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The effect of dissolved air and natural isotopic distributions on the density of water*

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ABSTRACT

The effects of dissolved air and of natural isotopic distributions on the density of water have been determined at 1 atm by using a magnetic float densimeter. Dissolved gases were found to decrease the density by $3.0 \pm 0.2 \times 10^{-6} \text{ g cm}^{-3}$ at 4°C. The apparent molal volumes of air were found to be nearly independent of saturation concentration and temperatures between 0° and 30°C. The decrease in density (to $\pm 0.2 \times 10^{-6}$) can be determined from, $\Delta d = -2.6 \times 10^{-3} \times c$ where c is the total concentration of air in moles/liter (O_2 , N_2 , Ar and CO_2) over the saturation and temperature range of ocean waters. The dissolved air experimental results were found to be in good agreement with those determined from partial molal volume data for gases determined by other workers. The ion exchanged Miami water used in our density studies was found to be $1 \times 10^{-6} \text{ g cm}^{-3}$ lower than distilled standard mean ocean water (SMOW) and Mediterranean deep water (MDW). All of our isotopic measurements were found to obey ($\pm 0.7 \times 10^{-6}$) the relationship developed by Menaché (1967)

$$\Delta d = 2.3 \times 10^{-7} \Delta\delta(^{18}\text{O}) + 1.8 \times 10^{-9} \Delta\delta(\text{D})$$

where Δd is the density difference (in g cm^{-3}) at 4°C between other waters and SMOW, and $\Delta\delta$ is the isotopic difference (in ppt).

1. Introduction

A study of the density of seawater solutions has recently been initiated in this laboratory (Millero, Gonzalez and Ward, 1975). In these studies, ion exchanged Miami tap water has been used as a density standard. To compare these seawater densities with those obtained by other workers (Knudsen, Forch and Sørensen, 1902), (Cox, McCartney and Culkin, 1970), and (Kremling, 1972), it is necessary to specify our standard water (hereafter designated as MIAMI) as accurately as possible relative to the other water standards.

To specify the density of water at a given temperature and at a pressure of one normal atmosphere (1.013b) to within one part per million (1 ppm), as discussed

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by Menaché (1967) one must know both the isotopic composition and the content of dissolved air. In order to compare the standard MIAMI water with established standards, covering the density range of purified natural waters, its density has been compared to other waters of known isotopic composition. To define the most suitable conditions for comparison, the effect of dissolved air on water density was also determined. The purpose of the present paper is to establish the relative density of MIAMI water to standard mean ocean water (SMOW) which will probably become a standard for future density studies (Girard and Menaché, 1972).

a. Isotope effect. In natural waters, according to Menaché (1967), the four major molecular species occur in the approximate proportions $H_2^{16}O/H_2^{18}O/H_2^{17}O/H^{16}OD = 997280/2000/400/320$. The isotope effect on the vapor pressure varies inversely with the molecular weight, leading to fractionation in natural precipitation and evaporation processes. The isotopic proportions of the heavier species decrease with increasing latitude and increasing altitude. These species distributions are determined in a mass spectrometer relative to those of a standard water. The isotopic ratios, D/H , $^{17}O/^{16}O$ or $^{18}O/^{16}O = R_x$, are expressed relative to those of a standard water as the per millage enrichment, $\delta = [(R \text{ sample}/R \text{ standard}) - 1] \times 10^3$. Determination of the absolute isotopic ratios in the standard water establishes the reported δ 's on an absolute scale. Using certain assumptions regarding the volumes of the molecular species, the absolute ratios may be used to predict the effect on density of the observed isotopic distribution.

Assuming the volumes of the molecular species to be equal, Menaché (1967) has deduced that

$$\rho_{MAX} - \rho_{MAX} (SMOW) = 0.23 \times 10^{-6} \Delta\delta(^{18}O) + 0.018 \times 10^{-6} \Delta\delta(D) \quad (1)$$

where the Δ quantities refer to the differences between two water samples in densities and in absolute per millage differences of isotopic ratios. The minor effect of ^{17}O on density is assumed to be 1/10 that of ^{18}O on the basis of the species concentration ratios and the mass differences of the oxygen isotopes. Menaché further simplified (1) by assuming that, for natural systems, $(\Delta\delta D)/(\Delta\delta^{18}O) = 8$, giving

$$\Delta d(10^{-6} g \text{ cm}^{-3}) = 0.37 \Delta\delta(^{18}O) \quad (2)$$

which, according to Dansgaard (1964) corresponds to a single-stage Raleigh enrichment process at 20°C.

