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The solubility of neon, nitrogen and argon in distilled water and seawater

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Abstract

Large discrepancies in published neon and nitrogen solubility data limit the interpretation of oceanic measurements of these gases. We present new solubility measurements for neon, nitrogen and argon in distilled water and seawater, over a temperature range of 1–30 °C. Water was equilibrated with air at measured temperatures, salinities and pressures. Dissolved Ne concentrations were then determined by isotope dilution using a quadrupole mass spectrometer. Ratios of O₂/N₂/Ar were measured on a stable isotope ratio mass spectrometer, from which absolute N₂ and Ar concentrations were calculated using published O₂ solubilities. We propose new equations, fitted to the data, for the equilibrium concentrations of Ne, N₂ and Ar with estimated errors of 0.30%, 0.14% and 0.13%, respectively. The Ar results matched those of most previous researchers within 0.4%. However, the Ne and N₂ results were greater than those of Weiss (1971b, 1970) by 1% or more.

1 Introduction

The dependence of gas solubility on temperature and salinity primarily controls the concentrations of inert

gases dissolved in natural waters. Although the concentration of a gas like argon varies by fifty percent from warm subtropical waters to the cold deep ocean, the range in Ar saturation (the difference between observed Ar concentrations and predicted equilibrium concentrations) is usually less than a few percent (Spitzer and Jenkins, 1989; Emerson et al., 1995; Hamme and Emerson, 2002). Neon and nitrogen are also generally within a few percent of equilibrium (Well and Roether, 2003). These deviations from equilibrium are forced by diffusive and bubble-mediated air-sea gas exchange, rapid temperature change, and atmospheric pressure (Craig and Weiss, 1971; Schudlich and Emerson, 1996; Hamme and Emerson, 2002), with ice processes dominant in some areas (Hood et al., 1998; Hohmann et al., 2002). Over the last few decades, the analytical error in measuring these gases has decreased by close to an order of magnitude, resulting in precisions of a couple tenths of a percent (e.g. Hamme and Emerson, 2004). These advances are allowing gas biogeochemistry to expand into many new applications. However, all these applications depend on accurately determining the departure of gas concentrations from their equilibrium values, which requires solubility curves with an accuracy similar to that of the field measurements.

Many of these applications rely on a suite of gases with different solubilities and temperature dependencies, such as Ne, N₂ and Ar (Figure 1), to determine the rates of

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physical processes such as gas exchange and temperature change (Craig and Weiss, 1971; Bieri, 1971; Hamme and Emerson, 2002). For example, inert gas measurements are used to separate physical from biological processes acting to produce oxygen supersaturation in the upper ocean, and hence to determine carbon export from net biological O_2 production (Craig and Hayward, 1987; Spitzer and Jenkins, 1989; Emerson et al., 1997). This technique is moving toward employing moored gas tension devices to measure N_2 and estimate the bubble-induced supersaturation of O_2 (Emerson et al., 2002). Accurate gas saturations are critical for this application. Emerson et al. (1995) showed that a 0.3% error in their N_2 and Ar saturations led to a 65% error in the net biological O_2 production value they derived from the gas measurements. Further modeling work with a time-series of Ne, N_2 , and Ar data collected in 2000–01 near Hawaii has shown that 0.2% errors in the measured gas saturations would alter estimated O_2 fluxes through bubble-mediated gas exchange by 45% (Hamme and Emerson, unpublished data).

Accurate measurements of Ne, N_2 and Ar saturations are also important to a variety of other geochemical applications. N_2 /Ar ratios in suboxic areas of the ocean yield estimates of excess N_2 produced during denitrification (Codispoti et al., 2001). The paleotemperature of ground waters can be determined from Ne, N_2 and Ar (Stute et al., 1992; Stute and Schlosser, 1993). Neon is useful in correcting tritium/ ^3He flux estimates for injected air from bubbles (Jenkins, 1988), and in determining the amount of helium released from the earth's mantle and crust (Craig and Weiss, 1971; Roether et al., 1998, 2001). Therefore, we must not only have accurate methods to measure gas concentrations, but also solubility relationships accurate to within a few tenths of a percent over the range of temperatures and salinities found in natural waters.

The most recently published solubility measurements for Ne in distilled water and seawater disagree by more than one percent (Table 1). Discrepancies of greater than one percent also exist among published values for N_2 solubility in distilled water. In contrast, Ar solubilities determined by these same researchers were generally within 0.4%, except for the seawater values of Murray and Riley (1970), which were shown by Weiss (1971a) to have an unusual dependence on salinity. (See Clever (1979), Battino (1982) and Clever (1980) for a full review of the older Ne, N_2 and Ar solubility data not presented

