

NOTICE: THIS MATERIAL MAY BE PROTECTED
BY COPYRIGHT LAW (TITLE 17 U.S. CODE)

A standard table for predicting equilibrium dissolved oxygen concentrations in salt lakes dominated by sodium chloride

J.E. Sherwood¹, F. Stagnitti¹, M.J. Kokkinn² and W.D. Williams³

¹Faculty of Aquatic Science, Deakin University, Warrnambool, Victoria, 3280, Australia.

²School of Pharmacy, University of South Australia, North Terrace, Adelaide, South Australia, 5000, Australia.

³Department of Zoology, University of Adelaide, GPO Box 498, Adelaide, South Australia, 5001, Australia.

Key Words: dissolved oxygen, saline, lakes

Abstract

An equation of state was used to prepare a standard table for the solubility of oxygen in sodium chloride solutions at temperatures between 0 and 35°C and for concentrations up to saturation (260 ppt). The uncertainty introduced by linear interpolation between DO values in the table is less than the experimental uncertainty of data which was used to generate the equation of state. Where pressures differ from 1 atm the DO value from the table can be corrected provided the equilibrium vapour pressure of the salt solution is known. Where this is not the case an approximate correction (± 0.5 per cent) can be used provided atmospheric pressure is in the range 950 to 1030 mbar.

Predictions made using the standard tables will provide near but probably low ($<0.2 \text{ mg L}^{-1}$) estimates of DO in salt lakes where sodium chloride is the dominant electrolyte (>70 per cent by mass).

Introduction

Limnologists studying salt lakes have not had access to standard tables for equilibrium dissolved oxygen (DO) of the sort available to oceanographers and those working in estuarine and fresh waters. This is due, in part, to the highly variable ionic composition

of these lakes world-wide (see table 1, Williams (1966) for example). Different electrolytes affect the solubility of oxygen to differing degrees and so a single "universal" table is not possible. Most salt lakes however are dominated by sodium chloride. In Australia for example, this electrolyte commonly accounts for 70–90 per cent of the total dissolved solids (Hart and McKelvie, 1986). We have completed a study of equilibrium DO concentrations in sodium chloride solutions (Sherwood *et al.*, 1991). This covered an environmentally significant temperature range (0–35°C) and salt concentrations up to saturation (*ca.* 260 parts per thousand, ppt). Comparisons of equilibrium DO values for NaCl solutions with those reported for salt lakes and artificial salt mixtures were made (Sherwood *et al.*, 1991). These showed that predictions based on NaCl were likely to provide near (within 0.2 mg L⁻¹) but low estimates of DO in salt lakes in which NaCl was the dominant electrolyte (>70 per cent). Predictions of equilibrium DO values based on sodium chloride therefore have great utility for limnologists working on these lakes. Accordingly, we present here a standard table for DO in NaCl solutions based on our experimental studies. This table will provide, for the first time, a convenient reference for limnologists in the field.

Procedure

The experimental methods used in our investigation are described elsewhere (Sherwood *et al.*, 1991). An equation of state of the following form gave the best fit to our experimental data:

$$\ln C^*_0 = a_0 + \frac{a_1}{T} + a_2 \ln T + a_3 T + a_4 T^2 + S (a_5 + a_6 T + a_7 T^2) + a_8 S^2 \dots(1)$$

In this equation C^*_0 is the unit standard atmospheric concentration by volume and is defined as the concentration of dissolved oxygen per unit volume of solution (measured at the equilibrium temperature) when it is in equilibrium with an atmosphere of standard composition and saturated with water vapour at a total pressure (including that of the water vapour) of 1 atm (Benson and Krause, 1980); T is the water temperature in Kelvin; S is the total dissolved solids in parts in per thousand and a_i are the empirical constants found by multiple regression. The values for a_i are listed in Table 1.

