# Oxygen solubility in seawater: Better fitting equations

*Abstract*—We examined uncertainties associated with the routine computation of $O_2$ solubility ($C_o*$) at 1 atm total pressure in pure water and seawater in equilibrium with air as a function of temperature and salinity. We propose formulae expressing $C_o*$ (at STP, real gas) in $cm^3$ $dm^{-3}$ and $\mu mol$ $kg^{-1}$ in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 42\‰$) based on a fit to precise data selected from the literature.

Precise and accurate values of oxygen solubility in seawater are important for estimating oxygen utilization, oxygen-nutrient equivalent relations, air–sea gas exchange, etc. Green (1965 and references therein) reported measurements of $O_2$ solubility in seawater. However, Carpenter (1966) and Murray and Riley (1969) obtained more precise results, and Benson and Krause (1984) published yet more precise $O_2$ solubility data. For limnological work, Mortimer (1981) proposed using the results of Benson and Krause (1980), and Millero (1986) recommended those of Benson and Krause (1984) for oceanographic work. More recently, Sherwood et al. (1991) have examined $O_2$ solubility in hypersaline solutions of NaCl and other salts.

In the past, $O_2$ solubility was difficult to use for several purposes because it was tabulated for integral values of temperature and salinity (or chlorinity). More recently, several empirical formulae have been proposed for expressing the dependence of the logarithm of $O_2$ solubility on temperature and salinity (Gilbert et al. 1968; Weiss 1970). The effect of salinity on the logarithm of $O_2$ solubility is often expressed with the empirical Setschenow relation at constant temperature,

$$\ln C_o* = A + BS, \qquad (1)$$

where $C_o*$ is the solubility of $O_2$ per mass or per volume of seawater at the temperature of equilibrium (the subscript o denotes $O_2$; the asterisk signifies equilibrium with an atmosphere of standard composition saturated with water vapor at a total pressure, including that of the water vapor, of 1 atm), $S$ is salinity in per mil, and $A$ and $B$ are constant coefficients. Clever (1982) reviewed the Setschenow relation. Because seawater is a complex multicomponent solution, disagreement exists on an expression for, and thermodynamic basis of, an empirical formula for routine computation of $C_o*$ which fits the experimental data precisely and accurately while covering the thermohaline range of the world ocean (Battino et al. 1983). This disagreement complicates the use and interpretation of $C_o*$ data.

We examined uncertainties associated with $C_o*$ computations in seawater as functions of temperature and salinity and evaluated several formulae for its routine estimation. Our main concern is that the formulae that have been proposed for routine computation of $C_o*$ in seawater do not behave well at the extremes of the experimental data, especially at low temperatures. Although no precise $O_2$ solubility data in seawater are available below ~0.5°C, workers use empirical formulae to extrapolate to lower temperatures (Weiss 1970; Chen 1981). These formulae do not fit the data well at temperatures below ~1°C and at high salinity. Based on the experimental values of Carpenter (1966), Murray and Riley (1969), and Benson and Krause (1984), we propose a high-precision formula for estimating $C_o*$ (at STP, real gas) by the method of least-squares; it covers oceanic ranges of temperature and salinity. This new fit is well behaved in the temperature and salinity ranges of the data and it does not appear to deviate significantly at the extremes of temperature and salinity of the measurements. We provide formulae and solubility coefficients for estimating $C_o*$ in seawater as a

function of temperature and salinity in $cm^3$ $dm^{-3}$ and $\mu mol$ $kg^{-1}$.

Weiss (1970) proposed a least-squares regression (LSR) fit for computing $O_2$ solubility (at STP, real gas) in seawater in the range ($-1 \geq t \geq 40°C$; $0 \geq S \geq 40‰$) with the experimental data of Carpenter (1966) in the range ($0.5 \geq t \geq 36°C$; $5.2 \geq Cl \geq 20‰$) and Murray and Riley (1969) in the range ($0.7 \geq t \geq 35°C$; $0 \geq S \geq 40‰$):

$$\ln C_o^* = A_1 + A_1 T^{-1} + A_2 \ln T + A_3 T \\ + S(B_0 + B_1 T + B_2 T^2) \quad (2)$$

