Effects of Isotopic Composition, Temperature, Pressure, and Dissolved Gases on the Density of Liquid Water *

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A review is made of measurements of the effect of temperature, pressure, isotopic composition, and dissolved atmospheric gases on the density of liquid water at temperatures to 100 °C. The molar volume is expanded as a multiple power series in the variables, and the coefficients determined. A number of gaps become evident in our knowledge of properties that are within the capacity of current measurements. For example, there appears to be no measurement of the effect of oxygen isotopes on the compressibility. Data on the thermal expansion of D_2O are strikingly inconsistent. The partial molar volumes of dissolved gases are only sketchily known. At 0 °C, equilibration with the oxygen, nitrogen, and argon of the atmosphere lowers the density about 3 p.p.m., while atmospheric carbon dioxide raises it about 0.3 p.p.m. Appendix I discusses the care needed to obtain various degrees of precision in practical density measurements, and the effect of isotopic uncertainties on them. Appendix II treats the representation of the equation of state of water at slightly higher pressures.

Key words: Aqueous solutions of gases; compressibility; equation of state; heavy water; isotopic waters; partial molar volume of aqueous gases; *PVT*; thermal expansivity; water.

Contents

1. Introduction

The density of liquid water is a function of externally imposed variables, such as temperature and pressure, and of compositional ones that include isotopic composition as well as dissolved substances. The latter category includes in principle all aqueous solutions, but only the dissolved atmospheric gases are considered here. In particular, the effects of salinity and related oceanographic parameters are not considered, although there is an extensive literature on that subject. Treatments of the effect of isotopic variations on the density of natural water have been given by Menaché [1],[1] Girard and Menaché [2], and Millero and Emmet [3], but the present paper adopts a somewhat different notation and considers a wider range of conditions.

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[1] Figures in brackets indicate the literature references.

TABLE 1. Isotopic masses and abundances [a]

	Atomic weight A	Natural abundance			SMOW	
		Mole fraction	Weight fraction	Formula weight [b, c]	Mole fraction	Formula weight [c]
^1H	1.007825	0.99985	0.99970		0.999842	
^2H (D)	2.014102	0.00015	0.00030		0.000158	
^3H (T)	3.016049	$2.\times10^{-16}$	$6.\times10^{-16}$		0	
H (weighted)				1.0079		1.007984
^{16}O	15.994915	0.99759	0.99732		0.997640	
^{17}O	16.999133	0.00037	0.00039		0.000371	
^{18}O	17.99916	0.00204	0.00229		0.001989	
O (weighted)				15.999_4		15.999274
H_2O (weighted)				18.015_2		18.015242

[a] Masses are on the scale $^{12}C = 12$ exactly.

[b] While the masses of the isotopes are known with higher precision, the variations of the isotopic ratio between different terrestial samples limit the precision.

[c] From equations (2), (3) and (4).

For most purposes the volumic mass, or massic density,[2] is the useful quantity, but as the volumes of isotopic mixtures are nearly ideal, expressions will first be derived in terms of volumes, and only converted to densities later. The molar volume V of liquid water may be expressed as a function of the following variables.

$$V = V(t, p;\ [D],[T];\ [^{17}O],[^{18}O];\ [N_2],[O_2],[Ar],[CO_2],[NH_3]), \qquad (1)$$

where t is the temperature, p the pressure, and square brackets denote concentrations; the first group of concentrations gives the abundance of hydrogen isotopes in the water itself, the second that of the oxygen isotopes, while the last refers to dissolved substances. The evolution of work on density has been in the direction of giving a more complete analysis of the composition. Equation (1) is purely formal, and this paper, after choosing a suitable way to express each variable, considers a systematic series expansion in terms of these variables: data from the literature then yield values for most coefficients, while a few important gaps become evident. Section 2 will treat the expression of isotopic composition and the evaluation of the molecular weight. Subsequent sections will then review the data on density as they bear on the evaluation of the various parameters in the expansion.

2. Molecular Weights and the Specification of Isotopic Composition

2.1. General Treatment

The molar volumes of the isotopic waters are approximately equal, but engineering and laboratory work is usually done on a mass basis. More important for the present study, weighings can be made with high accuracy more easily than can determinations of isotope fractions. We thus work here on a mole basis, but in such a way as to minimize the effect of errors in the molar concentrations.

The isotopic masses, taken from "Atomic Weights of the Elements 1973" [4], are included in table 1 which revises a table given earlier [5]. There are three isotopes of hydrogen, two of them stable, namely ^1H or light hydrogen (or simply H if contrasted with D or T) and ^2H or D, deuterium or heavy hydrogen, while ^3H or T, tritium, is radioactive with a half-life of 12.33 yr. If the mole (or number) fraction of ^2H is denoted by x_2, and that of ^3H by x_3, so that the fraction of ^1H is $1-x_2-x_3$, then the atomic weight of a sample of hydrogen is

$$A(H) = 1.007825 + 1.006277x_2 + 2.008224x_3. \qquad (2)$$

There are three stable isotopes of oxygen. (Radioactive isotopes ^{14}O, ^{15}O, ^{19}O, and ^{20}O have half-lives of seconds (2 min for ^{15}O) and no data are available on waters containing them.) If y_{17} denotes the mole fraction of ^{17}O, and y_{18} that of ^{18}O, so that the fraction of ^{16}O is $1-y_{17}-y_{18}$, the atomic weight of a sample of oxygen is

$$A(O) = 15.994915 + 1.004218y_{17} + 2.00424_5y_{18}. \qquad (3)$$

Adding these two equations together, to correspond to the stoichiometry H_2O, gives the molecular weight of water as

$$M_w(H_2O)/\text{g mol}^{-1} = 18.010565 + 2.012554x_2 + 4.016448x_3 + 1.004218y_{17} + 2.00424_5y_{18}. \qquad (4)$$

This equation shows that the molecular weight is known to 6 decimal places, that is to ~1 in 2 × 10^7, provided the isotope fractions are known to 1 in 10^6, except for solutions rich in ^{18}O when the accuracy falls to 5 decimal places. This accuracy of measurement of isotopic composition is not

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[2] As the French word *densite* has the meaning of specific gravity and implies a relative measurement, some English authors use "absolute density" for volumic mass to avoid confusion. In this paper "massic density" is used with this meaning. In this we parallel the admittedly unhappy double use of molar as in molar volume and its reciprocal molar density. For the present paper the reciprocal of the massic density is the massic volume (Fr. *volume massique*). The word "specific" is reserved to refer to species such as $HD^{16}O$ or HCO_3^-. Throughout the paper ρ is the massic density and V is the molar volume.

easily reached, nor is the corresponding accuracy of density measurements.

In practice a somewhat different method is usually used to express the composition of waters not too different from natural water. Denote the concentration of the heavier hydrogen and oxygen isotopes by the abundance ratios

$$ {}^{2}r = [{}^{2}\mathrm{H}]/[{}^{1}\mathrm{H}] = x_2/(1-x_2-x_3), \qquad (5) $$

$$ {}^{3}r = [{}^{3}\mathrm{H}]/[{}^{1}\mathrm{H}] = x_3/(1-x_2-x_3), $$

$$ {}^{17}r = [{}^{17}\mathrm{O}]/[{}^{16}\mathrm{O}] = y_{17}/(1-y_{17}-y_{18}), \qquad (6) $$

$$ {}^{18}r = [{}^{18}\mathrm{O}]/[{}^{16}\mathrm{O}] = y^{18}/(1-y_{17}-y_{18}). $$

The isotopic ratios defined by ${}^{i}r$ can be determined directly when a mass spectrometer is used.

In the present paper we wish, however, to work in terms of mole fractions. As the mole fraction of ^{1}H is $(1+{}^{2}r+{}^{3}r)^{-1}$, the mole fractions are given in terms of ${}^{i}r$ by

$$ x_2 = \frac{{}^{2}r}{1+{}^{2}r+{}^{3}r}\,; \qquad (7) $$

and similarly for the other isotopic species.