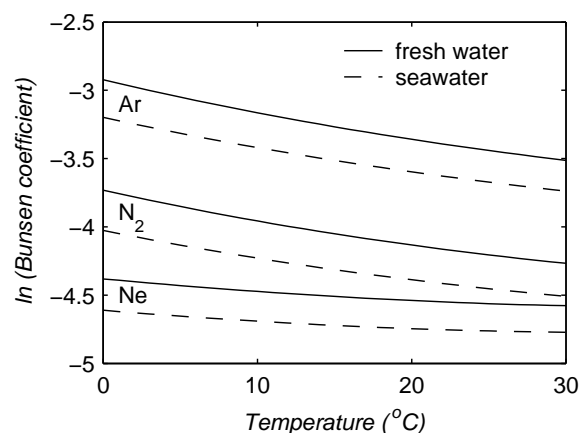


Figure 1: Comparison of the natural log of Bunsen solubilities determined for Ne, N_2 and Ar for both fresh water and seawater. The slope of the lines indicates the degree to which gas solubilities are dependent on temperature, demonstrating that Ar and N_2 have similar temperature dependencies while Ne is less than half as dependent on temperature. The y-intercept of the lines shows the overall solubility of the gas, demonstrating that Ne is about three times less soluble than Ar and that N_2 is about two times less soluble than Ar.

here.) Although different techniques were used by different groups to determine solubility (Table 1), no clear source of systematic error has been identified for any one method. Still, a pattern emerges in which lower solubility values have been measured for the more insoluble gases (Ne and N_2) by determining the change in the volume of a closed system as a pure gas dissolves into initially degassed water.

Because solubility discrepancies on the order of one percent produce drastic errors in the emerging field of biological O_2 determination and other applications, we have redetermined the solubilities of Ne, N_2 , and Ar in distilled water and seawater over a temperature range of 1–30 °C. Briefly, we equilibrated water with atmospheric air and measured the concentrations of dissolved gases by our field methods. This yielded a direct measurement of Ne solubility, while N_2 and Ar solubilities were further derived from the published O_2 solubility curve of García and

Table 1: Comparison of this work with the methods and results of previous solubility determinations

Gas / Salinity	reference	method	deviation from this work
(a) Neon			
distilled	Benson and Krause (1976)	pressure measurement ¹	0.36±0.45 %
distilled	Weiss (1971b)	volume change ²	-0.94±0.61 %
distilled	Top et al. (1987)	concentration measurement ³	-0.97±0.45 %
seawater	Weiss (1971b)	volume change ²	-1.54±0.83 %
seawater	Top et al. (1987)	concentration measurement ³	-0.39±0.63 %
(b) Nitrogen			
distilled	Klots and Benson (1963)	pressure measurement ¹	0.29±0.29 %
distilled	Emerson et al. (1999)	concentration measurement ³	0.07±0.12 %
distilled	Douglas (1964)	volume change ²	-1.00±0.19 %
distilled	Murray et al. (1969)	volume change ²	-0.96±0.54 %
distilled	Weiss (1970)	compilation ⁴	-0.92±0.10 %
seawater	Douglas (1965)	volume change ²	-1.24±0.24 %
seawater	Murray et al. (1969)	volume change ²	-1.09±0.54 %
seawater	Weiss (1970)	compilation ⁴	-1.13±0.02 %
(c) Argon			
distilled	Klots and Benson (1963)	pressure measurement ¹	0.07±0.17 %
distilled	Emerson et al. (1999)	concentration measurement ³	0.00±0.12 %
distilled	Douglas (1964)	volume change ²	-0.15±0.05 %
distilled	Murray and Riley (1970)	volume change ²	-0.26±0.18 %
distilled	Weiss (1970)	compilation ⁴	-0.12±0.06 %
seawater	Douglas (1965)	volume change ²	-0.35±0.12 %
seawater	Murray and Riley (1970)	volume change ²	-0.72±0.37 %
seawater	Weiss (1970)	compilation ⁴	-0.33±0.04 %

¹ After equilibration of degassed water with a pure gas, the pressure of the dissolved gas and of the gas headspace were measured.

² The volume change of a system was measured as pure gas dissolved into degassed water. Geometries of the systems and exact techniques varied slightly between the groups.

³ After equilibration of water with atmospheric air of a known pressure, the concentration of the dissolved gas of interest was measured. This was also the method used for this study.

⁴ Weiss (1970) used the results of Douglas (1964), Douglas (1965) and Murray et al. (1969) to construct a curve for N₂, but only the results of Douglas (1964) and Douglas (1965) to construct an Ar curve.

Gordon (1992). Our Ne results were slightly below the data of Benson and Krause (1976), but generally 1% or more above the data of Weiss (1971b) (Table 1). Our N₂ results agreed well with those of Klots and Benson (1963) and Emerson et al. (1999), but were about 1% higher than those determined by the volume change method. Finally, our Ar results supported the majority of other recently published results within 0.4%.

2 Methods

We slightly modified the method of Emerson et al. (1999) to produce water equilibrated with the atmosphere at known temperatures and pressures. Approximately 3 l of water was placed in a 5-l glass sphere. The sphere had three valves at the top to allow for water sampling and flushing of the headspace (Figure 2). We used either distilled deionized water or seawater collected from 1000m at the Hawaii Ocean Time-series station and stored at 4 °C. Saturated HgCl₂ solution was added to the water to eliminate biological activity (3 ml in early experiments, 1.2 ml in later ones). The sphere was immersed in a 225-l water bath, using round, flexible, lead weights to hold it down. A small stirbar and an air-driven magnetic stirrer, supplied by an air pump, kept the water inside the sphere well-mixed.

