinity ( $S$ ) is determined from the ratio of the conductivity of the sample relative to a KCl solution or a standard seawater solution of known conductance. By definition, seawater with a salinity of 35.000 has a conductivity ratio of 1.0000 with a solution of KCl (32.4356 g  $kg^{-1}$ ) at 15°C.

of equivalents in the solution. By using a simple additivity relationship, it can be shown that the apparent equivalent property ( $\Phi$ ) of a mixed electrolyte is equal to the sum of the weighted apparent equivalent properties of the salts ( $\phi_{MX}$ ) by

$$\Phi = \sum_M \sum_X E_M E_X \phi_{MX}, \quad (3)$$

where  $E_i$  is the equivalent fraction of the ionic constituent  $i$  ( $E_i = e_i/e_T = Z_i M_i/e_T$ ) and  $\phi_{MX}$  is the apparent equivalent property of  $MX$  at the total ionic strength of the solution. The values of  $\phi_{MX}$  at a given ionic strength ( $I$ ) are determined from the physical properties (density, compressibility, heat capacity, etc) of the electrolytes that make up the solution. The values of  $\phi_{MX}$  properties are normally fitted to functions of molality in some empirical form. The input needed to determine the values of  $\Phi$  is the concentration of the ionic components of the solution ( $M$  and  $X$ ). For the mixture containing the major seasalts, equation (3) becomes

$$\Phi = E_{\text{Na}} E_{\text{Cl}} \phi_{\text{NaCl}} + E_{\text{Na}} E_{\text{SO}_4} \phi_{\text{Na}_2\text{SO}_4} + E_{\text{Mg}} E_{\text{Cl}} \phi_{\text{MgCl}_2} + E_{\text{Mg}} E_{\text{SO}_4} \phi_{\text{MgSO}_4}. \quad (4)$$

Recently I have constructed computer programs (Millero, 1999) that can be used to determine the density and compressibility of electrolyte mixtures from 0 to 50°C and  $I = 0$  to 6 m containing the major components of seawater (Na, Mg, Ca, K, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, Br, CO<sub>3</sub>, B(OH)<sub>4</sub>, and F). For more concentrated solutions one has to consider the excess properties of mixing which are available for the major sea salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>) (Millero, 1999).

For the dilute solutions considered in this paper these terms are not important and one can use properties of the ionic components of the solution to estimate the apparent molal property of the solution

$$\Phi = \sum_i E_i \phi_i, \quad (5)$$

where the ionic values  $\phi_i$  can be estimated from equations of the form

$$\phi_i = \phi_i^0 + S_V I_V^{1/2} + B_i I_V, \quad (6)$$

where  $S_V$  is the Debye-Hückel limiting slope (0.934 and 1.868, respectively, for monovalent and divalent ions),  $B_i$  is empirical constant and  $I_V$  is the volume ionic strength (Millero, 1973a,b; 1974; 1975; 1999). The values of  $\phi_i$  and  $B_i$  used in this equation have been fitted to quadratic functions of temperature ( $t$ , °C)

$$\phi_i = A + Bt + Ct^2, \quad (7)$$

$$B_i = A' + B't + C't^2, \quad (8)$$

and the coefficients ( $A$ ,  $B$ ,  $C$  etc.) for volumes are given in the appendix. These ionic values are determined from the  $\text{Cl}^-$  salts for cations and  $\text{Na}^+$  salts for anions. It neglects the interactions of ions of opposite sign (e.g.,  $\text{Mg}^{2+}$ - $\text{SO}_4^{2-}$ ) that are important at higher ionic strengths. For the density of a solution the apparent molal volume for the mixture is given by (Millero, 1974)

$$\Phi_V = 1000(\rho_0 - \rho)/e_T\rho_0 + M_T/\rho_0, \quad (9)$$

where  $\rho$  is the density of the solution and  $\rho_0$  is the density of water and  $M_T$  is the mean equivalent weight of the ionic components ( $i$ ),  $M_T = \frac{1}{2} \sum_i (E_i M_i)$  where  $M_i$  is the equivalent weight. The rearrangement of this equation gives

$$1000(\rho - \rho_0) = (M_T - \Phi_V \rho_0)e_T \quad (10)$$

and the substitution of equations (5) and (6) lead to

$$1000(\rho - \rho_0) = AI_V + BI_V^{1.5} + CI_V^2, \quad (11)$$

where  $A = k[M_T - \sum_i E_i \phi_V^0(i)]$ ,  $B = -k\rho_0 \sum_i E_i S_V(i)$  and  $C = -k\rho_0 \sum_i E_i B_i$ . The constant  $k = e_T/I_V$  relates the total equivalent molarity and the total ionic strength of the solution. For dilute solutions the  $C$  term is quite small and the density is largely related to the sum of the apparent equivalent volumes of the ions in pure water,  $\phi_V^0(i)$  since the limiting slope,  $S_V$ , is constant for ions of the same charge.