where $T$ is temperature in Kelvin and $A_i$ and $B_i$ are constants. Equation 2 is based on the Van't Hoff and the Setschenow relations for, respectively, $T$ and $S$ effects. Weiss indicated a root-mean-square (rms) deviation of $\pm 0.016$ $cm^3$ $dm^{-3}$ from the combined data of Carpenter and Murray and Riley. Similarly, Chen (1981) examined the same data, proposing LSR fits for $C_o^*$ in the range ($0 \geq t \geq 35.5°C$; $0 \geq S \geq 40‰$) with an rms deviation of $\pm 0.015$ $cm^3$ $dm^{-3}$.

$$\ln C_o^* = A_0 + A_1 T^{-1} + A_2 \ln T + A_3 T \\ + S(B_0 + B_1 T^{-1}) + C_0 S^2. \quad (3)$$

Benson and Krause (1984) made measurements of the Henry's coefficient for $O_2$ in seawater ($K_o$) in the range ($0.2 \geq t \geq 45°C$; $0 \geq S \geq 50‰$), and proposed an LSR fit with an rms deviation from the measurements of $\pm 0.08\%$. They expressed $C_o^*$ (at STP, real gas) in mol $kg^{-1}$ as a function of $K_o$ at unit standard atmospheric concentration per unit mass of seawater:

$$C_o^* = 0.20946 F(1 - P_{wv})(1 - B_o) \\ \cdot (K_o M_w)^{-1} \quad (4)$$

where $P_{wv}$ is the equilibrium water vapor pressure in air (Green and Carritt 1967), $F$ and $M_w$ are a salinity factor and the gram molecular mass of water, respectively (Millero 1982), $B_o$ is the second virial coefficient for $O_2$ (Benson and Krause 1980), and the constant 0.20946 is the mole fraction of $O_2$ in dry air (Glueckauf 1951).

For Eq. 4, Benson and Krause (1984) indicated an uncertainty of $\pm 0.1\%$ or better.

For routine computations of $C_o^*$ from Eq. 4, they fitted values in several units (at STP, ideal gas) in the range ($0 \geq t \geq 40°C$; $0 \geq S \geq 40‰$):

$$\ln C_o^* = A_0 + A_1 T^{-1} + A_2 T^{-2} \\ + A_3 T^{-3} + A_4 T^{-4} A_4 \\ + S(B_0 + B_1 T^{-1} \\ + B_2 T^{-2} + B_3 T^{-3}). \quad (5)$$

Given the high precision of the current $O_2$ solubility data, it is not clear from Eq. 2, 3, and 5 that all provide the same values over oceanic ranges of $T$ and $S$. The uncertainty arises because certain formulae are more robust (statistical sensitivity to the experimental data). The behavior of the gas solubility formulae at high and low $T$ and $S$ is of importance. It is critical that a gas solubility equation behaves well at the extremes of the experimental values. The $C_o^*$ data of Carpenter, Murray and Riley, and Benson and Krause do not cover the whole range of temperature of the world ocean and extrapolation is required.