By using the world-wide ^{18}O distribution data of Dansgaard (1961), Menaché concluded that $\delta^{18}O$ for undiluted ocean water varied only within 1%, which corresponds to 0.37 ppm in density; while in water influenced by continental runoff, particularly in high latitudes, values of $\delta^{18}O$ had been found corresponding to 10 ppm difference in density. Recently, Menaché and Girard (1970) have performed

density measurements on waters of known isotopic composition and have established that the constants in equation (1) are correct to within 10%.

The above described correlation between density and mass spectroscopic data is well established and useful. However, for the purposes of our study, we have chosen to compare directly, using a magnetic float densimeter, our standard water with other standard waters of known composition.

b. Effect of dissolved air. Marek (1891) measured the density differences at different temperatures between air-free water and water saturated at one atmosphere. From 0° to 14°C, the density decreased about 3 ppm during saturation, and the effect was smaller at higher temperatures. Chappuis (1910) proceeded to repeat the work of Marek and concluded that, after 4 days of undisturbed exposure to air, water which had been initially air-free was only 74% saturated to a depth of 12 cm. Afterwards, by precise measurements, Chappuis (1910) found that at 3° and 5°C, air-free water decreased 3 ppm in density during saturation. Richards and Harris (1916), using a float equilibrium technique, reported that the decrease in density during air saturation at 20°C was 0.2 ppm, which is only half Marek's value. Emeléus *et al.* (1934) using essentially the same technique, observed a 2 ppm decrease in density accompanying air saturation at 20°C which is five times Marek's 20°C value.

Because of the sketchy and contradictory information available, this study was undertaken which was specifically designed to meet our requirements. These results describe the effect on density of different concentrations of air in water at 4°C and in saturated solutions at 4°, 15° and 25°C.

2. Experimental

The density measurements were made with a magnetic float apparatus which is described in detail elsewhere (Millero, 1967). The solenoid was constructed with fewer turns than used in previous studies to increase the sensitivity (Millero, 1967) — 65 μ amp for a 1 ppm change in density. Once the system was calibrated it was not removed from its support so as to eliminate errors due to positioning. Samples (65 cm³) were introduced into the solution cell by means of a Teflon syringe needle threaded through the stopcock bore on the top of the cell. The densimeter was calibrated at 4°C using ion exchanged (Millipore Super Q) water using a density of 0.999972 g cm⁻³ (Kell, 1967).

The densimeter was completely immersed in a 30 liter constant temperature bath. A Hallikainen Thermotrol was used to regulate the temperature of the bath to $\pm 0.001^\circ\text{C}$. The bath temperature was set with a platinum resistance thermometer calibrated by the National Bureau of Standards and a G-2 Mueller Bridge. The temperature was monitored with a Hewlett-Packard quartz crystal thermometer.

The isotopic standard waters used in this study were obtained from IAEA in

Table 1. Absolute isotopic analyses of six standard waters.

Sample	$D/H \times 10^{-6}$	$^{18}O/^{16}O \times 10^{-6}$	$\delta D(\text{‰})$	$\delta^{18}O(\text{‰})$
MDW	157.2	1996.0	+9.3	+1.3
SLAP	89.02	1883.8	-428	-55.0
MIAMI	154.4	1989.2	-9.0	-2.1
SMOW	155.76	1993.4	0.0	0.0
NBS-I	148.3	1977.6	-48.0	-7.9
NBS-IA	127.2	1944.9	-183.4	-24.3

Vienna, sealed in glass ampules. The NBS-I sample is distilled Potomac River water, the NBS-IA sample is distilled Yellowstone National Park water, and the SLAP sample is distilled precipitation obtained in the Antarctic called standard light Antarctic precipitation. The SMOW sample (Craig, 1961) is distilled standard mean ocean water. The MIAMI water is 18 meg Ω ion exchanged (Millipore Super Q) tap water. The isotopic ratios assigned to SMOW were $^{18}O/^{16}O = (1993.4 \pm 2.5) \times 10^{-6}$ (Craig, 1961) and $D/H = (155.76 \pm 0.05) \times 10^{-6}$ (Hagemann, Nief and Roth, 1970). Also included in this study is a sample of distilled Mediterranean deep water (MDW) which was the density standard used by Cox *et al.* (1970). The isotopic ratios of this sample relative to SMOW were found by Menaché (personal communication, 1972) to be 1996.0×10^{-6} for $^{18}O/^{16}O$ and 147.2×10^{-6} for D/H . The sample of MIAMI was analyzed by Friedman (personal communication, 1972) as 1989.2×10^{-6} for $^{18}O/^{16}O$ and 154.4×10^{-6} for D/H . The absolute isotopic ratios and per millage enrichment factors for the six standard waters are given in Table 1.