Craig [6] has introduced the concept of Standard Mean Ocean Water (SMOW) to provide a uniform standard for reporting D and ^{18}O concentrations of natural waters. No sample of SMOW exists, although there are several close approximations; there is, accordingly, no vat of SMOW from which samples can be taken for density studies. Rather, SMOW was first defined in terms of the U.S. National Bureau of Standards "reference sample 1" [7]. Small samples of a closely similar standard, intended as a calibration standard for mass spectrometry, are available from the International Atomic Energy Agency [8]. Compositions relative to SMOW are usually expressed in terms of the per millage enrichment δ‰ which is defined by

$$ {}^{i}\delta‰ = [({}^{i}r_{\mathrm{sample}}/{}^{i}r_{\mathrm{SMOW}})-1]\times 1000. \qquad (8) $$

Parameter ${}^{i}r$ offers conveniences for the discussion of equilibria, for example the isotopic separation factor ${}^{i}\alpha$ is

$$ {}^{i}\alpha = {}^{i}r_{\mathrm{product}}/{}^{i}r_{\mathrm{initial}}. \qquad (9) $$

For thermodynamic purposes ${}^{i}\delta‰$, $\triangle{}^{i}\delta‰$, or ${}^{i}\alpha$ are inferior to Δx_j or Δy_k because they give a less complete specification of the composition. In the long run only x and y will be of interest, and the correlations here are reported in terms of them. Craig gives ${}^{2}r = 1/6328$, giving $x_2 = (158.\pm 2.)\times 10^{-6}$ for SMOW; for thermodynamic purposes x_3 is zero in natural waters. For D in near-normal waters we then have from eq (7)

$$ x_{2,\mathrm{sample}} = 158.\times 10^{-6} + 0.9997({}^{2}r_{\mathrm{sample}} - {}^{2}r_{\mathrm{SMOW}}), \qquad (10) $$

or in terms of δ, with the same restriction to near-normal water,

$$ x_{2,\mathrm{sample}} = 158.\times 10^{-6}\left(1+\frac{{}^{2}\delta‰}{1000}\right). \qquad (11) $$

Similarly, for ${}^{i}\alpha$, with the same restriction,

$$ \begin{aligned} \triangle x_2 &= x_2(\mathrm{product}) - x_2(\mathrm{initial}), \\ &= 158.\times 10^{-6}({}^{2}\alpha - 1). \qquad (12) \end{aligned} $$

These are the conversion relations used in this paper.

All three stable isotopes must be taken into account in specifying the isotopic composition of ordinary oxygen. However, the definition of SMOW [6] did not mention ^{17}O, an isotope present in greater mole fraction than is D.

We here follow Girard and Menaché [2] in adopting the value ${}^{18}r = 1993.4\times 10^{-6}$ as given by Craig [6], and adopt their value ${}^{17}r = 372.\times 10^{-6}$. There is then, paralleling eq (10),

$$ y_{17,\mathrm{sample}} = 371.\times 10^{-6} + 0.9950({}^{17}r_{\mathrm{sample}} - {}^{17}r_{\mathrm{SMOW}}), \qquad (13) $$

$$ y_{18,\mathrm{sample}} = 1989.\times 10^{-6} + 0.9902({}^{18}r_{\mathrm{sample}} - {}^{18}r_{\mathrm{SMOW}}). $$

Similarly, paralleling eq (11) there is obtained

$$ y_{17,\mathrm{sample}} = 371.\times 10^{-6}\left(1+\frac{{}^{17}\delta‰}{1000}\right), \qquad (14) $$

$$ y_{18,\mathrm{sample}} = 1989.\times 10^{-6}\left(1+\frac{{}^{18}\delta‰}{1000}\right). $$

and paralleling eq (12)

$$ \Delta y_{17} = 371.\times 10^{-6}\,({}^{17}\alpha - 1), \qquad (15) $$

$$ \Delta y_{18} = 1989.\times 10^{-6}\,({}^{18}\alpha - 1). $$

The coefficients entering into eqs (10) to (15) are experimental and subject to future revision. More important, Coplen and Clayton [9] point out that the standard water from the International Atomic Energy Agency [8], to which reference has already been made, differs slightly from SMOW as originally defined by Craig [6].[3] Determinations of D in light or heavy water vary greatly in accuracy. The error given by Hagemann et al. of 0.05×10^{-6} for x_2 in SMOW is only attained in the best work. An error of per-

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[3] In commenting on the manuscript of this paper, Menache points out that it would be better to take the isotopic abundances of SMOW as given by Hagemann et al. [8] for hydrogen, and by Baertschi [95] for ^{18}O; the latter paper was not available when the present paper was written. These give for SMOW $10^{6}x_2 = 155.74 \pm 0.05$ and $10^{6}y_{18} = 2000.45 \pm 0.45$. Adoption of these values would not change the patterns of isotopic effects to be deduced below. A meeting on stable isotope standards held in Vienna, September 1976, resolved that henceforth only the material distributed by the I.A.E.A. should be called SMOW and, if necessary to avoid ambiguity, it may be designated as Vienna-SMOW or V-SMOW.

haps 2×10^{-6} in x_2 appears more usual, but even this corresponds to an error in the massic density of less than 1 p.p.m. The situation is similar for the oxygen isotopes. The uncertainty in the abundance of ^{18}O in SMOW produces an error in the density of less than 1 p.p.m. The uncertainty with respect to ^{17}O may be larger, and the measurements are not adequate to estimate its error. The abundances of the isotopes in SMOW, and the corresponding atomic weights, are included in table 1; these values were used in determining the numerical coefficients of eqs (10) to (15). The effect of isotopic errors on the density is similar to their effect on the molecular weight as given by eq (4); numerical values will be given in section 3.9. The effect of isotopic variations on practical density measurements is discussed in Appendix I.

Because of the fractionation on evaporation, seawater is richer than freshwater in the heavier isotopes, both deuterium and the heavy oxygens. Atmospheric oxygen is also richer in ^{18}O than either water, its composition being related to that of water by equilibria with CO_2, so that water prepared by burning hydrogen in air has this slightly heavier oxygen composition and an increase in density of about 7 p.p.m.

In the treatment here, attention has been focused on the isotopic composition of the solution as a whole, and the fraction of molecules of the species $H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$, etc., has not been used to describe the solution. To be sure, the specific abundances in SMOW are easily calculated by assuming random formation of the molecules; for each million molecules there are 997325 of $H_2{}^{16}O$, 1988 of $H_2{}^{18}O$, 371 of $H_2{}^{17}O$, 315 of $HD^{16}O$, 0.6 of $HD^{18}O$, 0.1 of $HD^{17}O$, 0.02 of $D_2{}^{16}O$, 5×10^{-5} of $D_2{}^{18}O$, and 9×10^{-6} of $D_2{}^{17}O$. When it is remembered that approximately 0.1 molecules per million have dissociated to give H_3O^+ and OH^-, it is clear that the least abundant species make a negligible contribution to the solution properties. The first reason for not pursuing a more detailed description is that such is not necessary, for the volume properties are described simply and adequately in terms of the overall composition. The second reason is that in a condensed phase the molecules are not isolated. In the low-pressure gas, in contrast, the fraction of time that a molecule spends in collision is small compared to the time it spends alone, and, at least in principle, $H_2{}^{16}O$, $HD^{16}O$, etc., are seen distinctly in optical and mass spectra. But in the liquid the vibrations of each molecule are strongly coupled to the motions of its neighbors, so the species are not seen separately.

On the other hand, each water with monoisotopic hydrogen and oxygen can be prepared pure, so there must be terms for each in the equations representing the properties. This question will be returned to in connection with the equation for the molar volume and in section 3.7 on nonideality.

If SMOW is to be accepted as a reference composition for density measurements, it is desirable that the same material be used as the isotopic standard for tabulating the vapor pressure and for defining the triple point as it is used in thermometry. The triple point of water is the fundamental point for the IPTS-68 and the water used for its realization is now required to have "substantially the isotopic composition of ocean water" [10]. This is given as about $^{2}r = 0.00016$, $^{17}r = 0.0004$, and $^{18}r = 0.002$, values that are less precise than those used here for SMOW but not in conflict with them. The triple point temperature is relatively insensitive to the isotopic composition.