### Seawater

Before we can estimate the properties of Lakes, it is useful to examine the reliability of the method in determining the relative density ( $\rho - \rho_0$ ) and adiabatic compressibility ( $\beta - \beta_0$ ) of seawater. The values of  $\rho_0$  and  $\beta_0$  for water are taken from Kell (1967) and Kell (1970), respectively. The differences in the calculated and measured density and adiabatic compressibility of seawater at 25°C and  $S = 5$  to 40 are given in Table 1. The estimated densities agree with the measured values (Millero and Poisson, 1981) to within  $13 \times 10^{-6} \text{ g cm}^{-3}$ . The differences at higher salinities are greater than at low salinities where the ionic values of the apparent molal properties are affected by ion-ion interactions of all the components of the solution. The differences are small at salinities below  $S = 5$ , which includes most lakes and rivers. The estimated compressibilities agree with the measured values (Millero, 1982) to within  $0.7 \times 10^{-6} \text{ bar}^{-1}$ . Again the deviations are higher at the higher salinities.

### Lake Baikal Waters

The composition of Lake Baikal waters (Falkner et al., 1991) is given in Table 2. The total salinity of the lake is 0.0963‰. A comparison of the calculated relative

Table I. The comparison of the measured and calculated relative densities and adiabatic compressibilities of seawater at 25°C.<sup>a</sup>

Salinity	$10^3(\rho - \rho_0)$ g cm <sup>-3</sup>			$10^6(\beta - \beta_0)$ bar <sup>-1</sup>		
	Meas <sup>a</sup>	Calc	$\Delta$	Meas <sup>b</sup>	Calc <sup>c</sup>	$\Delta$
2.5	1.885	1.887	-0.002	-0.249	-0.249	0.000
5	3.764	3.770	-0.006	-0.494	-0.493	-0.001
10	7.511	7.521	-0.010	-0.974	-0.973	-0.001
15	11.257	11.268	-0.011	-1.446	-1.444	-0.002
20	15.005	15.018	-0.013	-1.910	-1.907	-0.003
25	18.761	18.774	-0.013	-2.368	-2.364	-0.004
30	22.525	22.537	-0.012	-2.820	-2.816	-0.004
35	26.298	26.311	-0.013	-3.267	-3.262	-0.005
40	30.083	30.095	-0.012	-3.710	-3.703	-0.007

<sup>a</sup> The measured densities were determined from the seawater equation of state (Millero and Poisson, 1981). The density of water (0.997045 g cm<sup>-3</sup>) is taken from Kell (1967).

<sup>b</sup> The measured adiabatic compressibilities were determined from the seawater values (Millero, 1989). The adiabatic compressibility of water ( $44.773 \times 10^{-6}$  bar<sup>-1</sup>) is taken from Kell (1970) and Millero (1982).

<sup>c</sup> The estimated adiabatic compressibilities have been made with a computer program that uses sound speed measurements on the major seasalts from Millero et al. (1977; 1982a).

densities ( $\rho - \rho_0$ ) and adiabatic compressibilities ( $\beta - \beta_0$ ) determined from molal volume data with the values from seawater measurements at  $S_T = 0.0963\text{‰}$  are given in Table 3. The calculated densities and adiabatic compressibilities are in good agreement with the seawater measurement (within  $7 \times 10^{-6}$  g cm<sup>-3</sup> in  $\rho$  and  $6 \times 10^{-6}$  bar<sup>-1</sup> in  $\beta$ ).

### Lake Malawi Waters

The composition of Lake Malawi waters (Wüest et al., 1996) is given in Table 2. The salinity of the lake is 0.205‰. A comparison of the calculated relative densities ( $\rho - \rho_0$ ) and adiabatic compressibilities ( $\beta - \beta_0$ ) determined from molal volume data with the values calculated from seawater at  $S_T = 0.205\text{‰}$  are given in Table 4. The calculated densities and adiabatic compressibilities are in good agreement with the seawater measurement (within  $12 \times 10^{-6}$  g cm<sup>-3</sup> in  $\rho$  and  $7 \times 10^{-6}$  bar<sup>-1</sup> in  $\beta$ ).