Equation (1) has been used to predict the DO values for Table 2. Temperature and salinity intervals have been selected so that linearly interpolated values differ from those predicted by eqn (1) by less than 0.03 mg L⁻¹ for any chosen salinity or temperature. This

is less than the experimental uncertainty in the original DO determinations (0.05 mg L^{-1} ; Sherwood *et al.*, 1991).

Table 1. Coefficients in eqn (1) used to predict C^*_0 in NaCl solutions.

Constant	Value
a ₀	$-6.85693750 \times 10^{+4}$
a ₁	$+1.28038367 \times 10^{+6}$
a ₂	$+1.32716777 \times 10^{+4}$
a ₃	$-4.59371240 \times 10^{+1}$
a ₄	$+2.65097198 \times 10^{-2}$
a ₅	$-4.29122353 \times 10^{-2}$
a ₆	$+2.06161380 \times 10^{-4}$
a ₇	$-2.68767762 \times 10^{-7}$
a ₈	$-3.60557809 \times 10^{-6}$

Discussion

Several factors must be considered when using Table 2 to estimate DO in salt lakes.

(a) Ionic composition of lake waters. The “salting out” effect (i.e. reduction of DO as salt concentration increases) of many limnologically significant electrolytes is lower than that for sodium chloride. Hence mixtures of salts which include NaCl will tend to have values of C^*_0 higher than predicted from Table 2. Comparison of these predictions to measured DO for magnesium sulphate/sodium chloride mixtures, with seawater, and with water from Laguna Tamaulipas, a hypersaline coastal lagoon in Mexico indicate that predictions may be low by up to 0.2 mg L^{-1} . At lower salinities and/or higher proportions of NaCl (*ca.* 90 per cent) the difference between measured and predicted values was less than 0.1 mg L^{-1} (Sherwood *et al.*, 1991). We are currently working on the preparation of equations of state for other limnologically important salts (e.g. MgSO_4) so that the presence of these can be taken into account for DO predictions.

(b) Measurement of total dissolved solids (S). Loss of water of hydration from electrolytes is dependent on drying temperature and so measured concentrations of total dissolved solids (S) will also be a function of drying temperature.

Table 2. Predicted values (mg L⁻¹) of C*₀ for pure NaCl solutions calculated from eqn (1) using coefficients in Table 1.