As the discussion of ^{17}O has made clear, even in the better work of today the concentration of ^{17}O is not usually determined, but rather ^{i}r is found for D and ^{18}O for the sample and for a standard; that is, $^{i}\delta$ is determined for the two components. Older or less pretentious work specifies less of the isotopic composition, possibly giving the concentration of D and asserting that the oxygen abundances are normal, while before the discovery of ^{17}O and ^{18}O in 1929, and of deuterium in 1932, water was regarded as an invariant substance. To cover the range of time and precision found in papers still cited it is, accordingly, necessary to consider a series of approximations ranging from those specifying more to those specifying less of the isotopic composition.

2.2. Approximations for the Concentration of ^{17}O

The relative abundances of D and ^{18}O characterize a sample of water sufficiently for most geochemical or environmental studies. However, the concentration of ^{17}O is required for a specification of composition, such as is required for a specification of the density, and as this concentration is seldom measured, some approximation is needed to provide an estimated value of ^{17}O for use in calculations. To a fairly good approximation the properties of ^{17}O are the geometric (or what is nearly equivalent, the arithmetic) mean of those of ^{16}O and ^{18}O. That is, in any process which changes the relative abundances the fractional change of y_{17} will be the mean of those of y_{16} and y_{18}, or

$$\frac{dy_{17}}{y_{17}}=\frac{dy_{16}}{2y_{16}}+\frac{dy_{18}}{2y_{18}}\ , \tag{16}$$

or, expressing y_{16} as $1-y_{17}-y_{18}$, we obtain for any near-normal water

$$\begin{aligned} y_{17,\mathrm{sample}} &= y_{17,\mathrm{SMOW}}+\frac{y_{17}\,(1-y_{17}-2y_{18})}{y_{18}\,(2-y_{17}-2y_{18})}\\ &\quad\times(y_{18,\mathrm{sample}}-y_{18,\mathrm{SMOW}}),\\ &= 371.\times10^{-6}+0.0931\,(y_{18,\mathrm{sample}}-y_{18,\mathrm{SMOW}}). \end{aligned} \tag{17}$$

In the approximation, good for near-normal waters, that y_{16} is the same in the sample as in SMOW, eq (17) can be expressed in terms of r as

$$\begin{aligned} {}^{17}r_{\mathrm{sample}} &= {}^{17}r_{\mathrm{SMOW}}+\frac{{}^{17}r(1-y_{17}-2y_{18})}{{}^{18}r(2-y_{17}-2y_{18})}\,({}^{18}r_{\mathrm{sample}}-{}^{18}r_{\mathrm{SMOW}}),\\ &=372.\times10^{-6}+0.0931\,({}^{18}r_{\mathrm{sample}}-{}^{18}r_{\mathrm{SMOW}}). \end{aligned} \tag{18}$$

Expressing this last equation in terms of δ gives

$$^{17}\delta = 0.4989\,^{18}\delta,$$

$$\simeq \tfrac{1}{2}\,^{18}\delta. \qquad (19)$$

Those who use δ as their parameter to describe isotopic composition usually start with the last equation as a self-evident relation.

2.3. *Meteoric Water*

Variations of hydrogen and oxygen isotopes are highly correlated in environmental water, as they are in laboratory purifications. Craig [11] has shown that for many rivers, lakes, rain, and snow the relation is approximately

$$^{2}\delta‰ = 8\,^{18}\delta‰ + 10, \qquad (20)$$

while deviations from this curve have been discussed by Payne [12]. In this equation the coefficient 8 represents the nearest integer rather than a carefully fitted value, and Menaché [1] says that the value can be as low as 5 in exceptional cases. The constant term would be zero for a line passing through the composition of SMOW. On substituting in eq (20) from eqs (11) and (14) there is obtained, for the natural waters described by equation (20),

$$x_2 = 0.6355y_{18} - 1.104 \times 10^{-3}, \qquad (21)$$

with coefficients close to those given by Craig [6].

2.4. Liquid-Vapor Equilibrium

Many processes must be involved in producing the isotopic variations in natural water given by the correlation of eq (20). An attempt to model the central processes involved may be made under laboratory conditions either in systems containing air [13, 14], which has a bearing on atmospheric processes, or on systems containing only the water isotopes at their vapor pressure. Equilibrium studies are often reported in terms of vapor pressures or vapor-pressure ratios, closely related to, but not identical with α, and in many papers such equilibria are reported in terms of species such as HDO. A critical review of the literature has recently been given by Jancso and Van Hook [15], so we cite here only papers sufficient for our purposes without justifying the choices by a more complete bibliography.

The equilibrium fractionation of deuterium has been given by Majoube [16]. The isotopic separation factor $^{2}\alpha$ (the present α is the reciprocal of the one used in that paper) changes with temperature and in the interval $0 \leq t \leq 100$ °C can be represented by

$$\ln {}^{2}\alpha = -52.612\times10^{-3} + \frac{76.248}{T} - \frac{24.844\times10^{3}}{T^{2}}, \qquad (22)$$

which gives $^{2}\alpha$ as 0.899 at 0 °C, 0.922 at 20 °C, and 0.974 at 100 °C, in adequate agreement with the values given by Merlivat, Botter, and Nief [17]. The recent data by Stewart and Friedman [18] lie between those two sets. Equation (12) then shows these values to correspond to enrichments in the equilibrium vapor of $-10^{6}\Delta x_2 = 16$ at 0 °C, 12 at 20 °C, and 4 at 100 °C. These figures show that, as far as hydrogen is concerned, there is appreciably less fractionation in a distillation made at 100 °C than in one made at lower temperatures. At 0 °C the deuterium concentration in the equilibrium vapor is reduced to 90% of its value in the liquid. However, if the equilibrium vapor were completely condensed, then its density, as far as the contribution from deuterium is concerned, would be only decreased by 1 p.p.m. If the vapor in equilibrium with the liquid is removed during the course of a distillation at 20 °C, when half the liquid has been evaporated the deuterium concentration in the liquid has risen 10 p.p.m., and the density 1 p.p.m. When the amount of liquid is halved again the deuterium concentration rises a further 10 p.p.m. The final 1% has a concentration of 221 p.p.m. of D, compared to 158 p.p.m. in the starting material, and the density has increased about 6 p.p.m. This is significantly less than the difference in density of 20 p.p.m. between the first and last fractions of distilled tap water as reported by Christiansen, Crabtree, and Laby [19].

For equilibria involving the oxygen isotopes we will follow Borowitz [20] and Majoube [16]. The latter gives the temperature dependence of $^{18}\alpha$ for $0 \leqq t \leqq 100$ °C as

$$\ln {}^{18}\alpha = 2.0667\times10^{-3} + \frac{0.4156}{T} - \frac{1.137\times10^{3}}{T^{2}}, \qquad (23)$$

which gives $^{18}\alpha$ as 0.988 at 0 °C, 0.990 at 20 °C, and 0.995 at 100 °C. Using eq (15) these correspond to $-10^{6}\Delta y_{18} =$ 24 at 0 °C, 20 at 20 °C, and 10 at 100 °C.

Borowitz found the ratio $(^{17}\alpha - 1)/(^{18}\alpha - 1)$ to be about 0.52, rather than 0.499 as would be given by eq (18). Using this ratio, the separation factor for ^{17}O is

$$^{17}\alpha = 1 + 0.52(^{18}\alpha - 1), \qquad (24)$$

which gives values of 0.9938 at 0 °C, 0.9948 at 20 °C, and 0.9974 at 100 °C. Using eq (15) these correspond to $-10^{6}\Delta y_{17} = 2.3$ at 0 °C, 1.9 at 20 °C, and 1.0 at 100 °C.

In the approximation that the molar volume of each species is the same, an increase of 1 p.p.m. in *either* D or ^{18}O increases the density by 1/9 p.p.m., while an increase of 1 p.p.m. in ^{17}O increases the density 0.06 p.p.m. As the concentration increase of ^{18}O is greater than that of D at the same temperature, the density increases more from the change of oxygen composition. Hence, returning to the question of the density change during a single distillation discussed above, when the variation of oxygen is considered the effects on the density are about 2½ times as great as from hydrogen alone, and it is thus quite possible that Christiansen et al. [19] did see a density variation of 20 p.p.m. between the first and last fractions of a single distillation that arose from isotopic variations. At the same time the concentration change of ^{17}O is about 1/20 as much as that of ^{18}O, less than 1 p.p.m. in an equilibrium distillation from SMOW.