The bath and associated equipment were housed in a controlled-temperature room set at the temperature of the water bath. Humidity in the room was regulated at 50–70% to discourage evaporation from the water bath, which would cool the surface of the water and could create temperature gradients in the water bath. The temperature of the water was stabilized with a NesLab circulating constant temperature water bath. The temperature of the bath was measured and recorded every minute with a Sea-Bird Electronics SBE 39 temperature recorder to an estimated accuracy of ± 0.002 °C. After the sphere was immersed in the water bath, room air was gently bubbled into the water for 2–4 d, to encourage the gases to approach equilibrium, by inserting a 3/16" ID tube connected to an aquarium air pump into the central dip tube of the sphere. Air for the room's ventilation system was drawn in from the receiving area of the building, which was in good communication with outside air. After the bubbling, the sphere remained open to the atmosphere for 1–2 d before all the

valves were closed. The room pressure as the sphere was isolated from the atmosphere was determined from measurements made nearby with a Vaisala PTB 220A silicon capacitive pressure sensor at the Atmospheric Sciences Department of the University of Washington. Adjusted for height differences, this sensor has an accuracy of 0.2 hPa. Experiments with a Hg manometer and an MKS Baratron 1000-Torr pressure gauge showed that the pressure inside the room was not significantly different from atmospheric pressure outside the building. These instruments were not used to determine the starting pressure directly, because the Hg manometer could not be read as precisely, and the Baratron pressure gauge was highly affected by room temperature and a slow drift in the zero reading (Hyland and Tilford, 1985).

The main differences between this method of producing equilibrated water and that of Emerson et al. (1999) were: (1) a SeaBird temperature sensor was used in place of reversing thermometers to monitor the temperature of the bath; (2) an air-driven stirrer was used instead of an electric one to eliminate a source of heat in the bath; (3) air was bubbled through the water to encourage equilibration, not just flowed through the headspace; (4) the entire experiment and sampling were carried out in a temperature and humidity controlled room; and (5) actual seawater was used in place of a NaCl solution.

About two weeks after closing the sphere, the experiment was sampled. First, the Baratron pressure gauge was attached to one of the headspace valves with a 1/2" Cajon Ultra-Torr union O-ring compression fitting, so that the pressure inside the sphere could be measured. The dead space trapped inside the valve neck by the pressure gauge was initially at the current room pressure, but was only about 0.4% of the volume of the sphere's headspace leading to at most a 0.15 hPa error in the pressure reading. For each experiment, the Baratron pressure gauge was calibrated against the Atmospheric Sciences Department measurements to determine corrections for room temperature and zero reading fluctuations. After measuring the pressure, the sphere was removed from the bath, a tygon tube inserted into the neck of the middle valve, and a flow of water started by siphon. Three Winkler oxygen samples were collected and preserved, followed by 3–4 O₂/N₂/Ar samples and 3–4 Ne samples interspersed, followed by 2 more oxygen samples, and finally a salinity sample for seawater experiments.

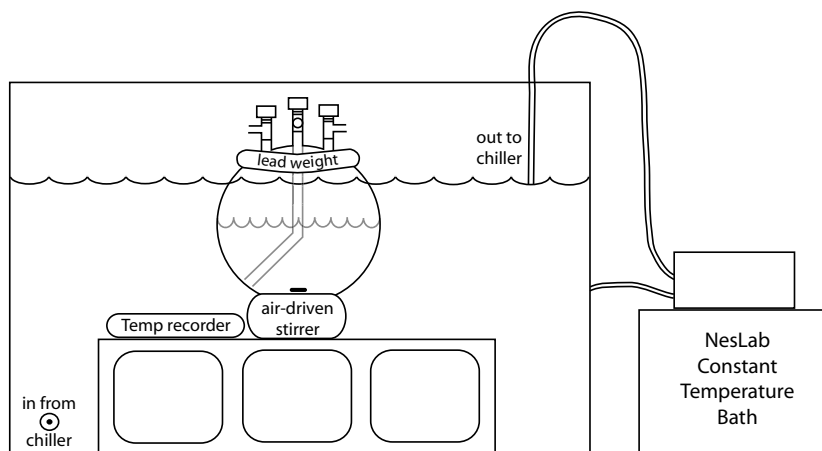


Figure 2: Schematic of the system used to produce air-equilibrated water. The apparatus was placed on cinder blocks in the water bath to allow for a greater volume of water and therefore thermal mass. Three 9-mm, Louwers Hapert, glass, O-ring sealing valves were located at the top of the sphere. The central valve was connected to a glass dip tube that extended to near the bottom of the sphere for water sampling.

Oxygen samples were analyzed by Carpenter-Winkler titration using a visually determined endpoint. For each experiment, the O_2 measurement was standardized with a solution freshly prepared from desiccated KIO_3 crystals purchased from WAKO and oven-dried for four hours at $100^\circ C$. Comparisons with standard solutions prepared from Aldrich reagent-grade KIO_3 agreed to $0.05 \pm 0.15\%$ after a 0.3% correction for impurities (Emerson et al., 1999). Titration blanks were determined on water identical to that used for the experiment. We estimate a routine accuracy of 0.2% for the O_2 measurements (Emerson et al., 1999), while our precision was 0.08% based on analysis of replicate samples.