Concentration (ppt)	Temperature (°C)																	
	0	1	2	3	4	5	6	8	10	12	14	15	16	18	20	25	30	35
0	14.60	14.20	13.82	13.46	13.11	12.79	12.47	11.88	11.34	10.83	10.35	10.13	9.91	9.49	9.10	8.22	7.49	6.92
2	14.40	14.01	13.64	13.28	12.95	12.63	12.32	11.74	11.20	10.70	10.23	10.01	9.79	9.38	9.00	8.13	7.42	6.85
5	14.12	13.74	13.37	13.03	12.70	12.39	12.09	11.52	11.00	10.51	10.05	9.84	9.63	9.22	8.85	8.00	7.30	6.75
10	13.65	13.29	12.94	12.61	12.29	11.99	11.71	11.17	10.66	10.20	9.76	9.55	9.35	8.96	8.60	7.79	7.12	6.59
15	13.20	12.85	12.52	12.20	1.90	11.61	11.34	10.82	10.34	9.89	9.47	9.27	9.08	8.71	8.36	7.58	6.93	6.42
20	12.76	12.43	12.11	11.81	11.52	11.24	10.98	10.48	10.02	9.60	9.19	9.00	8.82	8.46	8.13	7.38	6.75	6.26
25	12.33	12.01	11.71	11.42	11.14	10.88	10.63	10.16	9.72	9.31	8.92	8.74	8.56	8.22	7.90	7.18	6.58	6.11
30	11.92	11.61	11.32	11.05	10.78	10.53	10.29	9.84	9.42	9.02	8.65	8.48	8.31	7.98	7.67	6.98	6.41	5.95
35	11.51	11.22	10.94	10.68	10.43	10.19	9.96	9.53	9.12	8.75	8.39	8.22	8.06	7.75	7.45	6.79	6.24	5.80
40	11.12	10.84	10.58	10.33	10.09	9.86	9.64	9.22	8.84	8.48	8.14	7.98	7.82	7.52	7.24	6.60	6.07	5.65
45	10.74	10.48	10.22	9.98	9.75	9.53	9.32	8.93	8.56	8.21	7.89	7.74	7.59	7.30	7.03	6.42	5.91	5.51
50	10.37	10.12	9.88	9.65	9.43	9.22	9.02	8.64	8.29	7.96	7.65	7.50	7.36	7.08	6.82	6.24	5.75	5.37
55	10.01	9.77	9.54	9.32	9.11	8.91	8.72	8.36	8.02	7.71	7.41	7.27	7.14	6.87	6.62	6.06	5.59	5.23
60	9.67	9.44	9.22	9.01	8.81	8.62	8.43	8.09	7.77	7.47	7.18	7.05	6.92	6.67	6.43	5.89	5.44	5.09
65	9.33	9.11	8.90	8.70	8.51	8.33	8.15	7.82	7.52	7.23	6.96	6.83	6.71	6.46	6.24	5.72	5.29	4.95
70	9.00	8.79	8.59	8.40	8.22	8.05	7.88	7.57	7.28	7.00	6.74	6.62	6.50	6.27	6.05	5.56	5.15	4.82
75	8.69	8.48	8.29	8.11	7.94	7.78	7.62	7.32	7.04	6.78	6.53	6.41	6.30	6.08	5.87	5.40	5.00	4.69
80	8.38	8.19	8.01	7.83	7.67	7.51	7.36	7.07	6.81	6.56	6.32	6.21	6.10	5.89	5.69	5.24	4.86	4.57
90	7.79	7.62	7.45	7.30	7.15	7.00	6.87	6.61	6.37	6.14	5.93	5.82	5.72	5.53	5.35	4.94	4.59	4.32
100	7.24	7.08	6.93	6.79	6.66	6.53	6.40	6.17	5.95	5.75	5.55	5.46	5.37	5.19	5.03	4.65	4.33	4.09
110	6.72	6.58	6.45	6.32	6.20	6.08	5.97	5.76	5.56	5.37	5.19	5.11	5.03	4.87	4.72	4.37	4.09	3.86
120	6.24	6.11	5.99	5.87	5.76	5.66	5.56	5.36	5.19	5.02	4.86	4.78	4.71	4.56	4.42	4.11	3.85	3.65
130	5.78	5.67	5.56	5.46	5.36	5.26	5.17	5.00	4.84	4.68	4.54	4.47	4.40	4.27	4.15	3.86	3.63	3.44
140	5.36	5.26	5.16	5.06	4.97	4.89	4.81	4.65	4.51	4.37	4.24	4.18	4.12	4.00	3.88	3.63	3.41	3.24
150	4.96	4.87	4.78	4.70	4.62	4.54	4.47	4.33	4.20	4.07	3.96	3.90	3.84	3.74	3.64	3.40	3.21	3.06
160	4.59	4.51	4.43	4.35	4.28	4.21	4.15	4.02	3.90	3.79	3.69	3.64	3.59	3.49	3.40	3.19	3.01	2.88
170	4.24	4.17	4.10	4.03	3.97	3.91	3.85	3.74	3.63	3.53	3.44	3.39	3.35	3.26	3.18	2.99	2.83	2.71
180	3.92	3.86	3.79	3.73	3.67	3.62	3.57	3.47	3.37	3.28	3.20	3.16	3.12	3.04	2.97	2.80	2.65	2.55
190	3.62	3.56	3.51	3.45	3.40	3.35	3.30	3.22	3.13	3.05	2.98	2.94	2.91	2.84	2.77	2.62	2.49	2.39
200	3.34	3.29	3.24	3.19	3.14	3.10	3.06	2.98	2.91	2.84	2.77	2.74	2.70	2.64	2.58	2.45	2.33	2.25
220	2.84	2.80	2.76	2.72	2.68	2.65	2.62	2.55	2.50	2.44	2.39	2.36	2.34	2.29	2.24	2.13	2.04	1.98
240	2.40	2.37	2.34	2.31	2.28	2.26	2.23	2.18	2.14	2.10	2.05	2.03	2.01	1.98	1.94	1.86	1.78	1.73
260	2.03	2.00	1.98	1.96	1.94	1.92	1.90	1.86	1.83	1.79	1.76	1.75	1.73	1.70	1.67	1.61	1.55	1.51