The ratio $\Delta x_2/\Delta y_{18}$ for an equilibrium vaporization is a function of temperature, with values falling from 0.7 at 0 °C to 0.4 at 100 °C. The coefficient 0.64 given in eq (21) for meteoric waters corresponds to the lower temperature part of the range. If density changes are measured on distillation and a factor such as 0.6 assumed to relate changes in D to ^{18}O, then the composition change of both hydrogen and oxygen can be approximated. There have been many papers on the determination of deuterium concentrations from density or other measurements [21], but it is clear from the analysis just given that density measurements alone are insufficient, and some second measurement giving knowledge of the oxygen isotopes is needed if either density or a full compositional description is to be obtained. We conclude that no relation along the lines of eq (20) is generally valid for laboratory waters prepared by distillation.

3. Molar Volume of Water

3.1. Equations for Molar Volume and Density

The reference density to which all others will be related is that of SMOW at its maximum density at a pressure of one atmosphere,

$$\rho_{\max}\,(\text{SMOW}) = 999.975\ \text{kg m}^{-3}, \qquad (25)$$

as provisionally recommended by Girard and Menaché [22]. Taking the molecular weight from table 1, the molar volume corresponding to this density is 18.01569 cm³ mol⁻¹.

The series expansion corresponding to eq (1) will, however, be made about 0 °C, rather than about the temperature of maximum density, and about atmospheric pressure, 1 atm = 1.01325 bar = 101325 Pa. Analogous to the use of T for the absolute temperature and t for the Celsius one with a shifted zero, P is used for pressure and p for the shifted pressure

$$p = \mathrm{P} - 1\ \text{atm}. \qquad (26)$$

The molar volume V_w is a multiple power series in p, t, and the mole fractions of the isotopic components.

$$\begin{aligned} V_w = {} & (A_{00} + A_{10}t + A_{01}p + A_{11}tp + \ldots) \\ & + (B_{00} + B_{10}t + B_{01}p + \ldots)x_2 + (C_{00} + \ldots)x_3 \\ & + (D_{00} + \ldots)y_{17} + (E_{00} + \ldots)y_{18} \\ & + (F_{00} + \ldots)x_2y_{17} + (G_{00} + \ldots)x_2y_{18} + \ldots \\ & + (Q_{00} + Q_{10}t + Q_{01}p + \ldots)x_2x_1 . \qquad (27) \end{aligned}$$

Except in the terms Q, x_1 and y_{16} do not appear explicitly in this equation, just as they do not appear in eq (4). This omission recognizes both that ordinary water is nearly $H_2{}^{16}O$ and that the values of that component are most precisely known. (For extensive application of the equation to heavy water it would be most convenient to rearrange the equation, and eq (4) as well, so that the hydrogen isotopes are expressed as x_1, $(1 - x_1 - x_3)$, and x_3.)

While eq (27) can represent non-ideal behavior if a sufficient number of cross terms in the mole fractions are included, the leading terms describe ideal behavior. If water is an ideal solution of pure components $^iH_2{}^jO$ of molar volume V_{ij} at the temperature and pressure under consideration, the molar volume is

$$V_W = \Sigma x_i y_j V_{ij}, \Sigma x_i = 1, \Sigma y_j = 1 . \qquad (28)$$

Considering for the moment only two hydrogen isotopes, H and D, and two oxygen ones, ^{16}O and ^{18}O, in order to limit the number of terms written in the following equation, writing $(1 - x_2)$ for x_1 and $(1 - y_{18})$ for y_{16}, and rearranging gives

$$\begin{aligned} V_W = {} & V_{H_2{}^{16}O} + (V_{D_2{}^{16}O} - V_{H_2{}^{16}O})x_2 + (V_{H_2{}^{18}O} - \\ & V_{H_2{}^{16}O})y_{18} + (V_{D_2{}^{18}O} + V_{H_2{}^{16}O} - V_{D_2{}^{16}O} - \\ & V_{H_2{}^{18}O})x_2y_{18} . \qquad (29) \end{aligned}$$

Comparison with eq (27) shows that the coefficients A give the temperature and pressure dependence of $V_{H_2{}^{16}O}$, the B relate to $(V_{D_2{}^{16}O} - V_{H_2{}^{16}O})$, etc.

The massic density ρ_w of a sample of pure water is then obtained by dividing the molecular weight, as given by eq (4), by the molar volume, given by eq (27),

$$\rho_w = M_w/V_w . \qquad (30)$$

In a previous paper [23] the density of the isotopic waters was represented by the rational polynomial

$$\rho = \frac{a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5}{1 + bt} . \qquad (31)$$

This form provides a smoother representation of the data than does a power series, but has the disadvantage that it is not clear how to generalize it to incorporate variations of isotopic composition. It should be noted, however, that the work of Steckel and Szapiro [24] implies that up to a temperature of about 70 °C the density is adequately given by

$$\rho = \rho_{\max}\left\{1 - F\tau^2\left(1.74224 + \frac{482.502}{\tau + 77.861}\right) \times 10^{-6}\right\}, \qquad (32)$$

where $\rho_{\max}$, the maximum density, might be approximated as a linear function of x_2, y_{17}, and y_{18}, F depends only on x_2, and $\tau = t - t_m$ is the temperature above the maximum density t_m, where t_m might also be approximated by a linear function of x_2, y_{17}, and y_{18}. Equation (27) fails to express the high correlation that exists between the volumes and compressibilities of waters of different compositions, e.g. it does not recognize that all species show rather similar density maxima and compressibility minima, but it has been preferred here because an equation such as (32) presupposes the nature of the relation between the densities of the various isotopic forms, which is what we wish to elucidate.

3.2. Density of Ordinary Water or SMOW

The density of ordinary water or SMOW as a function of temperature at atmospheric pressure has recently been reviewed by Aleksandrov and Trakhtengerts [25], who represented the density as a polynomial in the temperature, and by Kell [26], who represented the data by eq (31) as had been done for waters of various isotopic compositions in an earlier paper [23]. The coefficients of eq (31) as given in this most recent version, with the maximum density adjusted to that of SMOW are given in table 2.

All functions discussed here, whether of the form of eq (27) or (31), have been obtained by least squares; the problem of fitting volumes and densities in an equivalent way using least squares is discussed elsewhere [27]. The calculations in the present paper have used the algorithm outlined there. This means that, although it is volumes that appear in eq (27), it may be considered that the input data, which were mostly densities, have been fitted as densities and the results reported as volumes.

TABLE 2. Coefficients and properties of functions representing the density of liquid water. The coefficients are for the rational function given by equation (31). The D_2O represented here has the same composition of the oxygen isotopes as SMOW.

	H_2O (SMOW)	D_2O
$a_0/\text{kg m}^{-3}$	999.84252	1104.7056
a_1	16.945227	28.88152
10^3a_2	−7.9870641	−7.652899
10^6a_3	−46.170600	−136.61854
10^9a_4	105.56334	534.7350
$10^{12}a_5$	−280.54337	−1361.843
10^3b	16.879850	25.91488
Range of function/°C	0—150	5—100

My 1967 paper [23] tried to find an equation that was both accurate in following the experimental data and efficient in the sense that alternating signs did not necessitate carrying many figures in the calculation because of losses on subtraction. That quest for efficiency has not been pursued in this paper, although we note here that the following function for the density of SMOW, with nine parameters and only positive signs, is equivalent to eq (31) to within experimental uncertainty.

$$\rho_{(\text{SMOW})}/\text{kg m}^{-3} = (999.8427 + 67.8782\times10^{-3}t + 103.1412\times10^{-6}t^3 + 15.95835\times10^{-9}t^5 + 636.8907\times10^{-15}t^7)/(1 + 9.090169\times10^{-6}t^2 + 1.4511976\times10^{-9}t^4 + 134.84863\times10^{-15}t^6 + 2.008615\times10^{-18}t^8),\ 0 \leqq t/°\text{C} \leqq 150\ . \qquad (33)$$

The molar volume of SMOW as a function of temperature at 1 atm is represented by the nine-parameter power series

$$V_{\text{SMOW}}/\text{cm}^3\ \text{mol}^{-1} = 18.018\,070 - 1.218\,4846\times10^{-3}\,t + 162.727\,55\times10^{-6}t^2 - 1.769\,7126\times10^{-6}t^3 + 22.156\,063\times10^{-9}t^4 - 207.211\,87\times10^{-12}t^5 + 1.289\,6330\times10^{-12}t^6 - 4.595\,4939\times10^{-15}t^7 + 7.048\,1250\times10^{-18}t^8,\ 0 \leqq t/°\text{C} \leqq 150\ . \qquad (34)$$

This has more parameters than eq (31), and gives a less smooth fit; differences between it and eq (31) are, however, less than experimental uncertainties.