Neon measurements were made by isotope dilution on a UTI 100C quadrupole mass spectrometer (see Hamme and Emerson, 2004, for a full description). A precise amount of ^{22}Ne was first added to evacuated 160 mL glass flasks. During sampling, water was sucked into the flasks until they were about half-full. The water was equilibrated with the headspace and then removed, leaving most of the gas behind. This gas sample was then cryogenically processed to remove all gases except Ne and He before being introduced to the quadrupole mass spectrometer where the

$^{22}Ne/^{20}Ne$ ratio was measured. Daily measurements of the $^{22}Ne/^{20}Ne$ ratio in air samples were used to correct for mass fractionation. The accuracy of the Ne concentration determined by this method is estimated to be $\pm 0.18\%$. There is also an uncertainty of $\pm 0.2\%$ in the Ne concentration of air (Glueckauf, 1951), which we used as our standard. Combined, this results in an overall accuracy estimate of $\pm 0.27\%$. However, all published Ne methods rely on air as a standard, so this portion of the solubility error would cancel for those methods.

Ratios of $O_2/N_2/Ar$ were measured on a stable isotope ratio mass spectrometer (see Emerson et al., 1999, for a full description). Sampling and equilibration were the same as for the Ne method, except that no isotopic spike was added to the flasks before sampling. O_2/Ar , O_2/N_2 , and N_2/Ar ratios were then measured on a dual-inlet Finnigan MAT 251 mass spectrometer. The $O_2/N_2/Ar$ ratios determined this way were sensitive to the O_2 difference (here quantified by the O_2/N_2 ratio) between the gases in the two inlets of the mass spectrometer (Emerson et al., 1999). The solubility samples were run against a standard with a very similar O_2/N_2 ratio (0.515); however, the standard was calibrated against air, which has

an O_2/N_2 ratio of 0.268. This was the main source of possible systematic error in the $O_2/N_2/Ar$ measurements. We determined the O_2 difference correction factor for N_2/Ar by comparing the mass spectrometer's response to standards created by combining a single N_2/Ar mixture with different amounts of pure O_2 (Emerson et al., 1999). This technique worked well for N_2/Ar , but it was not precise enough to determine correction factors for O_2/Ar and O_2/N_2 , because the relative amount of O_2 and N_2/Ar added to the standards could not be controlled well enough. Instead, we chose to tune the O_2/Ar correction to force our distilled water O_2/Ar results to agree with those of Klots and Benson (1963) and Weiss (1970) near 15 °C where the published values agree best (within 0.03%). The O_2/N_2 correction factor could then be calculated from the O_2/Ar and N_2/Ar factors. The correction factors for the calibration of our main standard against air were 1.00024 ± 0.00049 for O_2/Ar , 0.99977 ± 0.00051 for O_2/N_2 , and 1.00048 ± 0.00013 for N_2/Ar .

3 Results

Fourteen equilibration experiments were completed at a range of temperatures and salinities (Table 2). The difference between the measured pressure at the beginning and end of the equilibration was never more than 1.4 hPa ($\sim 0.1\%$). We assumed that relative humidity was 100% inside the sphere as it was closed, and used the starting pressure, which is subject to fewer errors, for all calculations. Oxygen concentrations measured by titration agreed well with previous researchers (Figure 3). In particular, our O_2 results were within $0.11 \pm 0.07\%$ of equilibrium values from García and Gordon (1992) for the temperature, salinity and starting pressure of the experiments, which is within our analytical error of 0.2%. All O_2 solubilities used for calculations in this study were taken from the fit of García and Gordon (1992, 1993) to the data of Benson and Krause (1984).

Our O_2 measurements indicate that dissolved O_2 came to equilibrium with the headspace by the time the experiment was sampled. This must have been true for Ar as well, since both gases have very similar solubilities, temperature dependencies and diffusion coefficients. In contrast, Ne and N_2 are both less soluble, but this would not have resulted in disequilibria for these gases. The bub-

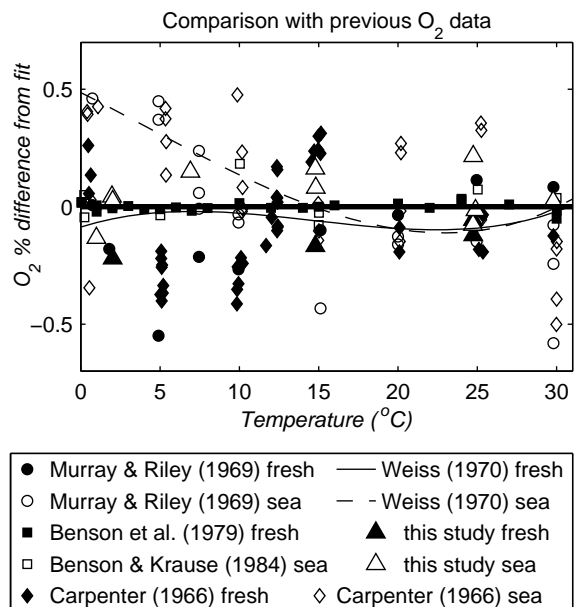


Figure 3: Each symbol shows the percent difference between the predicted O_2 equilibrium value calculated from García and Gordon (1992) and the O_2 solubility data from this study or the published results of Carpenter (1966), Murray and Riley (1969), Benson et al. (1979), or Benson and Krause (1984). Equilibrium values were calculated for the temperature and salinity corresponding to each experiment (heavy center line at 0%). Fresh (filled symbols) indicates data from distilled water, while sea (open symbols) indicates data from experiments with salinity ζ 25 (PSS). The differences between the fits proposed by Weiss (1970) and García and Gordon (1992) are also shown for salinities of 0 and 35.