We compared the $C_o^*$ values derived from the formulae of Weiss (Eq. 2), Chen (Eq. 3), and Benson and Krause (Eq. 5) in the range ($-2 \geq t \geq 40°C$; $0 \geq S \geq 42‰$). We considered temperatures greater than or equal to the freezing point ($t_F$) from Fofonoff and Millard (1983). Using the formulae and coefficients of Weiss (1970) and Chen (1981), we converted their $C_o^*$ values from $cm^3$ $dm^{-3}$ to $\mu mol$ $kg^{-1}$ at a molar volume of $O_2$ of 22,391.6 $cm^3$ $mol^{-1}$ and the equation of state of seawater of Millero and Poisson (1981). The difference between the molar volume of $O_2$ (at STP) as an ideal gas and as a real gas is $\sim 0.1\%$. Thus, all $C_o^*$ values (at STP, real gas) were expressed in units independent of pressure and temperature. A computer program was written to fit the $C_o^*$ values from Eq. 4 by singular value decomposition in the least-squares sense. Our objective was to examine the relative precision of the fit of these solubility equations over the oceanic range of $T$ and $S$ when Eq. 2, 3, and 5 were used to fit values from Eq. 4. We also examined the relative precision of these equations to estimate the data of
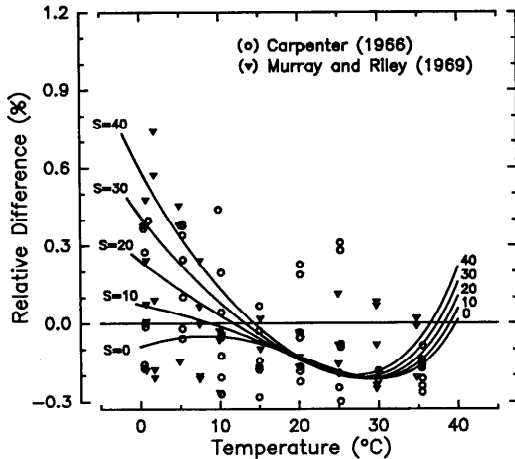
Fig. 1.  Difference between the $C_o$* values from Weiss (1970, curves), Carpenter (1966, o), and Murray and Riley (1969, ▼), relative to the results of Benson and Krause (1984).
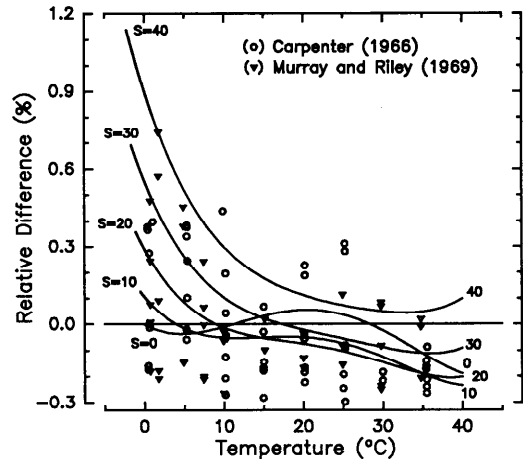


Fig. 2.  As Fig. 1, but for the results of Chen (1981).

Carpenter (1966) and Murray and Riley (1969). In each case, we used from 2 to 10 $T$ terms to fit the constant coefficients of Eq. 1. Because of its empirical nature, we also examined addition of $S$ terms to the Setschenow relation. After adding a $T$ or $S$ term, we analyzed the goodness-of-fit and behavior of the fit at the extremes of the $C_o$* data.

Because of the behavior of the equation of state of seawater, chemical concentration units on a per-mass basis should be compared separately from those on a per-volume basis. Other than for the seawater density effect, systematic deviations in one set of dissolved $O_2$ concentration units apply in others. Figure 1 shows the relative percent deviation between the $C_o$* values from Eq. 4 and those of Weiss (Eq. 2) in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 40‰$). The maximum and minimum relative deviations between their $C_o$* values were +0.7% (2.60 $\mu$mol kg$^{-1}$) and -0.2% (0.51 $\mu$mol kg$^{-1}$), respectively, with an rms deviation of ±0.3% (±1.01 $\mu$mol kg$^{-1}$). Similarly, Fig. 2 shows the relative deviations between the $C_o$* values from Eq. 4 and those of Chen (Eq. 3) in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 40‰$). In this case, the minimum, maximum, and rms deviations in the range ($0 \geq t \geq 35.5°C$; $0 \geq S \geq 40‰$) were, respectively, -0.2% (0.40 $\mu$mol kg$^{-1}$), + 0.9%

(3.01 $\mu$mol kg$^{-1}$), and ±0.3% (±0.85 $\mu$mol kg$^{-1}$). In all cases, the discrepancy between $C_o$* values derived from these fits was significant at low $T$ and high $S$.