Table II. The composition of the major components of Lake Baikal<sup>a</sup>, Lake Malawi<sup>b</sup>, and Lake Tanganyika<sup>c</sup>.

Ion	Molecular weight	Lake Baikal		Lake Malawi		Lake Tanganyika	
		mM	Salinity ‰	mM	Salinity ‰	mM	Salinity ‰
Na <sup>+</sup>	22.9898	0.155	0.0036	0.875	0.0212	2.72	0.063
Mg <sup>2+</sup>	39.1020	0.126	0.0009	0.3075	0.0120	1.65	0.040
Ca <sup>2+</sup>	24.3050	0.402	0.0032	0.4525	0.011	0.27	0.011
K <sup>+</sup>	40.0800	0.0241	0.0161	0.16	0.0064	0.82	0.032
Cl <sup>-</sup>	35.4530	0.0124	0.0004	0.14	0.0050	0.62	0.022
SO <sub>4</sub> <sup>2-</sup>	96.0576	0.0574	0.0055	0.0775	0.0074	0.06	0.003
HCO <sub>3</sub> <sup>-</sup>	61.0172	1.093	0.0667	2.309	0.1422	6.52	0.398
CO <sub>3</sub> <sup>2-</sup>	60.0092			0.0055	0.0003		
$S_T =$			0.0963		0.205		0.568
$e_T =$		1.228		2.585		7.32	

<sup>a</sup> Falkner et al. (1991).

<sup>b</sup> The values for Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and K<sup>+</sup> were taken from Edmond (1974) and the values of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were taken from Degens et al. (1991).

<sup>c</sup> Wüest et al. (1994).

Table III. Comparison of the measured and calculated relative densities and adiabatic compressibilities of Lake Baikal as a function of temperature.

Temp. °	10 <sup>3</sup> ( $\rho - \rho_0$ ) g cm <sup>-3</sup>			10 <sup>6</sup> ( $\beta - \beta_0$ ) bar <sup>-1</sup>		
	Meas <sup>a</sup>	Calc	$\Delta$	Meas <sup>b</sup>	Calc <sup>c</sup>	$\Delta$
0	0.079	0.075	0.004	6.066	6.072	-0.006
5	0.077	0.076	0.001	4.383	4.385	-0.002
10	0.076	0.076	0.000	2.972	2.974	-0.002
15	0.075	0.077	-0.002	1.792	1.794	-0.002
20	0.074	0.078	-0.004	0.807	0.809	-0.002
25	0.073	0.078	-0.005	-0.009	-0.008	-0.001
30	0.072	0.078	-0.006	-0.682	-0.681	-0.001
35	0.072	0.079	-0.007	-1.228	-1.228	-0.000
40	0.072	0.079	-0.007	-1.663	-1.663	-0.000

<sup>a</sup> The measured densities were determined from the seawater equation of state (Millero and Poisson, 1981) at  $S_T = 0.0963\text{‰}$ .

<sup>b</sup> The measured adiabatic compressibilities were determined from the seawater values (Millero, 1982) at  $S_T = 0.0963\text{‰}$ .

Table IV. Comparison of the measured and calculated relative densities and adiabatic compressibilities of Lake Malawi as a function of temperature.

Temp. °C	$10^3(\rho - \rho_0)$ g cm <sup>-3</sup>			$10^6(\beta - \beta_0)$ bar <sup>-1</sup>		
	Meas <sup>a</sup>	Calc	$\Delta$	Meas <sup>b</sup>	Calc <sup>c</sup>	$\Delta$
0	0.169	0.157	0.012	6.051	6.058	-0.007
5	0.165	0.158	0.007	4.369	4.372	-0.003
10	0.162	0.158	0.004	2.959	2.961	-0.002
15	0.159	0.159	0.000	1.780	1.782	-0.002
20	0.157	0.160	-0.003	0.796	0.798	-0.002
25	0.155	0.160	-0.005	-0.020	-0.019	-0.001
30	0.154	0.161	-0.007	-0.692	-0.692	0.000
35	0.153	0.161	-0.008	-1.238	-1.238	0.000
40	0.152	0.162	-0.010	-1.673	-1.673	0.000

<sup>a</sup> The measured densities were determined from the seawater equation of state (Millero and Poisson, 1981) at  $S_T = 0.205\text{‰}$ .

<sup>b</sup> The measured adiabatic compressibilities were determined from the seawater values (Millero, 1982) at  $S_T = 0.205\text{‰}$ .