The samples of MIAMI water used in the dissolved gas measurements were saturated by bubbling filtered air through a shallow volume maintained at a fixed temperature. Two types of density measurements were made: 1. Measurements of water samples at a fixed temperature (4°C) that were saturated at different temperatures. These measurements were made to determine the apparent molal volume of air at different concentrations and a fixed temperature. 2. Measurements of saturated water samples at the same temperature at which they were saturated. These measurements were made to determine the temperature dependence of the apparent molal volume of air at saturation. For the first type of measurement, the samples were transferred to the densimeter cell (kept at 4°C) using a Teflon syringe. The density of the sample was measured after thermal equilibrium (within 1/2 hr). During the equilibrium period the sample was isolated from the atmosphere. The cell was emptied for degassing by using a Teflon syringe and needle that extended to the bottom of the solution container of the densimeter. The saturation was approached from both under and over saturation at four temperatures (4° , 20° , 30° and 50°C). The mean deviation of the densities determined on these samples was ± 0.2 ppm. The samples were degassed by using a vacuum system and repeatedly

Table 2. The effect of dissolved air on the density of water.

Experiment 1

Temp °C	$c \cdot 10^4$ ^a mol l ⁻¹	M g mol ⁻¹	$-\Delta d \cdot 10^6$ g cm ⁻³	ϕ_v cm ³ mol ⁻¹
4	5.7	29.71	2.2 ± 0.2	33.5 ± 0.4
	7.1	29.76	2.4 ± 0.2	33.1 ± 0.3
	8.4	29.80	2.5 ± 0.2	32.8 ± 0.2
	12.0	29.75	3.0 ± 0.2	32.3 ± 0.1

Experiment 2

Temp °C	$c \cdot 10^4$ mol l ⁻¹	M g mol ⁻¹	$-\Delta d \cdot 10^6$ g cm ⁻³	ϕ_v cm ³ mol ⁻¹
4	12.0	29.75	3.0 ± 0.2	32.3 ± 0.1
15	9.3	29.81	2.0 ± 0.2	32.0 ± 0.2
25	7.7	29.78	1.7 ± 0.2	32.0 ± 0.2

a) The molarities were determined at the saturation temperatures, respectively, 50°, 30°, 20° and 4°C.

shaking the flask until no bubbles could be nucleated (~ 1/2 hr). The densities of the degassed samples were measured on the same sample previously air saturated. For the second type of measurements the samples were saturated at a given temperature (15° and 25°C) and transferred to the cell kept at the same temperature. The degassing was accomplished in a manner similar to that used in the first type of measurements.

The density of the six standard waters was determined as described above. Since the specific resistances of the samples received were low, the samples were distilled before use. The distillation apparatus and procedure was patterned after the methods of Cox *et al.* (1968), which as shown by Menaché (1971) did not change the isotopic composition. Since our recovery was greater than 99.5%, it is unlikely that the one-stage distillation we made could introduce an appreciable error. Similar distillations on MIAMI ion-exchanged water had no effect on the density (i.e., within our experimental precision ± 0.2 ppm). The isotopic waters were saturated with air at 4°C before use. The air saturation condition was chosen because there were insufficient quantities of the isotopic samples to completely fill the densimeter cell and the samples could not be completely isolated from the air. At the saturated condition the densities were found to not drift during the measurement (about 1 hr). The changes in atmospheric pressure during an experiment were not sufficient to change the density (a millibar change in pressure changes the density by 0.5 ppm).

3. Results and discussion

The effect of dissolved air on the density of water has been determined at various concentrations at 4°C and at saturation at 4°, 15° and 25°C. The results are given

in Table 2. The maximum decrease in density was found at saturation and at 4°C. The decrease in density becomes smaller at higher temperatures and when the solution becomes undersaturated, as one would expect. To analyze this density data it is useful to determine the apparent molal volume (ϕ_V) of air defined by

$$\phi_V = -10^3 \Delta d/d^0 c + M/d^0 \quad (3)$$

where $\Delta d = d - d^0$ is the difference in the density (g cm^{-3}) of the solution and of degassed pure water (Kell, 1967), c is the total molarity (moles/liter) of the dissolved gases and M is the mean molecular weight of air in an aqueous solution. The total molarity is equal to the sum of the molarities of the major dissolved gases N_2 , O_2 , Ar and CO_2 . The values of c given in Table 2 have been determined from the tabulations of Weiss (1970, 1975) and Kester (1975) at a total pressure of 1 atm with a composition of 0.7808 atm of N_2 , 0.2095 atm of O_2 , 9.34×10^{-3} atm of Ar and 3.3×10^{-4} atm of CO_2 (Kester, 1975). The mean molecular weight of air is determined from