bling procedure during set-up of the experiment could have produced a supersaturation of the gases in the water, but we have several lines of evidence that this did not prevent the gases from reaching equilibrium with the headspace by the end of the experiment. First, as will be shown later, our N_2 results agree closely with those of Emerson et al. (1999), who used nearly the same equilibration procedure but without bubbling at the beginning of the experiment. Second, bubbles with a diameter of about 0.5 cm were produced by the aquarium pump at

Table 2: Temperature, salinity, pressure and oxygen concentrations of equilibration experiments

Expt. #	Length (days)	Temp (°C)	Salinity (PSS)	Starting pressure (hPa)	Ending pressure (hPa)	O ₂ (μmol/kg)	ΔO ₂ (%)
6	35	2.016±.004	34.537	1018.2	1019.5	333.45±0.07 (n=4)	0.02
7	22	2.012±.002	0.074	1015.3	1015.6	431.77±0.47 (n=5)	-0.22
8	21	24.734±.055	34.607	1020.2	1020.2	209.50±0.18 (n=5)	-0.08
9	16	24.725±.017	0.074	1022.9	1022.1	262.50±0.25 (n=5)	-0.06
10	9	14.786±.006	34.447	1013.0	1013.0	250.11±0.17 (n=5)	0.16
11	9	14.785±.006	0.030	1016.5	1016.6	317.27±0.23 (n=5)	-0.17
12	14	1.970±.003	34.442	1021.4	1021.5	335.00±0.37 (n=5)	0.04
14	15	6.907±.004	34.469	1014.0	1013.7	295.83±0.16 (n=5)	0.15
15	15	14.816±.007	34.493	1016.8	1016.9	250.64±0.20 (n=5)	0.08
16	14	24.743±.018	34.531	1016.5	1017.0	209.39±0.34 (n=5)	0.22
17	13	29.789±.010	34.586	1015.5	1015.1	192.32±0.11 (n=2)	0.02
18	14	24.888±.006	34.511	1014.9	1015.0	208.15±0.08 (n=5)	-0.01
19	14	24.748±.008	0.030	1016.5	1015.0	260.63±0.17 (n=5)	-0.12
20	17	0.991±.002	34.481	1013.8	-	340.29±0.14 (n=5)	-0.13

Length refers to the time between when the sphere was closed and sampled. The error in temperature is the standard deviation of recorded temperatures over the course of the experiment. Pressures include the contribution from water vapor (1 hPa = 1 mbar). The degree of oxygen supersaturation, ΔO₂, is based on García and Gordon (1992). n is the number of oxygen samples included in the mean. – indicates a missing measurement.

10-cm depth in the sphere. While small bubbles cause preferential supersaturation of low solubility gases, modelling results demonstrate that bubbles of this size would produce nearly equal supersaturations for all the gases (Memery and Merlivat, 1985; Fuchs et al., 1987). At most, a 1% supersaturation in all the gases could be generated at the beginning of the experiment by bubbling. Based on their diffusion coefficients, Ne and N₂ would then be expected to approach equilibrium at least as fast as O₂. Third, no relationship was observed between the length of time an experiment was allowed to equilibrate and the deviation of the O₂ measurements from equilibrium or the difference between the Ne, N₂ and Ar results and the Weiss (1971b, 1970) curves. This suggests that the experiments were not still approaching equilibrium when they were sampled. Finally, while our results for Ne and N₂ are higher than those determined by the volume change technique, they more closely agree with those generated by alternate techniques (Table 1). Based on these four arguments, the bubbling procedure could not have been responsible for the difference between our results

and those generated by the volume change technique.

The average precision in the Ne measurement was ± 0.23%, as determined from the replicate water samples for each experiment (Table 3). This was almost two times worse than the precision obtained by this method for field samples. The average precisions of the O₂/N₂, O₂/Ar, and N₂/Ar ratios were ± 0.066, ± 0.048, and ± 0.037 %, respectively, for these experiments. These values were close to the mass spectrometer precision for the repeated introduction of the same gas, ±0.04% (Emerson et al., 1999). The somewhat larger errors in Ne, compared with field samples, and in O₂/N₂, compared with standard runs, were probably due to complications in sampling a small volume of water and variability in gas handling. We observed no trend in the Ne concentrations or O₂/N₂/Ar ratios with the order in which the samples were taken. Also, oxygen samples collected before and after the inert gas sampling were not significantly different. This suggests that worse precision was not caused by drift in the dissolved gas concentrations during sampling.