For reference purposes, IUPAC Commission I.4 recommends [28], for the range $0 \leqq t/°\text{C} \leqq 40$, a particular table of the density of SMOW based on the analysis by Bigg [29]. This table gives densities greater than eq (31) by 2 p.p.m. at 40 °C; the differences are less at lower temperatures. Such differences are comparable to those we accept in writing a power series representation such as eq (27) in place of (31). The IUPAC recommendation is being adopted as a standard, particularly for oceanography, by a number of organizations. Because of the narrowness of the temperature range considered by Bigg, as well as the slight disagreement with the values at higher temperatures, it seems better for thermodynamic purposes to ignore the IUPAC recommendation and to permit each author to make his own evaluation of the experimental data. A preliminary report is available of new experimental work between the maximum density and 40 °C [30]. At 40 °C these results will be about 5 p.p.m. lower than eq (31), and hence outside the range given by the differences between the measurements of Chappuis [31] and Thiesen et al. [32], which have often been implicitly considered to give the range within which the correct value lies.[4]

The standard errors of ρ_{SMOW} have been discussed previously [26]. At 100 °C these errors included a scatter of ~5 p.p.m., and other errors were estimated as ~10 p.p.m. Adding variances gives a total estimated error of 12 p.p.m. Errors should be approximately equal to the square of the temperature interval from maximum density, that is approximately equal to the square of the Celsius temperature, but they are not because most data were obtained either below 40 °C or above that temperature, and there are uncertainties about how the two regions join. Hence, it is better to consider the error of ρ_{SMOW} as rising linearly from the temperature of maximum density, where its value is defined to be zero, to 12 p.p.m. at 100 °C.

The compressibility of ordinary water at 1 atm has been reviewed recently [26], and the results of that analysis will

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[4] Commenting on the manuscript of this paper, Bell informs me that the latest results of the Australian CSIRO lie between those of Thiesen and Chappuis at 40 °C.

be followed here. Recent work by Kroebel and Mahrt [33] indicates that the isothermal compressibility $\kappa_T = (\partial \ln \rho / \partial P)_T$, found most accurately for liquid water from the speed of sound, has systematic errors between different data sets of ~2 Gbar^{-1}. This error is negligibly small for present purposes, as the compressibility is known for only a few isotopic compositions. The data of reference 26 were expressed as molar compressibilities $(\partial V_\mathrm{W}/\partial P)_T$, and this quantity represented by the power series

$$(\partial V_\mathrm{SMOW}/\partial P)_T/\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{Mbar}^{-1} = -916.843 +$$

$$6.971\,95\,t - 166.126\,9\times10^{-3}t^2 + 2.499\,971\times10^{-3}t^3 -$$

$$32.516\,6\times10^{-6}t^4 + 286.324\,4\times10^{-9}t^5 -$$

$$1.484\,224\times10^{-9}t^6 + 3.321\,54\times10^{-12}t^7,$$

$$0 \leqq t/{}^\circ\mathrm{C} \leqq 100. \qquad (35)$$

The errors of the compressibility, also discussed previously [26], are predominantly quadratic in the temperature and amount to ~8 Gbar^{-1} at 100 °C. Two factors not discussed previously are the effect of the uncertainty of isotopic composition on the compressibility and the effect of uncertainties of the absolute temperature scale. Can differences between the measurements be ascribed to differences in isotopic composition? Equation (35) was based on the data of Del Grosso [34, 35]. The compressibilities from those data are about 3 Gbar^{-1} lower (corresponding to velocities 0.04 m s^{-1} higher) than those of Barlow and Yazgan [36] and McSkimin [37], both using doubly distilled water, and those of Carnvale et al. [38], using distilled water not otherwise specified. The water used by Kroebel was distilled water, not otherwise specified, but considered suitable as a baseline for the study of sea water. We may only conclude that the water samples used by these workers may differ in isotopic composition by amounts similar to those found in density studies. As shown in section 2.4, if the oxygen isotopes remain normal, the mole fraction of deuterium increases 10^{-5} for every p.p.m. increase in density. Mathieson and Conway [39] have shown that the velocity of sound increases almost linearly with mole fraction in H_2O–D_2O mixtures, by approximately 100 m s^{-1} over the whole composition range. That is, an increase of 1.5 p.p.m. in density produces an increase of 1 p.p.m. in the velocity of sound; if measured velocity is used, and the change of density has not been allowed for, there is a decrease of 0.5 Gbar^{-1} in the compressibility obtained. Accordingly, while the differences between the data sets cannot be definitely ascribed to isotopic uncertainty, they are within the range of such variations. To reflect this, the error estimate for the compressibility above should be increased about 1 Gbar^{-1}, independent of temperature.

The isothermal molar compressibility is obtained from the speed of sound by the following relation

$$(\partial V/\partial p)_T = -M\rho^{-2}(\partial\rho/\partial p)_T = -M\rho^{-2}(u^{-2} + T\alpha^2/C_p), \qquad (36)$$

where M is the molecular weight, ρ the massic density, u the velocity of sound, α the thermal expansivity $(-\partial \ln \rho/\partial_T)_p$, and C_p the massic heat capacity at constant pressure Errors in realizing the absolute temperature scale would have their largest effect on the α^2 of this equation.[5] Evidence has been offered by Guildner and Edsinger [40] that the 1968 thermodynamic scale may be 0.03 K too high at 100 °C. Approximately, the relation is

$$\theta = T - 3\times10^{-4}t, \qquad (37)$$

where θ is Guildner's gas-thermometer scale, and T and t are, as everywhere in this paper, the absolute and Celsius temperatures on the IPTS-68. Hence $dT/d\theta = 1.0003$, and α in equation (36) is not changed enough to affect the error estimates for the compressibility.

3.3. Heavy Water

Existing correlations of the density of D_2O are unsatisfactory in two respects. First, most of them give undue weight to early measurements made on limited samples. Secondly, much of the work is weakened by inadequate control of the abundances of the oxygen isotopes. It is now possible to give a much more authoritative treatment of the oxygen isotopes, and something can be said about the pure forms $D_2{}^{17}O$ and $D_2{}^{18}O$, and by subtraction about $D_2{}^{16}O$.

For purposes of a correlating equation, D_2O will be taken to be 100% D_2O, with the oxygen isotopes in the same abundance as SMOW, i.e. with a molecular weight of 20.027 478. The choice of this concentration of oxygen isotopes has been made so that the difference between the representations for SMOW and heavy water will depend only on the hydrogen isotopes. Heavy water commonly is about 99.8% D, 0.2% H, and has no close control on the oxygen isotopes. We might expect that the greatest source of error in the data sets where the oxygen isotopes were not measured lies in inadequate normalization of the oxygen composition. If this is correct, the various data sets should be approximately parallel.

The method used here to compare the data follows that of reference 26. An approximate equation (that of reference 23 expressed on the IPTS-68) was taken, and the deviations of the various sets of reliable data from this are plotted in figure 1. This shows the data sets to be far from parallel. In 1967 I concluded that the baseline of the figure was probably accurate to 1 in 10^5 at the lower temperatures and to 5 in 10^5 at 100 °C [23]. The differing thermal expansions in recent measurements show that claim to be overly optimistic. However, the situation has improved in that there are now two measurements where the concentrations of oxygen isotopes were measured. Hence the molecular weight, and thus the molar volume, to be ascribed to D_2O is known within narrower limits than before.

The most fully described determination of the density of

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[5] Ref. 26 erroneously states that the change from the IPTS-48 to the IPTS-68 has a negligible effect on C_p. As the values of the heat capacity of water have been obtained by differentiation of calorimetric quantities, if C_{48} refers to the heat capacity when t_{48}, the temperature on the IPTS-48, is used, then $C_{68} = C_{48}\,dt_{48}/dt_{68}$. Hence the change of temperature scale has similar effects on α and C_p.