## Lake Tanganyika Waters

The composition of Lake Tanganyika waters (Degens et al., 1971; Edmond, 1974) is given in Table 2. The salinity of the lake is  $0.568\text{‰}$ . A comparison of the calculated relative densities ( $\rho - \rho_0$ ) and adiabatic compressibilities ( $\beta - \beta_0$ ) determined from molal volume data with the values calculated from seawater at  $S = 0.568\text{‰}$  are given in Table 5. The calculated densities and adiabatic compressibilities are in good agreement with the seawater measurement (within  $2 \times 10^{-6}$  g cm<sup>-3</sup> in  $\rho$  and  $6 \times 10^{-6}$  bar<sup>-1</sup> in  $\beta$ ).

## 2. Direct Measurements of Density of Lake Tanganyika Waters

The model calculations shown above for the densities and compressibilities demonstrate that the physical properties of lakes are the same within experimental error to those of seawater diluted to the same salinity. Direct measurements are needed to confirm these calculations. This can be done from the density measurements we have made on Lake Tanganyika waters collected in 1973 and 1975. The measurements were made at 25°C with a vibrating densimeter that is described elsewhere (Picker et al., 1974). The measured densities of the lake waters are given in Table 6. The 1975 results are shown plotted versus depth in Figure 1. The surface waters have a relative density ( $\rho - \rho_0$ ) =  $430 \times 10^{-6}$  g cm<sup>-3</sup> while the waters below 400 meters have a relative density ( $\rho - \rho_0$ ) =  $475 \times 10^{-6}$  g cm<sup>-3</sup>. The calculated relative density of  $430 \times 10^{-6}$  g cm<sup>-3</sup> determined from the composition data given in Table 2 are in excellent agreement with the measured value for the surface waters. The

Table V. Comparison of the measured and calculated relative densities and adiabatic compressibilities of Lake Tanganyika as a function of temperature.

Temp. °C	$10^3(\rho - \rho_0) \text{ g cm}^{-3}$			$10^6(\beta - \beta_0) \text{ bar}^{-1}$		
	Meas <sup>a</sup>	Calc	$\Delta$	Meas <sup>b</sup>	Calc <sup>c</sup>	$\Delta$
0	0.466	0.464	0.002	50.839	50.845	-0.006
5	0.456	0.456	0.000	49.156	49.158	-0.002
10	0.447	0.448	-0.001	47.745	47.747	-0.002
15	0.440	0.442	-0.002	46.565	46.567	-0.002
20	0.434	0.436	-0.002	45.580	45.582	-0.002
25	0.430	0.431	-0.001	44.764	44.765	-0.001
30	0.426	0.428	-0.002	44.091	44.092	-0.001
35	0.423	0.425	-0.002	43.545	43.545	-0.000
40	0.421	0.423	-0.002	43.110	43.110	-0.000

<sup>a</sup> The measured densities were determined from the seawater equation of state (Millero and Poisson, 1981) at  $S_T = 0.568\text{‰}$ .

<sup>b</sup> The measured adiabatic compressibilities were determined from the seawater values (Millero, 1982) at  $S_T = 0.568\text{‰}$ .

composition data of Edmond (1974) shows an increase in the deep waters for  $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SiO}_2$  in the deep waters. The increase in the density due to these increases in the concentrations of these constituents can be estimated from the equation

$$10^3(\rho - \rho^0) = [\text{MW} - \phi_V^0 \rho_0] \Delta M, \quad (12)$$

where MW is the molecular weight,  $\phi_V^0$  is the apparent molal volume of the solute and  $\Delta M$  is the increase in the molar concentration. The calculated increase in the density due to the increase in concentration of various solutes is shown in Table 7. The calculated increase in density of  $46 \times 10^{-6} \text{ g cm}^{-3}$  is in excellent agreement with the measured increase of  $45 \times 10^{-6} \text{ g cm}^{-3}$ .

The salinities of the Lake waters as a function of depth (Table 6) have been determined from the density measurements using the equation of state of seawater (Millero and Poisson, 1981). The least squares best fit of the total salinity as a function of depth ( $z$ ) gives (std. dev. 0.005)

$$S_T(\text{‰}) = 0.578 + 1.28305 \times 10^{-1}z - 7.32604 \times 10^{-5}z^2. \quad (13)$$

To determine the stability of Lake Tanganyika waters, this increase in salinity with depth must be considered (Chen and Millero, 1977).

### 3. Calculation of Salinity

The densities and compressibilities for the lakes shown above support the contention that the PVT properties of most lakes are similar to seawater diluted to



Table VI. The Relative Densities of Lake Tanganyika waters at 25°C.