Table 3: Neon concentrations and O₂/N₂/Ar gas ratios of equilibration experiments

Expt. #	Ne (nmol/kg)	O ₂ /N ₂	O ₂ /Ar	N ₂ /Ar
6	7.948±.023 (n=4)	0.5572±0.0002	20.441±0.006	36.687±0.007 (n=4)
7	9.870±.005 (n=4)	0.5483±0.0003	20.488±0.013	37.356±0.004 (n=4)
8	6.687±.017 (n=3)	0.5319±0.0004	20.346±0.010	38.259±0.011 (n=3)
9	8.110±.019 (n=4)	0.5249±0.0002	20.401±0.006	38.869±0.008 (n=4)
10	7.089±.013 (n=4)	0.5429±0.0001	20.383±0.006	37.547±0.007 (n=4)
11	8.708±.042 (n=4)	0.5352±0.0002	20.426±0.008	38.164±0.010 (n=4)
12	7.980±.008 (n=3)	0.5572±0.0004	20.445±0.008	36.694±0.018 (n=3)
14	7.570±.005 (n=3)	0.5513±0.0009	20.404±0.034	37.013±0.005 (n=3)
15	7.129±.018 (n=4)	0.5429±0.0001	20.384±0.005	37.548±0.008 (n=4)
16	6.682±.022 (n=4)	0.5317±0.0004	20.348±0.009	38.275±0.011 (n=4)
17	6.517±.012 (n=4)	0.5264±0.0004	20.346±0.010	38.656±0.013 (n=4)
18	6.685±.012 (n=4)	0.5322±0.0003	20.369±0.004	38.274±0.025 (n=4)
19	8.106±.018 (n=4)	0.5238±0.0011	20.381±0.010	38.910±0.061 (n=3)
20	8.030±.032 (n=3)	0.5577±0.0001	20.426±0.009	36.626±0.010 (n=3)

Ne concentrations are not corrected for pressure. O₂/N₂/Ar ratios are corrected for the mass spectrometer’s sensitivity to O₂ differences between the sample and standard. n is the number of measurements for either the Ne concentration or the O₂/N₂/Ar ratios.

4 Fitting equations

The goal of this research was to produce accurate empirical formulas that express the dependence of the solubilities of Ne, N₂ and Ar on temperature and salinity. Using the pressure measured at the beginning of the experiment, the measured Ne concentrations (Table 3) were corrected to 1-atm pressure of air including water vapor. The N₂ and Ar concentrations for each experiment were derived from the O₂/N₂ and O₂/Ar ratios (Table 3) and the O₂ solubility of García and Gordon (1992) for the temperature and salinity of the experiment.

Most proposed solubility equations have expressed the dependence on salinity using the Setchenow relation, which states that the natural logarithm of solubility is linearly related to salinity at any one temperature. With data at only two salinities, we could not independently evaluate the Setchenow relation and so accepted it. Several different forms have been proposed for the dependence of gas solubilities on temperature. Weiss (1970), Weiss (1971b), and Top et al. (1987) use the integrated form of the van’t Hoff equation to express temperature dependence, while Benson and Krause (1976) suggest a simple polynomial in 1/T. The temperature dependence of any of the previously

proposed solubility equations did not fit our data better than any other. García and Gordon (1992) showed that their form of the solubility equation was able to reduce errors associated with fitting O₂ solubility data. Based on this, we chose to adopt the temperature dependence of their polynomial:

$$\ln C = A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 + S(B_0 + B_1 T_s + B_2 T_s^2) \quad (1)$$

with

$$T_s = \ln\left(\frac{298.15 - t}{273.15 + t}\right), \quad (2)$$

where C is the gas concentration at equilibrium with a moist atmosphere at 1-atm pressure (nmol/kg for Ne and $\mu\text{mol/kg}$ for N₂ and Ar), t is the temperature ($^{\circ}\text{C}$), and S is the salinity (PSS).

To produce an initial guess of the coefficients (Table 4) for Equation 1, a singular value decomposition was performed on the means of the gas data for each experiment. This was followed by a Nelder-Mead, multidimensional, unconstrained, nonlinear minimization designed to minimize the sum of the squares of the differences between the data and the equation’s predictions. We used an F

Table 4: Coefficients for the calculation of Ne, N₂ and Ar solubilities from Equation 1.

Coef.	Ne (nmol/kg)	N ₂ (μmol/kg)	Ar (μmol/kg)
A ₀	2.18156	6.42931	2.79150
A ₁	1.29108	2.92704	3.17609
A ₂	2.12504	4.32531	4.13116
A ₃	0	4.69149	4.90379
B ₀	$-5.94737 * 10^{-3}$	$-7.44129 * 10^{-3}$	$-6.96233 * 10^{-3}$
B ₁	$-5.13896 * 10^{-3}$	$-8.02566 * 10^{-3}$	$-7.66670 * 10^{-3}$
B ₂	0	$-1.46775 * 10^{-2}$	$-1.16888 * 10^{-2}$
Check:	7.34121	500.885	13.4622
check values at temperature of 10 °C and salinity of 35 (PSS)			

Zeros in the table indicate that the inclusion of this term was not significant to the fit.

test, which relates the decrease in the sum of the squares between two polynomial fits to the decrease in degrees of freedom, to determine whether the addition of each term to the polynomial produced a statistically better fit at the 95% confidence level. This test showed that while all the terms in Equation 1 were significant for N₂ and Ar, some of the terms were not significant for Ne, as indicated by zeros in Table 4. In contrast to the van't Hoff and 1/T based polynomials, the addition or removal of terms from the García and Gordon (1992) polynomial had only a small effect on the coefficients of the other terms, which reinforced our confidence in the choice of this form.