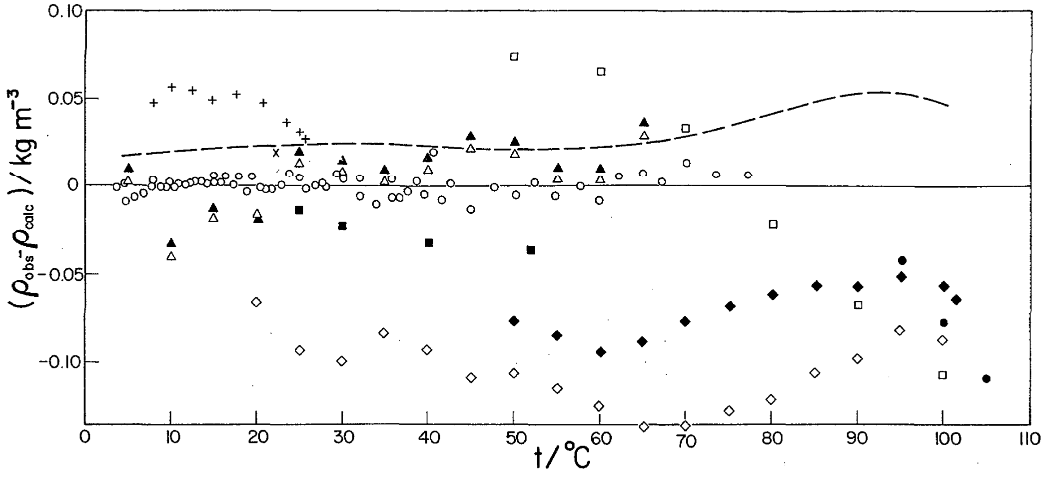

FIGURE 1. Deviations of the density of heavy water. The baseline is the correlation given earlier by the present author [23]. × Ceccaldi et al. [41]; + Babeliowsky et al. [43, 44]; Δ, ▲ Millero et al. [46]; o Steckel and Szapiro [24]; ◆ Chang and Tung [48]; ◊ Schrader and Wirtz [49]; • Grossmann-Doerth [50]; □ Rivkin [51]; ■ Shatenshtein et al. [47]; --- eq (31) of this paper with coefficients from table 2.

D_2O is by Ceccaldi, Girard, Menaché, and Riedinger [41] who made observations at 22.300 °C (IPTS-68) on samples with $x_2 \sim 0.9994$, $y_{17} = 380\times10^{-6}$ (by calculation by equation (18)), and $y_{18} = 0.002055$. By calculations similar to those here they obtained a density of 1104.750 kg m^{-3} for $D_2{}^{16}O$ at that temperature. This value is the mean of measurements on two samples differing by 0.003 kg m^{-3}. For D_2O, with oxygen isotopes as in SMOW, this corresponds to 1104.991 kg m^{-3}. Even after a value has been chosen for the maximum density of SMOW, differences of a few parts per million exist in estimates of the density at at 22.3 °C because of the use of different tables of thermal expansion. Ceccaldi et al. took their thermal expansion from Chappuis [31], employing the value 997.7086 kg m^{-3} for SMOW at that temperature. Equation (34) of the present paper gives 997.7052 kg m^{-3}. As we are concerned with a self-consistent surface, we replace the 1104.991 calculated above by 1104.987 kg m^{-3}. This means that if eq (34) should be replaced by another polynomial the other terms in eq (27) relating to other compositions would be little changed. The value obtained by Ceccaldi et al. cannot be considered in conflict with the baseline of figure 1 as a previous correction by Isberg and Lundberg [42] to the density of D_2O to correct for a previous error in the normalization of the oxygen isotopes had raised the density by 0.09 kg m^{-3}.

In a pair of briefer papers, Brulmans et al. [43, 44] have reported a density of 1104.481±0.003 kg m^{-3} at 25.000 °C on the IPTS-48 (Brulmans, private communication) for D_2O (100% D) with an oxygen composition of $y_{17} = 0.000375$ (calculated) and $y_{18} = 0.002039$, again slightly different from the oxygen composition of SMOW. Densities were also given at eight other temperatures from 8 to 26 °C; these two papers together have been treated as a single body of data. The authors' calibration was made on the assumption that ordinary water has a maximum density of 999.973 kg m^{-3} at 1 atm, and has a temperature dependence following the equation given by Tilton and Taylor [45]; they do not report the precautions taken to control the isotopic composition of their light water. The thermal expansion of Tilton and Taylor is close to that of eq (34). Adjusting for light water to have the density of SMOW, and adjusting to the oxygen isotope concentration standard adopted here, either by the method used by Ceccaldi et al. or by the different algorithm given by Babeliowsky and Brulmans [43], gives a density at 25 °C (IPTS–48) of 1104.477 kg m^{-3}. The other values in this body of data have been adjusted to this standard. The authors have made a comparison with previous values of the density of D_2O at 25 °C, adjusting all values to the same concentration of oxygen isotopes. The range of variations is 0.07 kg m^{-3}, with their value near the high end. The comparison of this value with that of Ceccaldi et al. is not straightforward. As figure 1 shows, if their thermal expansions are ignored and the baseline of the figure accepted, their value is 0.012 kg m^{-3} above that of Ceccaldi, the difference being about twice the combined estimated errors. If the Brulmans thermal expansions are accepted the difference doubles. The temperature dependence found by Brulmans does not parallel that of any other data set (parallelism is generally absent from the figure). The deviations are perhaps no larger than the experimental errors (the error of the data defining the baseline is larger than that of Brulmans), but, as it seems wiser to take the temperature dependence from data sets covering a wider temperature range, these values have largely been ignored. The determination of the absolute density is not to be ignored, and has been given about half the weight of the value of Ceccaldi; the new curve was started at 0.023 kg m^{-3} above the baseline between 20 and 25 °C.

The mole fraction of deuterium in the heavy water used by Millero, Dexter, and Hoff [46] was determined from the density and so has no authority for the density. Nevertheless, the measurements were made in a device calibrated against light water, so the measurements should have information on the thermal expansivity of heavy water. The figure, however, shows the scatter in the values to be ~1 in 10^5, except for the point at 70 °C which is in error by 17 in 10^5, well off the figure in the upward direction. Between 20 and 30 °C the thermal expansion data of Brulmans et al. [44] and Shatenshtein et al. [47] suggest that the density might be falling relative to the baseline with increasing temperature, while Millero's data show a rising trend in this range. In this situation, there is no reason to change the slope from that of the baseline, which here follows Steckel and Szapiro [24]. For display in figure 1, the published values of Millero et al. [46] were adjusted to 100% D_2O (accepting the authors' concentrations), to the density standard for SMOW adopted here, and for the differences in the density of light water between references [23] and [26]; i.e. at higher temperatures the densities have been increased by a few parts per million. All these adjustments are small compared to the apparent uncertainty.

The treatment of the other data in figure 1 has been straightforward. Chang and Tung [48], Schrader and Wirtz [49], Grossmann-Doerth [50], and Rivkin [51] all have experimental errors of several times 0.01 kg m^{-3}, and all report the ratios of light and heavy water. As this ratio varies only slowly with temperature and pressure, the densities for light water accepted here have been used with those ratios to obtain the points shown in figure 1. Had the values of Chang and Tung and Schrader and Wirtz been raised the 0.09 kg m^{-3} suggested by Isberg and Lundberg they would be in agreement with the baseline to about their precision. The values of Grossmann-Doerth and Rivkin were based on measurements at saturation. They agree with each other, but disagree with the others by an amount much greater than the uncertainties in adjustment to atmospheric pressure.

The apparent error of the four values of Shatenshtein et al. [47] is a little less than that of the data discussed in the preceding paragraph, and the trend of the data is in adequate agreement with the thermal expansion of the baseline of the figure.