Year	Station	Depth (m)	$(\rho - \rho_0)10^3$	$S_T$ (‰) <sup>a</sup>
1975	7	250	469	0.620
	7	400	470	0.621
	7	700	472	0.624
	7	1220	478	0.632
	10	100	443	0.586
	10	150	450	0.595
	10	200	456	0.603
	10	250	464	0.613
	10	300	465	0.615
	10	400	470	0.621
	10	500	470	0.621
	11	5	432	0.571
	11	35	433	0.572
	11	60	445	0.589
	11	600	475	0.628
	11	700	479	0.633
	11	800	478	0.632
	11	900	474	0.627
	11	1000	476	0.629
	11	1100	473	0.625
	11	1200	475	0.628
	11	1300	474	0.627
	2	5	430	0.569
	2	447	466	0.616
	3	12	429	0.567
	3	359	469	0.620
	4	5	433	0.572
	4	290	468	0.619

<sup>a</sup> The values of total salinity  $S_T$  (‰) were determined from the density measurements using the equation of state for seawater (Millero and Poisson, 1981).

the same total salinity. The measured densities for Lake Tanganyika are in good agreement with the calculated values from the composition of the waters (Degens et al., 1971; Edmond, 1977). The salinities determined from density measurements give a true representation of the total inorganic and organic solids in the lake and can be used to calculate its physical properties using the values for seawater dilute to this salinity. Since most experimental measurements made in lakes determine

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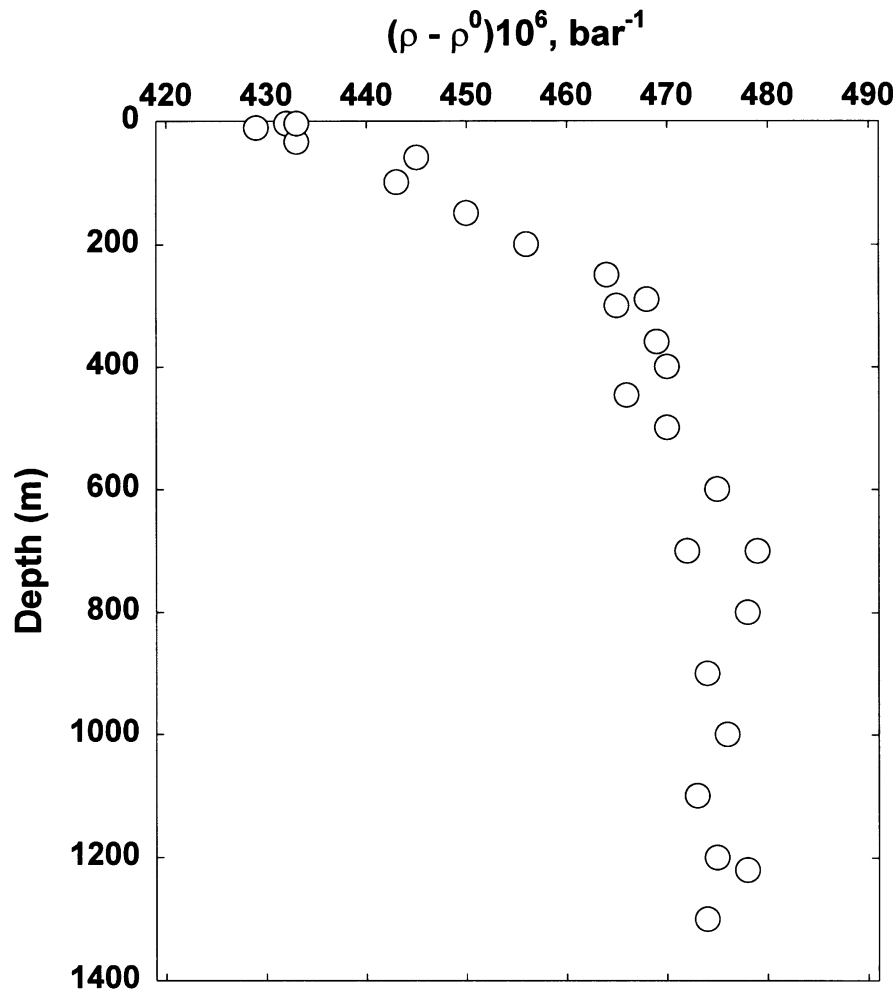


Figure 1. The density of Lake Tanganyika waters at 25°C as a function of depth.

the salinity by conductivity, it is appropriate to discuss the effect of composition of the conductivity of lakes and other natural waters.