The current recommended drying temperature for determination of S is 180°C (APHA, 1985). At this temperature for example, magnesium sulphate exists as the monohydrate ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) whereas at 105°C it is present chiefly as the dihydrate ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$). Since, in Table 2, all the dissolved salts are considered to be sodium chloride, inclusion of water of hydration will lead to elevated estimates of S. These will lead to lower estimates of DO.

(c) **Influence of atmospheric pressure.** Where DO in a salt solution equilibrates at a pressure other than 1 atm, the value of C^*_0 calculated from equation (1) will have to be corrected according to equation (2):

$$C_0 = C^*_0 \left(\frac{P - P_{wv}}{1 - P_{wv}} \right) \exp [B (P - 1)] \quad \dots(2)$$

$$\approx P C^*_0 \quad \dots(3)$$

where C_0 is the equilibrium DO at a total atmospheric pressure P measured in atmospheres; P_{wv} is the equilibrium vapour pressure (in atm) of the salt solution at temperature t , measured in °C; and B (atm^{-1}) is the second virial coefficient of oxygen gas at $t^\circ\text{C}$. B is given by equation (4).

$$B = -0.000975 + (1.426 \times 10^{-5} t) - (6.436 \times 10^{-8} t^2) \quad \dots(4)$$

The exponential term in equation (2) differs from unity by less than 0.01 per cent for temperatures between 0–35°C and pressures from 950 to 1030 mb.

Also, for many salt lakes the term $\left(\frac{P - P_{wv}}{1 - P_{wv}} \right)$ can be replaced by P as in equation (3). This approximation introduces an uncertainty of less than 0.5 per cent for typical values of P and P_{wv} . For example, at 35°C in distilled water P_{wv} , equals 0.0568 atm. When P equals 0.938 atm (950 mb), the term $\left(\frac{P - P_{wv}}{1 - P_{wv}} \right)$ equals 0.934 — a difference of 0.4 per cent. Raising P or lowering P_{wv} (by increasing salt concentration or lowering t) will further reduce the error in the approximation further. Equation (3) will thus provide a corrected C^*_0 (C_0) with an uncertainty within the likely uncertainty in the experimental data ($\pm 0.05\text{mg L}^{-1}$) for pressures in the range 950 to 1030 mbars and for temperatures between 0 and 35°C. Where pressures deviate substantially from this, the exact form (eqn (2)) should be used.

References

- APHA, 1985. **Standard Methods for the Examination of Water and Wastewater**. 16th edition. American Public Health Association, Inc., Washington, D.C.
- Benson, B.B., and Krause, D., 1980. The concentration and fractionation of gases dissolved in freshwater in equilibrium with the atmosphere: I. Oxygen. *Limnology and Oceanography* **25**: 662–671.
- Hart, B.T., and McKelvie, I.D., 1986. Chemical Limnology in Australia. In: P. De Deckker and W.D. Williams (Eds) **Limnology in Australia**. pp. 3–31. CSIRO and Junk, Melbourne and Dordrecht.
- Sherwood, J.E., Stagnitti, F., Kokkinn, M.J., and Williams, W.D., 1991. Dissolved oxygen concentrations in hypersaline waters. *Limnology and Oceanography* **36**(2): 235–250.
- Williams, W.D., 1966. Conductivity and the concentration of total dissolved solids in Australian lakes. *Australian Journal of Marine and Freshwater Research* **17**:169–176.