$$M = \sum N_i M_i \quad (4)$$

where $N_i = c_i/c$ (c_i is the molarity) is the mole fraction and M_i is the molecular weight of component i . Since N_i is slight dependent upon temperature, M is also slightly dependent upon temperature. The apparent molal volume of air determined from equation (3) is given in Table 2. The ϕ_V is slightly dependent upon concentration (see Figure 1) and can be fitted to the linear equation ($\pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$)

$$\phi_V = 34.5 + 0.18_4 \times 10^4 c \quad (5)$$

Since the concentration dependence of ϕ_V is small and nearly within our experimental error, it is not possible to be sure if this effect is real. The ϕ_V of more soluble nonelectrolytes are known to have a concentration dependence, but the effect is normally small. The saturation values of ϕ_V at various temperatures are constant within the experimental error of the measurements. The decrease in density can be determined from the rearranged form of equation (3)

$$\Delta d = 10^{-3} [M - \phi_V d^0] c \quad (6)$$

By assuming $\phi_V = 32.3 \text{ cm}^3 \text{ mol}^{-1}$ the value of $10^{-3} [M - \phi_V d^0]$ equals -2.6×10^{-3} . This equation predicts values for Δd that agree with the measured values to $\pm 0.3 \times 10^{-6}$ (with a maximum deviation of 0.7×10^{-6}) over the entire temperature and concentration range.

Since the partial molal volume $\bar{V} = \phi_V + (\partial \phi_V / \partial c) c$ of the dissolved gases N_2 , O_2 and CO_2 have been measured or calculated by other workers (Kritchevsky and Plüskaya, 1935; Enns, Scholander and Bradstreet, 1965; O'Sullivan and Smith, 1970; Millero and Berner, 1972; Bradshaw, 1973; and Weiss, 1975), it is possible

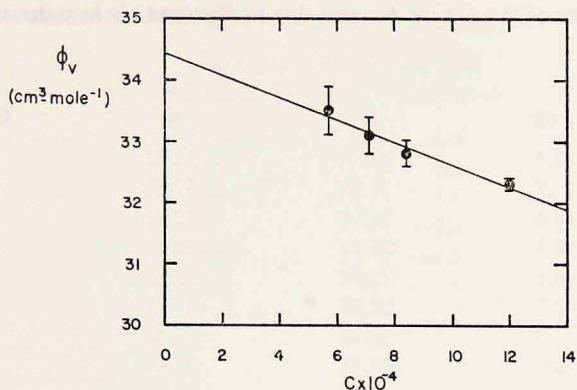


Figure 1. The apparent molal volume of dissolved air in water at 4°C plotted vs the total molarity of dissolved gases.

to estimate the ϕ_V of air. The value for the \bar{V} of N_2 , O_2 and CO_2 are all near $33 \text{ cm}^3 \text{ mol}^{-1}$ (see Table 3). By using the values of $\bar{V} = 33.0$ for N_2 , $\bar{V} = 32.0$ for O_2 , $\bar{V} = 32.3$ for CO_2 and assuming $\bar{V} = 32.0$ for Ar , we obtain the values $\phi_V = \bar{V}$ for air determined from

$$\bar{V} = \sum N_i \bar{V}_i \quad (7)$$

given in Table 4. The calculations have been made by assuming \bar{V} is independent of temperature and composition. The decrease in density calculated from these values of $\bar{V} = \phi_V$ and M are also given in Table 4. These calculated values agree with our measured results within the experimental error of our measurements ($\pm 0.2 \times 10^{-6}$) and the calculations ($\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ in ϕ_V is equivalent to an error of

Table 3. The partial molal volume of gases in water.

Gas	V ($\text{cm}^3 \text{ mol}^{-1}$)
N_2	32.8(25°C) ^a , 33.4(50°C) ^a , 33.3(25°C) ^b , 34.0(51.5°C) ^c , 32.76(51.5°C in 1 m NaCl) ^e
O_2	32.0(25°C) ^b
CO_2	34.3(25°C) ^b , 32.4(25°C) ^d , 32.3(12 to 40°C) ^e , 33.4(23°C) ^f

a) Kritchevsky and Il'inskaya (1935).

b) Enns, Scholander and Bradstreet (1965).

c) O'Sullivan and Smith (1970).

d) Millero and Berner (1972) recalculated using V° (NaHCO_3) = $22.75 \text{ cm}^3 \text{ mol}^{-1}$ (Millero and Gonzalez, in preparation).

e) Weiss (1975).

f) Bradshaw (1973).