The conductivity unlike the density responds only to the ionic components of the water. The conductivity salinity is thus a strong function of the composition of the waters. This has been demonstrated (Millero, 1984) by using the equivalent conductance's of the major components of seawater and river waters of different composition. The conductance of seawater in dilute solutions is larger than the values for "World" and St. Lawrence River waters. This is because the conductances

Table VII. Calculation of the increases in the density of deep waters of Lake Tanganyika.

Species	MW	$\phi_V$	$\Delta M$	$10^6 \Delta \rho^a$
Si(OH) <sub>4</sub>	96.116	56.0	$213 \times 10^{-6}$	$9 \text{ g cm}^{-3} \text{ H}_2\text{PO}_4^-$
	96.99	33.6	$6 \times 10^{-6}$	0.4
HCO <sub>3</sub> <sup>-</sup>	61.017	24.29	$0.65 \times 10^{-3}$	24
Na <sup>+</sup>	22.9898	-1.21	$0.28 \times 10^{-3}$	7
K <sup>+</sup>	39.102	9.03	$0.08 \times 10^{-3}$	0
Mg <sup>2+</sup>	24.305	-21.18	$0.05 \times 10^{-3}$	2
Ca <sup>2+</sup>	40.08	-17.86	$0.065 \times 10^{-3}$	4
			Sum	46

<sup>a</sup> Calculated from  $\Delta \rho = 10^3 [\text{MW} - \phi_V^0 \rho_0] \Delta M$ .

of Na<sup>+</sup> and Cl<sup>-</sup> are larger than Mg<sup>2+</sup>, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, the major components of river water.

Since the properties of lakes and seawater are the same at a given total salinity, it would be desirable to use the conductivity equations of seawater to determine a salinity that is consistent with the PVT properties. Since the effect of temperature and pressure are not strong functions of the composition, the relationship between the conductivity and the density salinity can be approximated by measurements or calculations at 25°C. The easiest way to determine this relationship is to make direct conductivity and density measurement on samples from the lake. Recently this has been done (Jellison et al., 1999) on samples from Mono Lake. This requires measurements of both conductivity and density as a function of temperature and composition of the lake waters of variable salinity. This is quite time consuming and essentially defines an equation of state for the Lake independent of seawater.

A more useful approach is to make density and conductivity measurements at 25°C on the waters collected from the lake and seawater of known salinity. This will allow one to use a semi-empirical correlation to relate the seawater salinity determined by conductivity to the lake conductivity

$$S(\text{Lake})_{\text{Cond}} = S(\text{Seawater})_{\text{Cond}} + \Delta_{\text{Cond}}, \quad (14)$$

where  $\Delta_{\text{Cond}}$  is an empirical function of the differences between the calculated salinity using the Practical Salinity Scale (UNESCO, 1981; Hill et al., 1986) for the lake and seawater. If density measurements are also made, one can develop a relationship between the conductance salinity and total salinity derived from density measurements using the equation of state of seawater (Millero and Poisson, 1981).

$$S(\text{Lake})_T = S(\text{Lake})_{\text{Cond}} + \Delta(\text{Dens} - \text{Cond}), \quad (15)$$

where  $\Delta(\text{Dens} - \text{Cond})$  is a constant or a function of  $S(\text{Lake})_{\text{Cond}}$ .

The methods outlined above can be used without any detailed knowledge of the composition of the lake. If it is not possible to make conductivity and density measurements on lake waters, the next best thing to do is to make measurements on artificially made lake waters. As I have shown, measurements of artificial waters can provide reliable densities and conductivities of river, estuarine, brine and sea waters of known composition (Millero, 1973a,b; Millero and Lepple, 1973; Millero et al, 1976a; 1982b; Millero and Chetirkin, 1980).

If only composition data are available one can determine the salinity from partial molal volume data as described above. The conductivity of the lake can be estimated from the conductivity of the components of the lake (Sorensen and Glass, 1987; Wüest et al., 1996) and dilute solution measurements on pure electrolytes (Robinson and Stokes, 1959). Wüest et al. (1996) have recently given equations for the equivalent conductivity of the major components of lakes as a function of temperature and composition. They have used these equations to estimate the conductivity of the waters from Lake Malawi. The validity of these methods needs to be examined by making direct measurements on waters of known composition as described above. To examine the approximate relationships between the conductivity of Lakes and seawater, I have determined the equivalent conductance of seawater and the lakes considered in this paper using the infinite dilution ionic conductance taken from Robinson and Stokes (1959) and Wüest et al. (1996). The equivalent conductance of the mixture ( $\Lambda_0$ ,  $\mu\text{S cm}^{-1} (\text{eq/L})^{-1}$ ) at infinite dilution is determined from

$$\Lambda_0 = \sum_i E_i \lambda_0(i), \quad (16)$$

where  $E_i$  is the equivalent fraction and  $\lambda_0(i)$  is the equivalent conductance of ionic component  $i$ . The values of  $\Lambda_0$  at 25°C determined from this equation are given in Table 9. The lake values are lower largely due to the decrease in the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$ . The ratio of  $\Lambda_0(\text{Lake})/\Lambda_0(\text{SW})$  at different temperatures are shown in Figure 2. The ratios are second degree functions of temperature and vary from 0.80 to 0.84. The conductance ratios for the lakes (0.82) can be compared to 0.88 for rivers (Millero, 1984).