For low-precision estimates of $C_o$*, deviations of ≤1% are probably unimportant. However, differences in $C_o$* at low $T$ and high $S$ are important in high-precision measurements for the following reasons. First, in recent years analytical precision in dissolved oxygen measurements in seawater at sea and in the laboratory have been improved to ±0.1% or better (Culberson et al. 1991). High precision and accuracy in measurements of dissolved $O_2$ and $C_o$* are important in the detection of ocean climatic changes where relatively small variations might be significant. Second, water masses responsible for the thermohaline characteristics of the deep ocean have $T$ and $S$ ranges where the greatest discrepancies occur between the $C_o$* values from Eq. 2, 3, and 5.

In pure water, Eq. 1 reduces to a form dependent on $T$, allowing the examination of solubility equations without consideration of $S$ effects. Because we use the same $C_o$* values (Eq. 4), LSR method, and the same equation of state for seawater, any differences between Eq. 2, 3, and 5 reflect their relative precision and accuracy, assuming that the data of Benson and Krause (1984) from Eq. 4 are the most precise and accurate. In pure water and in the range ($t_F \geq t \geq 40°C$), Eq. 2 and 3 attained an rms de-

viation from Eq. 4 of ±1.21%, ±0.16%, ±0.02%, and ±0.01% after addition of, respectively, two, three, four, and five $T$ terms. Additional $T$ terms did not significantly change the rms deviation of the Weiss extended equation. When Eq. 5 was used, four $T$ terms were required to obtain an rms deviation of ±0.01%. For seawater, terms must be added to Eq. 1 for the salinity effect on $\ln C_o^*$. For this case, we used the original form of the Weiss (Eq. 2) and Chen (Eq. 3) equations as well as extended forms, Eq. 6 and 7, respectively:

$$
\begin{aligned}
\ln C_o^* = A_0 &+ A_1 T^{-1} + A_2 \ln T + A_3 T \\
&+ A_4 T^2 + A_5 T^3 \\
&+ S(B_0 + B_1 T + B_2 T^2),
\end{aligned} \tag{6}
$$

and

$$
\begin{aligned}
\ln C_o^* = A_0 &+ A_1 T^{-1} + A_2 \ln T \\
&+ A_3 T + A_4 T^2 + A_5 T^3 \\
&+ S(B_0 + B_1 T^{-1} + B_2 T^{-2}) \\
&+ C_0 S^2.
\end{aligned} \tag{7}
$$

The extended or the original equations of Weiss and Chen gave greater rms deviations when fitting values from Eq. 4 over the oceanic thermohaline range than using Eq. 5. This is because a $T$ series of the form $T^{-n}$ fits the $\ln C_o^*$ values from Eq. 4 better than the Van't Hoff relation that Weiss or Chen used for the same number of coefficients. We examined several formulae to build a high-precision LSR fit for $C_o^*$ based on Eq. 4. From our analysis, Eq. 8 proved to be the best expression for estimating $C_o^*$ in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 42‰$):

$$
\begin{aligned}
\ln C_o^* = A_0 &+ A_1 T_s + A_2 T_s^2 + A_3 T_s^2 \\
&+ A_3 T_s^3 + A_4 T_s^4 + A_5 T_s^5 \\
&+ S(B_0 + B_1 T_s + B_2 T_s^2 + B_3 T_s^3) \\
&+ C_0 S^2
\end{aligned} \tag{8}
$$

where $T_s$ is a newly defined, scaled temperature: $T_s = \ln[(298.15 - t)(273.15 + t)^{-1}]$. This temperature ($T_s$) transformation significantly improves the rms deviation of the fit, particularly at high and low $T$ and $S$. A logarithmic transformation of the dependent or independent variables or both is common in LSR of curvilinear relations.

Though the Setschenow relation in its linear form has been shown to hold reasonably well within the experimental uncertainty of $C_o^*$ measurements in the past, it became evident from our analysis that a $S^2$ term is significant for the dependence of $\ln C_o^*$ on salinity. This finding is consistent with previous results (Carpenter 1966; Chen 1981; Sherwood et al. 1991). Values of $C_o^*$ in cm³ dm⁻³ and μmol kg⁻¹ can be obtained with Eq. 8 and the solubility coefficients in Table 1. The fit to Eq. 4 with Eq. 8 has rms deviations of ±4 × 10⁻⁴ cm³ dm⁻³ and ±10⁻³ μmol kg⁻¹ (Fig. 3) in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 42‰$).