Table 4. Calculation of the density decrease due to dissolved air in water using molal volume data.

Temp	$c \times 10^4$	M	ϕ_V	$-\Delta d \times 10^{-6}$	
				Calc ^a	Exp ^b
0°C	13.3	29.89	32.62	3.6	3.5
5	11.7	29.86	32.62	3.2	3.0
10	10.4	29.84	32.62	2.9	2.7
15	9.3	29.81	32.63	2.6	2.4
20	8.4	29.80	32.63	2.4	2.2
25	7.7	29.78	32.64	2.2	2.0
30	7.1	29.76	32.64	2.0	1.8
35	6.5	29.74	32.65	1.9	1.7
40	6.1	29.73	32.64	1.8	1.6

a) Determined from Equation (6) using the V , M and c data given in this Table.

b) Determined from Equation (6) using $10^{-3} [M - \phi_V d^0] = -2.6 \times 10^{-3}$.

$\pm 0.7 \times 10^{-6}$ in Δd). Similar calculations using the solubility of gases in seawater and assuming $\bar{V} = \phi_V$ is independent of ionic strength yield the same Δd 's (i.e., within $\pm 0.1 \times 10^{-6}$) as given in Table 4 at various temperatures. Thus, equation (6) can be used to determine the decrease in density in water and seawater at various concentrations of dissolved air (Weiss, 1970, 1975; Kester, 1975) from 0° to 40°C.

The density measurements made in our studies (Millero, *et al.*, 1975) and apparently for other workers (Cox *et al.*, 1970 and Kremling, 1972) were made on samples of seawater saturated with air. Since the water used to calibrate the densimeters was also saturated with air, the relative densities ($d - d^0$) or specific gravities are not affected (since the Δd due to air in water and seawater are nearly the same at a given temperature).

The relative densities at 4°C of the pure water samples of isotopic composition given in Table 1 are given in Table 5. Also given in this Table are the related densities determined from equation (1). With the exception of the NBS-IA sample, the measured densities agree with the calculated values to ± 0.5 ppm. Our measurements indicate that MIAMI water has a density that is 1 ppm lower than MDW, which is the same as SMOW. As was found by Menaché and Girard (1970), equation (1) predicts the density differences due to isotope changes to 10%. Our isotope results are not as consistent as was found by Menaché and Girard (1970), apparently due to small changes in isotopic composition during distillation (Menaché and Girard determined the isotopic composition after distillation). It should be pointed out that Menaché and Girard (1970) have suggested slightly different values for the constants of equation (1) [respectively, 0.211×10^{-6} and 0.015×10^{-6}]. This new equation also predicts Δd 's that are in good agreement with our measured values to ± 0.9 ppm (the largest differences occurring for SLAP).

Although it is not possible to fix the isotopic composition of the distilled water

Table 5. The relative density at 4°C of pure water from various sources.

Water Source	ρ (sample) - ρ (SMOW), ppm		δd , ppm
	Measured	Calculated	
SMOW ^a	0.0	0.0	0.0
MDW ^b	-0.1	0.4	0.5
MIAMI ^c	-1.1	-0.6	0.5
NBS-I ^d	-3.1	-2.6	0.5
NBS-IA ^e	-7.0	-8.7	1.7
SLAP ^f	-20.0	-19.9	0.1

- a) Distilled Standard Mean Ocean Water.
 b) Distilled Mediterranean Deep Water.
 c) Ion-exchanged Miami Water.
 d) Distilled Potomac River Water.
 e) Distilled Yellowstone National Park Water.
 f) Distilled Standard Light Antarctic Precipitation Water.

used by Knudsen *et al.*, it is possible to make a rough estimate by using the isotopic composition of Copenhagen tap water. The isotopic composition of Copenhagen tap water should be approximately equal to the value for Lista, Norway, determined by Dansgaard (1961). He found $\delta^{18}O = -7\text{‰}$ and $\delta D = -57\text{‰}$ which corresponds to a decrease in density of 2.6 ppm relative to SMOW. These comparisons indicate that the density measurements of Knudsen *et al.*, (1902) are about -2 ppm lower than our results (Millero, Gonzalez and Ward, 1975) while the results of Cox *et al.*, (1970) and Kremling (1971) are 1 ppm higher. These differences are well within the experimental error of the directly measured densities.

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