The specific conductances of the solutions are related to the equivalent conductances by

$$\kappa_0(\mu\text{Scm}^{-1}) = \Lambda_0 e_T, \quad (17)$$

where  $e_T = \frac{1}{2} \sum Z_i M_i$ . If one assumes that the value of  $\kappa_0$  is proportional to the salinity, one would expect that the values for the Lake should be proportional to the ratio of  $\kappa_0$ . The values of  $\kappa_0$  give ratios for  $\kappa_0(\text{Malawi})/\kappa_0(\text{Baikal}) = 2.06$  and  $\kappa_0(\text{Tanganyika})/\kappa_0(\text{Malawi}) = 2.77$  which are in reasonable agreement with the salinity ratios,  $S(\text{Malawi})/(\text{Baikal}) = 2.13$  and  $S(\text{Tanganyika})/S(\text{Malawi}) = 2.77$ .

## Conductance

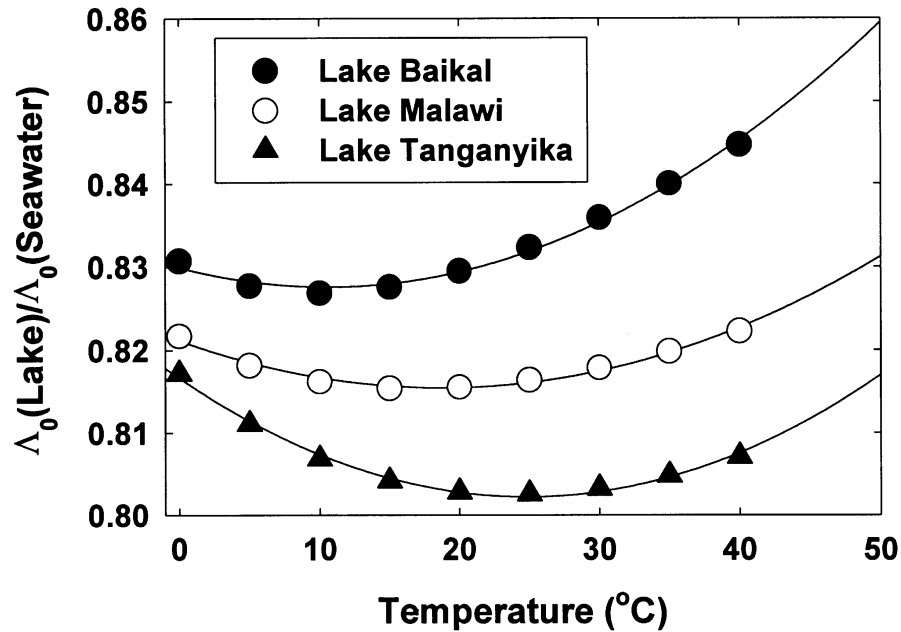


Figure 2. The ratio of the infinite dilution equivalent conductance of Lake Baikal, Malawi and Tanganyika and seawater,  $\Lambda_0(\text{Lake})/\Lambda_0(\text{Seawater})$ , as a function of temperature.

This simple comparison suggests that one can make a direct link of the conductivity to the total salinity that can be used to determine the PVT properties (Wüest et al., 1996). The calculated values of the total salinity can be related to  $\kappa$  by

$$S_T = k\kappa, \quad (18)$$

where  $k$  is a function of temperature and  $\kappa$  has been corrected for changes in the composition ( $\kappa = f\kappa_0$ , where  $f$  is a reduction coefficient, Wüest et al., 1996). Since the properties of seawater are accurately known as a function of the Practical Salinity, it is useful to make a direct link between the measured conductivity on this Scale to the total salinity determined from the composition (Equation 13). If seawater is diluted to the same total salinity (Table 8), the conductivity of seawater at 25°C is  $1.68 \pm 0.03$  larger than the values for the lakes. Direct measurements of the conductance are needed to determine if these methods are reliable. Finally it should be pointed out that changes in the composition of the deep waters (nutrients, carbon dioxide, etc.) can complicate the conversion of conductivity to total salinity that is directly related to the physical properties. The methods to account for these effects in ocean waters are discussed elsewhere (Brewer and Bradshaw, 1975; Millero et al., 1976; Millero, 1999).