Because of the agreement in the $C_o^*$ data of Carpenter and Murray and Riley (Weiss 1970), we examined the precision of Eq. 8 to estimate their measurements. Chlorinity (Cl, ‰) values were converted to salinity with the expression $S = 1.80655 \times Cl$ from Wooster et al. (1969). From this analysis, solubility coefficients for computing $C_o^*$ in cm³ dm⁻³ and μmol kg⁻¹ can be obtained from Table 1 and Eq. 8. The fit to the results of Carpenter and Murray and Riley has rms deviations from their combined data of ±0.015 cm³ dm⁻³ and ±0.67 μmol kg⁻¹. The rms deviations of the fit from Carpenter's data are ±0.013 cm³ dm⁻³ and +0.58 μmol kg⁻¹, while for Murray and Riley the rms deviations are ±0.018 cm³ dm⁻³ and ±0.78 μmol kg⁻¹. The rms deviations between the data of Carpenter and Murray and Riley from those of Benson and Krause are ±0.019 cm³ dm⁻³ and ±0.82 μmol kg⁻¹.

We compared our fits to the data of Carpenter, Murray and Riley, and Benson and Krause. When comparing the results of several workers, it is important to weight the precision of their data. When we assigned weights to the solubility data equal to their respective rms deviations from the experimental data, the resulting fit is significantly influenced by those fitted $C_o^*$ values with better precision. Although the rms of the fit to the data of Benson and Krause is considerably better, it is not clear that there are significant differences in accuracy between the $C_o^*$ data of Carpenter, Murray and Riley, and Benson and Krause. For this reason, we assigned equal weights to their solubility values to combine their fitted data. From this analysis, $C_o^*$ values in cm³ dm⁻³ and μmol kg⁻¹ can be obtained from the solu-
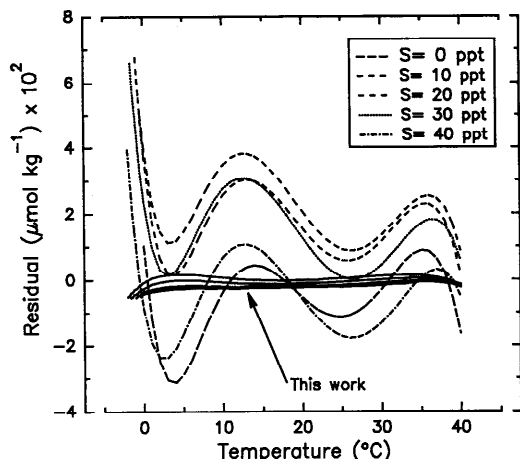
Fig. 3. Residual difference ($\mu$mol kg$^{-1}$) between the $C_o{}^*$ (at STP, real gas) values from Eq. 4 of Benson and Krause (1984) and their fit with Eq. 5 and our fit with Eq. 8 using coefficients in Table 1 in the range ($t_F \geq t \geq 40°C$; $0 \geq S \geq 40\text{‰}$). Solid lines represent the residual of our fit in the same range of $t$ and $S$.

bility coefficients in Table 1 and Eq. 8. The rms deviations of the fits from the combined measurements of Carpenter and Murray and Riley are ±0.016 cm³ dm⁻³ and ±0.72 $\mu$mol kg⁻¹. Similarly, the rms deviations of these fits from the results of Benson and Krause are ±0.005 cm³ dm⁻³ and ±0.23 $\mu$mol kg⁻¹.

We examined several empirical formulae for estimating $O_2$ solubility at 1 atm total pressure in pure water and seawater in equilibrium with air as a function of temperature and salinity. From our analysis of the data of Carpenter (1966), Murray and Riley (1969), and Benson and Krause (1984), we propose a new fit (Eq. 8) and solubility coefficients (Table 1) for the routine computation of $O_2$ (at STP, real gas) solubility in seawater ($t_F \geq t \geq 40°C$; $0 \geq S \geq 42\text{‰}$). This new fit estimates the $C_o{}^*$ data with relatively high precision in the ranges of $T$ and $S$ of the experimental values and seems to extrapolate more reliably beyond these ranges than do previous formulae. Clearly, extrapolation beyond the range of the experimental data should be viewed with caution. When relatively high precision of $C_o{}^*$ is not required, it probably makes no difference which $O_2$ solubility formula (Weiss 1970; Chen 1981; Benson and Krause 1984; this work) is used because the $C_o{}^*$ values