A free-hand curve was drawn starting 0.023 kg m^{-3} above the baseline of figure 1 between 20 and 25 °C, and continued parallel to the trend of the best data sets to higher and lower temperatures. As already discussed, the data of Steckel and Szapiro [24] have been given greatest weight. By starting the analysis by sketching a free-hand curve, rather than by doing a least-squares fit of separate data sets taken together, the jump at 80 °C of reference [23] is avoided. In the present case, above 80 °C the curve parallels Cheng and Tung most closely. Deviations of the resulting curve from the baseline were read at 5 degree intervals, and that curve fitted by least-squares. Two fits are reported, the first expressing the density as a rational function, eq (31); this is shown as the dashed line in figure 1 and its coefficients are included in table 2. The second fit expresses the molar volume as a polynomial of the sixth degree. Particularly for the rational function, the number of coefficients seems large for the range covered and the precision. This means that the data has been overfitted, and suggests that an attempt is being made to represent inconsistent data; it is not clear what data should be weighted less. The molar volume of D_2O with oxygen isotopes as in SMOW was found to be

$$V_{D_2O}/\text{cm}^3\,\text{mol}^{-1} = 18.128901 - 4.0016956\times10^{-3}t + 211.48069\times10^{-6}t^2 - 2.2696017\times10^{-6}t^3 + 22.478901\times10^{-9}t^4 - 133.77927\times10^{-12}t^5 + 347.5742\times10^{-15}t^6,\ 5 \leqq t/^\circ\text{C} \leqq 100. \tag{38}$$

Precise knowledge of the compressibility of heavy water is due to Millero [52, 53, 54]. Here we follow Fine and Millero [54] whose results are based on speed-of-sound measurements and are hence comparable to those for light water. In the case of heavy water it should be noted that the specific heat data are of lower quality than is the case for ordinary water, so the isothermal compressibilities would be of inferior quality at the higher temperatures even if the velocity data were of equal value. Fine and Millero gave a quadratic polynomial for the reciprocal of the compressibility of 99.82% D_2O that was based on the velocity data of Wilson [55]. Values of this compressibility were calculated at 5 degree intervals, adjusted to 100% D_2O, and multiplied by the molar volumes found above. A quadratic does not represent the data adequately, so a polynomial of the seventh degree was used to match eq (35).

$$(\partial V_{D_2O}/\partial P)_T/\text{cm}^3\,\text{mol}^{-1}\,\text{Mbar}^{-1} = -974.204 + 9.061\,85\,t - 210.515\,0\times10^{-3}t^2 + 3.101\,295\times10^{-3}t^3 - 37.840\,4\times10^{-6}t^4 + 311.543\,2\times10^{-9}t^5 - 1.507\,672\times10^{-9}t^6 + 3.195\,62\times10^{-12}t^7,\quad 5 \leqq t/^\circ\text{C} \leqq 100. \tag{39}$$

3.4. $H_2{}^{18}O$ and $D_2{}^{18}O$

It is not simple to express the data of Steckel and Szapiro [24] in the form used here as they have reported their reference densities at 30°C (IPTS–48) = 29.9906°C (IPTS–68), but have expressed functional representations in terms of the maximum densities of the various compositions. Further, their density for deuterium water is 1 in 10^4 lower than that accepted here. Accepting the present values for waters rich in $H_2{}^{16}O$ and $D_2{}^{16}O$, and their values for ones rich in $H_2{}^{18}O$ and $D_2{}^{18}O$ at 30°C, the values can be expressed in molar terms in the form of eq (27) as follows

$$V_w/\text{cm}^3\,\text{mol}^{-1} = 18.093\,94 + 0.059\,15x_2 - 0.013y_{17} - 0.026\,77y_{18} + 0.010x_2y_{17} + 0.019\,63x_2y_{18}, \tag{40}$$

where those authors have been followed (for the moment) in assuming that the molar volumes of $H_2{}^{17}O$ and $D_2{}^{17}O$ are the means of the forms with ^{16}O and ^{18}O.

Steckel and Szapiro measured the thermal expansion of a sample of $H_2{}^{18}O$ with hydrogen in natural abundance (which we take as being that of SMOW, i.e. $x_2 = 0.000158$), $y_{17} = 0.0038$, and $y_{18} = 0.9753$. Equation (40) gives the molar volume of this as 18.06779 cm^3 mol^{-1}. The temperature dependence of the molar volume is then represented by

$$V_{H_2{}^{18}O}/\mathrm{cm^3\,mol^{-1}} = 17.994\,066 - 1.209\,1347\times10^{-3}t + 152.007\,50\times10^{-6}t^2 - 1.231\,6963\times10^{-6}t^3 + 8.867\,695\times10^{-9}t^4 - 28.175\,669\times10^{-12}t^5,$$
$$1 \leqq t/°\mathrm{C} \leqq 79. \qquad (41)$$

where the argument is on the IPTS–68.

A similar analysis may be given of Steckel and Szapiro's thermal expansion measurements for $D_2{}^{18}O$, measurements made on a sample with $x_2 = 1$, $y_{17} = 0.0034$, and $y_{18} = 0.9798$. Equation (40) gives the molar volume of this at 30°C as 18.14610. The temperature dependence of the molar volume is then represented by

$$V_{D_2{}^{18}O}/\mathrm{cm^3\,mol^{-1}} = 18.124\,193 - 4.209\,8883\times10^{-3}t + 219.813\,33\times10^{-6}t^2 - 2.401\,4745\times10^{-6}t^3 + 21.334\,153\times10^{-9}t^4 - 83.406\,814\times10^{-12}t^5,$$
$$3.5 \leqq t/°\mathrm{C} \leqq 72. \qquad (42)$$

The four equations, (34), (38), (41), and (42), each associated with a well-defined isotopic composition, plus the assumption that the molar volume of water with ^{17}O is the mean of the volumes with ^{16}O and ^{18}O, which is adequate for the treatment of solutions where ^{17}O is dilute, permits the calculation of the temperature dependence of the volume of the four components $H_2{}^{16}O$, $H_2{}^{18}O$, $D_2{}^{16}O$, and$D_2{}^{18}O$, yielding the terms for those four components that appear in eq (45), below, as well as an approximation to the volumes of $H_2{}^{17}O$ and $D_2{}^{17}O$.

Other measurements of the density of $H_2{}^{18}O$ have been made by Ku and Chang [56], whose results agree with those of Steckel and Szapiro to experimental error. Additional data on $D_2{}^{18}O$ from 15 to 35°C were given by Kudish and Wolf [57]. Their values average 0.00045 cm^3 mol^{-1} lower than those of Steckel and Szapiro, and are quite smooth relative to the curve based on the latter data. They certainly should be given some weight, so the constant term in the equation originally based on data of Steckel and Szapiro has been lowered 0.00020 cm^3 mol^{-1} (1 in 10^5 in the massic density).

3.5. $H_2{}^{17}O$ and $D_2{}^{17}O$

Measurements by Kudish *et al.* [58] on waters containing up to 86% $H_2{}^{17}O$ were extrapolated by them to give the density of the pure component from 15 to 35°C. The results are scattered, but show that the molar volume is 0.042 ± 0.003 cm^3 mol^{-1} higher than the mean of $H_2{}^{16}O$ and $H_2{}^{18}O$. This is included in eq (45), and the coefficients for the other forms were recalculated for self-consistency. This means that although the molar volume of $H_2{}^{18}O$ is less than that of $H_2{}^{16}O$, the molar volume of $H_2{}^{17}O$ is greater. Despite this evidence that the properties of $H_2{}^{17}O$ are not the mean of those of $H_2{}^{16}O$ and $H_2{}^{18}O$, the higher terms included in eq (45) are such a mean, as in the absence of adequate information this is the best assumption that can be made.

There are no measurements of the density of $D_2{}^{17}O$. Its molar volume appears in eq (45) as 0.04 cm^3 mol^{-1} greater than the mean of $D_2{}^{16}O$ and $D_2{}^{18}O$, and in this case there is, of course, uncertainty about even the leading term.

3.6. T_2O

Based on Goldblatt's values [59] adjusted to pure T_2O, the molar volume at atmospheric pressure is

$$V_{T_2O}/\mathrm{cm^3\,mol^{-1}} = 18.16150 - 4.39208\times10^{-3}t + 178.7941\times10^{-6}t^2 - 773.641\times10^{-9}t^3,$$
$$5 \leqq t/°\mathrm{C} \leqq 55. \qquad (43)$$

Two runs differed by 0.006 cm^3 mol^{-1}, so the error of eq (43) is estimated as 0.01 cm^3 mol^{-1}.