Table VIII. The equivalence conductance of seawater and lake waters at 25°C.

Ion	$\lambda_0(i)$	Seawater <sup>a</sup>	Baikal	Malawi	Tanganyika
		$E_i \lambda_0(i)$	$E_i \lambda_0(i)$	$E_i \lambda_0(i)$	$E_i \lambda_0(i)$
Na <sup>+</sup>	49.92	38.66	6.30	16.90	18.55
Mg <sup>2+</sup>	53.04	9.25	10.89	12.62	23.91
Ca <sup>2+</sup>	60.96	2.07	39.92	21.34	4.50
K <sup>+</sup>	73.56	1.24	1.44	4.55	8.24
Sr <sup>2+</sup>	59.45	0.02	0.00	0.00	0.00
Cl <sup>-</sup>	76.41	68.87	0.77	4.14	6.47
SO <sub>4</sub> <sup>2-</sup>	79.97	7.46	7.48	4.80	1.31
HCO <sub>3</sub> <sup>-</sup>	44.50	0.13	39.62	39.75	39.64
Br <sup>-</sup>	78.14	0.11			
CO <sub>3</sub> <sup>2-</sup>	69.83	0.06		0.30	
F <sup>-</sup>	44.50	0.01			
B(OH) <sub>4</sub> <sup>-</sup>	55.40	0.01			
	$\Lambda_0 = \sum E_i \lambda_0(i)$	127.87	106.43	104.39	102.62
	$\kappa_0 = \Lambda_0 e_T$	80.26	0.131	0.270	0.751
	$\kappa_0(\text{SW})^a$		0.221	0.444	1.303
	$\kappa_0(\text{SW})/\kappa_0(\text{Lake})$		1.68	1.64	1.73

<sup>a</sup> Seawater diluted to same total salinity of the lake (at  $S_T = 35$ ,  $e_T = 0.6277$ ).

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### Appendix I. Coefficients for the apparent molal volume of the major sea salt ions as a function of temperature<sup>a</sup>

Ion	$\phi_V^0(i)^b$			$B_V(i)^c$		
	$A_i$	$B_i$	$C_i$	$A'_i$	$B'_i$	$C'_i$
Na <sup>+</sup>	-3.46	0.1092	-0.000768	2.698	-0.106	0.001651
Mg <sup>2+</sup>	-22.32	0.0868	-0.0016	2.017	-0.125	0.001457
Ca <sup>2+</sup>	-19.69	0.1058	-0.001256	1.617	-0.075	0.0008262
K <sup>+</sup>	7.26	0.0892	-0.000736	2.722	-0.101	0.00151
Sr <sup>2+</sup>	-18.44	0.0082	-0.0006	1.727	-0.067	0.00084
Cl <sup>-</sup>	16.37	0.0896	-0.001264	-1.494	0.034	-0.000621
SO <sub>4</sub> <sup>2-</sup>	9.26	0.284	-0.003808	0.4348	-0.0099143	-8.4762E-05
HCO <sub>3</sub> <sup>-</sup>	21.07	0.185	-0.002248	2.29	-0.006644	-3.667E-06
Br <sup>-</sup>	22.98	0.0934	-0.000968	-1.675	0.05	-0.001105
CO <sub>3</sub> <sup>2-</sup>	-8.74	0.300	-0.004064	5.65 <sup>d</sup>		
F <sup>-</sup>	-3.05	0.3276	-0.00352	1.271	-0.074	8.857E-05
B(OH) <sub>4</sub> <sup>-</sup>	15.85	0.1272	-0.002064	8.856	-0.235	0.002794
NO <sub>3</sub> <sup>-</sup>	25.51	0.1888	-0.001984	-0.654 <sup>d</sup>		
B(OH) <sub>3</sub>	36.56	0.130	-0.00081			
Si(OH) <sub>4</sub>	56.0					

<sup>a</sup> The values of the limiting slope can be determined from  $S_V = 1.4447 + 0.016799t - 8.4055E-06t^2 + 5.5153E-07t^3$ .

<sup>b</sup> From Millero (1983). The values for divalent ions must be divided by 2 to convert them to equivalents.

<sup>c</sup> The values for divalent ions must be divided by 2 to convert them to equivalents.

<sup>d</sup> The value at 25°C.

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