The root mean square deviations of the experimental data means from the fitting equations were 0.014 nmol/kg (0.18%) for Ne, 0.26 μmol/kg (0.0531%) for N₂, and 0.0055 μmol/kg (0.041%) for Ar (Figure 4). The maximum deviations were 0.31% for Ne, 0.10% for N₂, and 0.07% for Ar, with deviations of the experimental data evenly distributed above and below the fitting lines. To obtain an estimate of the total error in solubility predicted from these new curves, the mean square error (square root of the sum of the squares divided by the number of degrees of freedom) was compounded with our estimates of accuracy or systematic offsets in the methods. For Ne, this included the estimated 0.18% error of the Ne method and a 0.02% error in the pressure reading to yield a total 0.30% error. For N₂ and Ar, the estimate of accuracy included a 0.1% error from the O₂ solubility curve and the

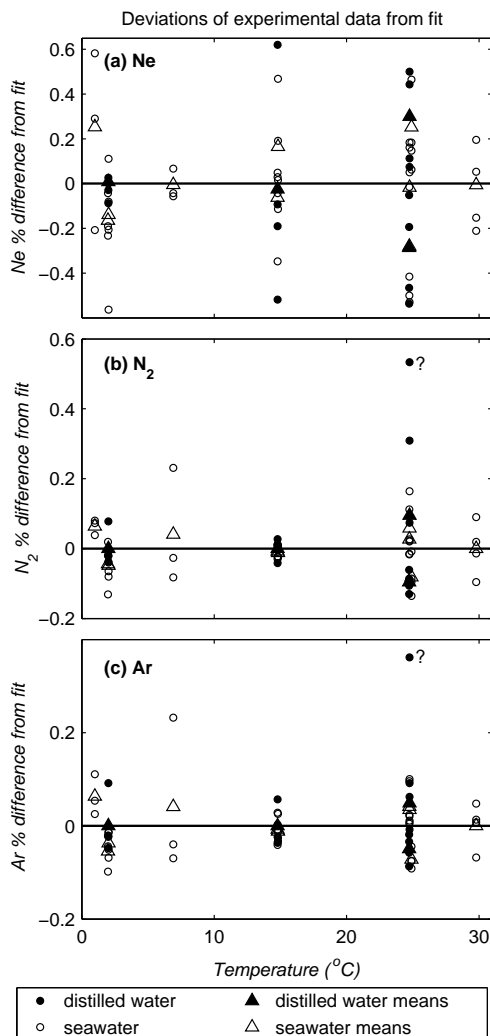


Figure 4: Percent deviations of the (a) pressure corrected neon, (b) nitrogen and (c) argon data from the proposed solubility curve at the actual temperature and salinity of each experiment. Each replicate is displayed along with the means of the experiments. Filled symbols are values from distilled water experiments, open symbols from seawater experiments. The ? designates a sample which was excluded as a flyer from the mean for that experiment.

estimated error in the mass spectrometer correction factors to yield total errors of 0.14% for N₂ and 0.13% for Ar.

The values from the fitting equations (in nmol/kg for Ne or $\mu\text{mol/kg}$ for N₂ and Ar) can be easily converted into the Bunsen coefficient, which describes the volume of pure dry gas at STP that will dissolve in a volume of water at equilibrium exposed to a partial pressure of 1 atm.

$$\beta = C * MV_C * \rho * (1 + vp) / \chi_C \quad (3)$$

where β is the Bunsen coefficient (L/L), C is concentration of the gas (mol/kg), MV_C is the molar volume of the gas at STP (L/mol), ρ is the density of the water (kg/L) (Millero and Poisson, 1981), vp is the saturation vapor pressure of the water (atm) (Millero and Leung, 1976; Ambrose and Lawrenson, 1972), and χ_C is the dry mole fraction of the gas in the atmosphere (Glueckauf, 1951). We use 22.425 L/mol for the molar volume at STP of Ne, 22.404 L/mol for N₂, and 22.393 L/mol for Ar, as calculated from the second virial coefficient of the gases (Dymond and Smith, 1980). The values from the fitting equations may be converted to the commonly used unit of cc of gas at STP / g of water using the molar volumes of the gases.