Table 1. Solubility constants for the routine computation of $C_o{}^*$ (at STP, real gas) in pure water and seawater with Eq. 8 and the data of Carpenter (1966), Murray and Riley (1969), and Benson and Krause (1984).

| Coef. | Benson and Krause | | Murray and Riley and Carpenter | | Combined fit | |
|---|---|---|---|---|---|---|
| | (cm³ dm⁻³) | ($\mu$mol kg⁻¹) | (cm³ dm⁻³) | ($\mu$mol kg⁻¹) | (cm³ dm⁻³) | ($\mu$mol kg⁻¹) |
| $A_0$ | 2.00907 | 5.80871 | 2.00805 | 5.80767 | 2.00856 | 5.80818 |
| $A_1$ | 3.22014 | 3.20291 | 3.22773 | 3.21049 | 3.22400 | 3.20684 |
| $A_2$ | 4.05010 | 4.17887 | 3.93008 | 4.05806 | 3.99063 | 4.11890 |
| $A_3$ | 4.94457 | 5.10006 | 4.68335 | 4.84125 | 4.80299 | 4.93845 |
| $A_4$ | $-2.56847 \times 10^{-1}$ | $-9.86643 \times 10^{-2}$ | 2.51836 | 2.78998 | $9.78188 \times 10^{-1}$ | 1.01567 |
| $A_5$ | 3.88767 | 3.80369 | $4.60916 \times 10^{-1}$ | $8.07948 \times 10^{-1}$ | 1.71069 | 1.41575 |
| $B_0$ | $-6.24523 \times 10^{-3}$ | $-7.01577 \times 10^{-3}$ | $-6.23669 \times 10^{-3}$ | $-7.00781 \times 10^{-3}$ | $-6.24097 \times 10^{-3}$ | $-7.01211 \times 10^{-3}$ |
| $B_1$ | $-7.37614 \times 10^{-3}$ | $-7.70028 \times 10^{-3}$ | $-6.49387 \times 10^{-3}$ | $-6.81863 \times 10^{-3}$ | $-6.93498 \times 10^{-3}$ | $-7.25958 \times 10^{-3}$ |
| $B_2$ | $-1.03410 \times 10^{-2}$ | $-1.13864 \times 10^{-2}$ | $-3.47040 \times 10^{-3}$ | $-4.50121 \times 10^{-3}$ | $-6.90358 \times 10^{-3}$ | $-7.93334 \times 10^{-3}$ |
| $B_3$ | $-8.17083 \times 10^{-3}$ | $-9.51519 \times 10^{-3}$ | $-4.27025 \times 10^{-4}$ | $-1.68803 \times 10^{-3}$ | $-4.29155 \times 10^{-3}$ | $-5.54491 \times 10^{-3}$ |
| $C_0$ | $-4.88682 \times 10^{-7}$ | $-2.75915 \times 10^{-7}$ | $-6.40583 \times 10^{-8}$ | $-1.25609 \times 10^{-7}$ | $-3.11680 \times 10^{-7}$ | $-1.32412 \times 10^{-7}$ |
| Check: | 6.315 | 274.610 | 6.318 | 274.735 | 6.316 | 274.647 |

(check values at temperature of 10°C and salinity of 35‰)

estimated from these formulae agree to within an rms deviation of $\pm 0.3\%$ ($\pm 1.01$ $\mu$mol kg$^{-1}$). The deviations in $C_o{}^*$ at low $T$ and high $S$, between these formulae, are of importance in the context of the current analytical precision of dissolved $O_2$ measurements and the need to extrapolate to the thermohaline range of the world ocean. For routine computation of $C_o{}^*$ in seawater, we recommend using Eq. 8 and the solubility coefficients in Table 1 derived from the more precise data of Benson and Krause (1984)

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