5 Conclusions

In general, our Ne distilled water results fall slightly below those of Benson and Krause (1976), but are greater than those of Weiss (1971b) and Top et al. (1987) by about 1% (Table 1, Figure 5). The difference between our results and Weiss (1971b) is even larger for seawater, especially at the temperature extremes. (For the seawater comparisons here and in Table 1, we have restricted the salinity range to 25–45 (PSS)). Our N₂ results agree quite well with those of Klots and Benson (1963) and Emerson et al. (1999) (Figure 6). In contrast, the data of Douglas (1964, 1965) and Murray et al. (1969) are lower than ours by about one percent. Except for the seawater data of Murray and Riley (1970), our Ar data falls within $\pm 0.4\%$ of other researchers. These discrepancies represent real differences between our gas data and those of previous investigators, and are not just based on differences in the choice of the form for the fitting equation.

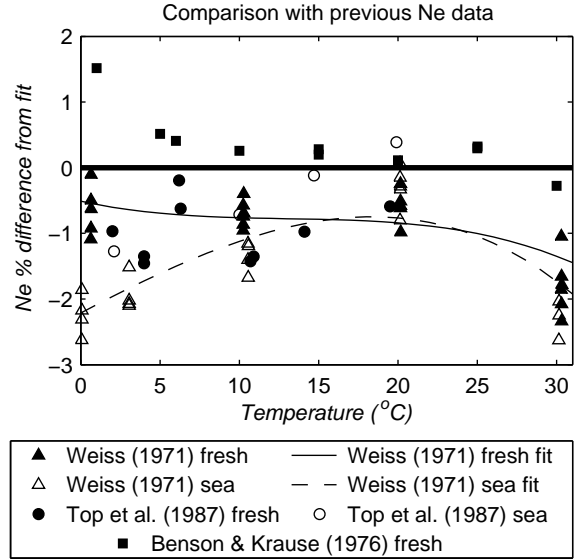


Figure 5: Each symbol shows the percent difference between Ne solubility data from the literature and our proposed solubility curve at the actual temperature and salinity of each data point (heavy center line at 0%). Fresh (filled symbols) indicates data from distilled water, while sea (open symbols) indicates data from experiments with salinity > 25 (PSS). The differences between the fits proposed by Weiss (1971b) and this study are also shown for salinities of 0 and 35.

We believe that Equation 1 combined with the coefficients listed in Table 4 represent the most accurate solubility estimates currently available for Ne, N₂, and Ar between 0 and 30 °C and for salinities spanning distilled water to seawater. We estimate that the errors in using these new curves to predict solubility are 0.30% for Ne, 0.14% for N₂ and 0.13% for Ar. More accurate estimates of O₂/N₂ and O₂/Ar can be obtained by combining our equations with that of García and Gordon (1992) for O₂, because this essentially reproduces our original ratio measurements. Our data for Ne and N₂ are both 1–2% higher than the curves commonly in use by oceanographers (Weiss, 1971b, 1970). This reevaluation of solubility will have a significant impact on estimates of the supersaturations of these gases in the ocean. For example,

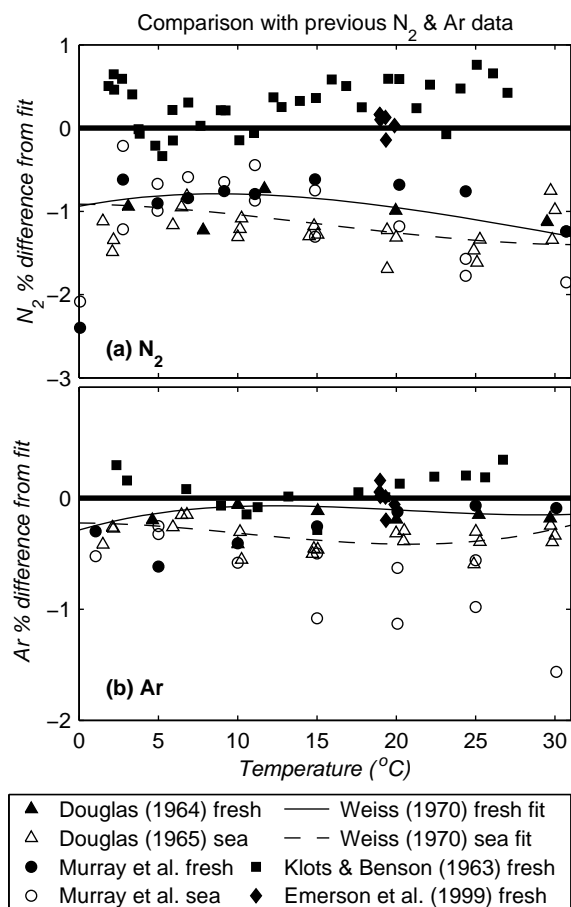


Figure 6: Same as Figure 5 except for (a)N₂ and (b) Ar. The differences between the fit proposed by this study and the compilation fits of Weiss (1970) are also shown for salinities of 0 and 35.

the revised average supersaturation values at the Hawaii Ocean Time-series are 1.6% for Ne and 0.24% for the N₂/Ar ratio (mean mixed layer, HOT cruises 117-127, Hamme (2003)), rather than 2.6% and 1.36%, respectively, as would have been calculated from the solubility curves of Weiss (1971b, 1970). These decreases in estimated mixed layer saturation on the order of 40% for Ne and 550% for N₂/Ar will have an enormous effect on estimates of air injection from bubbles at the ocean surface

and biological O₂ production estimates as well as on other applications.

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