3.7. Non-Ideality

We may distinguish two forms of non-ideality. The first, which has excited no comment, is implicit in eq (29). According to that equation the changes of volume produced by changing the isotopic composition of the hydrogen and those produced by changing the composition of the oxygen are not additive. Indeed, eq (40) shows the magnitude of the non-additivity to be comparable to that of the isotopic effects themselves. To the extent that eq (29) describes liquid water, the molar volume varies linearly if the hydrogen isotope composition is changed without variation of oxygen composition, or alternatively if the oxygen composition is changed holding the hydrogen composition constant. The dependence is not linear if both vary, as when $H_2{}^{16}O$ and $D_2{}^{18}O$, or $H_2{}^{18}O$ and $D_2{}^{16}O$, are mixed.

Non-ideality usually refers to a second effect, that of the molar volume being non-linear in the fractions of the hydrogen isotopes at constant oxygen composition. Longsworth [60] reported departures from ideality of light-heavy water solutions to be about 2×10^{-4} cm^3 mol^{-1}, while Swift [61] found them to have the opposite sign, but in both cases they are not significantly different from zero. Bottomley and Scott [62] have now reported that the excess volumes are close to symmetrical in the composition, with a maximum value of $+1.8\pm0.4\times10^{-4}$ cm^3 mol^{-1} at 25 °C, while at 4 °C it is -1.2×10^{-4} cm^3 mol^{-1}. As there is no information about the second derivative, it seems premature to speculate about how these values tie in with the patterns of maxima and minima in the properties of water. The same uncertainty about the pattern means that no corresponding term can be written for H_2O—T_2O mixtures; in any event, such a term is not needed at present since it would be smaller than the errors in the density of T_2O.

A straight line through these two values predicts large values of this non-ideality at higher temperatures. We have chosen to believe that the effect must be smaller than experimental error at the higher temperatures in our range, and have represented it by a quadratic equation, passing through the two values of Bottomley and Scott, and becoming zero at 125 °C. The quadratic term so obtained is the only one in the present paper that is justified only by weak arguments. The Q term of eq (27) then becomes

$$\begin{aligned} Qx_1x_2/\mathrm{cm^3\ mol^{-1}} = {}& (-0.000\,7616 + 0.072\,56\times10^{-3}t \\ & - 0.5316\times10^{-6}t^2)\,x_1x_2, \end{aligned} \tag{44}$$

with a maximum near 70 °C. The fitting of eq (45) has been done including this expression.

The origin of the nonplanarity of the molar volumes of $H_2{}^{16}O$, $D_2{}^{16}O$, $H_2{}^{18}O$, and $D_2{}^{18}O$ has not been explained. It is to be expected that non-linear terms in $y_{16}y_{18}$ would be somewhat smaller than the ones for x_1x_2, so they are probably too small for accurate measurement at present. On the other hand, eq (40) predicts a much larger effect if $H_2{}^{16}O$ and $D_2{}^{18}O$ are mixed; this would be well worth investigating, and a measurement of the thermal expansion of the equimolar mixture would be most useful for correlations like the present one.

Information on the compressibility of water is available only for H_2O and D_2O, with no information on the effects of oxygen isotopes. Knowledge of the non-linearity of $(\partial V/\partial p)_T$ in H_2O–D_2O mixtures could be obtained from measurements of the velocity of sound as from those made by Mathieson and Conway [39], but their observations have not been reported in such a way as to make this possible.

3.8. Comprehensive Equation

The equations already given can be combined into a single equation of the form of eq (27), namely

$$\begin{gathered}
V_\mathrm{w}/\mathrm{cm^3\ mol^{-1}} = 18.018\,091 - 1.218\,0767\times10^{-3}t \\
+ 162.743\,83\times10^{-6}t^2 - 1.770\,8337\times10^{-6}t^3 \\
+ (22.185\,652\times10^{-9}t^4 - 207.622\,81\times10^{-12}t^5 \\
+ 1.292\,6583\times10^{-12}t^6)\ (1 - x_3) \\
+ (-4.606\,4706\times10^{-15}t^7 + 7.064\,9600\times10^{-18}t^8) \\
(1 - x_2 - x_3) \\
+ (0.110\,806 - 2.783\,1566\times10^{-3}t + 48.718\,35\times10^{-6}t^2 \\
- 0.498\,4752\times10^{-6}t^3 + 0.295\,791\times10^{-9}t^4 \\
+ 73.731\,69\times10^{-12}t^5 - 944.3124\times10^{-15}t^6)\,x_2 \\
+ 0.029\,615\,y_{17} \\
- 0.024\,770\,y_{18} \\
+ [0.009\,6245\times10^{-3}t - 10.997\,72\times10^{-6}t^2 \\
+ 0.551\,9056\times10^{-6}t^3 - 13.630\,708\times10^{-9}t^4 \\
+ 183.642\,96\times10^{-12}t^5 - 1.322\,8188\times10^{-12}t^6 \\
+ (4.713\,9486\times10^{-15}t^7 - 7.229\,7994\times10^{-18}t^8) \\
(1 - x_2)](y_{18} + \tfrac{1}{2}y_{17}) \\
+ (0.019\,832 - 0.222\,2123\times10^{-3}t \\
+ 19.506\,27\times10^{-6}t^2 - 0.686\,562\times10^{-6}t^3 \\
+ 12.461\,793\times10^{-9}t^4 - 132.207\,09\times10^{-12}t^5 \\
+ 0.967\,9070\times10^{-12}t^6) \\
x_2\,(y_{18} + \tfrac{1}{2}y_{17}) \\
+ (0.143\,356 - 3.173\,99\times10^{-3}t + 16.0623\times10^{-6}t^2 \\
+ 998.393\times10^{-9}t^3)\,x_3 \\
+ (-0.000\,7616 + 0.072\,56\times10^{-3}t - 0.5316\times10^{-6}t^2)\,x_1x_2 \\
+ [-916.834 + 6.971\,62t - 166.1199\times10^{-3}t^2 \\
+ 2.499\,876\times10^{-3}t^3 - 32.5158\times10^{-6}t^4 \\
+ 286.3204\times10^{-9}t^5 - 1.484\,220\times10^{-9}t^6 \\
+ 3.321\,56\times10^{-12}t^7 \\
+ (-57.370 + 2.090\,23t - 44.3951\times10^{-3}t^2 \\
+ 0.601\,419\times10^{-3}t^2 - 5.3246\times10^{-6}t^4 \\
+ 25.2228\times10^{-9}t^5 - 0.023\,452\times10^{-9}t^6 \\
- 0.125\,94\times10^{-12}t^7)\,x_2]\times10^{-6}p.
\end{gathered} \tag{45}$$

In this equation t is the Celsius temperature on the IPTS–68, and p is the gage pressure in bars as defined by eq (26). The temperature range for the various isotopic components has been indicated in connection with the equations from which this has been derived, and the pressure term should not be used for a range exceeding 10 bar. The problems of representing the pressure dependence over a wider range are discussed in appendix II.

Equation (45) has been written to reproduce the starting equations when the appropriate isotope fractions are used, and to this end many more figures have been carried than are justified by the precision of most of the data. The uncertainties have been discussed for each of the components. Gathering this information together, the uncertainty of eq (45) is approximately

$$\epsilon/\mathrm{cm}^3\,\mathrm{mol}^{-1} = 2.2\times10^{-6}t + 2.\times10^{-11}p + (8. + 2.t)\times10^{-5}x_2 + 0.01x_3 + 0.005y_{17} + 0.0002y_{18} \qquad (46)$$

where the error of eq (25), possibly 8×10^{-5} cm^3 mol^{-1}, has not been included.

While it would be possible to take eq (45) and use it to refine some of the data on mixtures in order to obtain a better equation, this has not been done as the results would only make small changes that are negligible compared to the uncertainties.

3.9. Discussion

Equation (45) brings together all that is known about the molar volume of waters near atmospheric pressure. The surprising fact that has emerged is how poorly the thermal expansion of D_2O is known. As the molar volume at one temperature has been found with high precision by Ceccaldi et al. [41], the urgent need in connection with that composition is for thermal expansion measurements over a wide enough range that the higher derivatives with respect to temperature can be evaluated with confidence. Measurements with much smaller uncertainties than the spread of figure 1 are well within present capabilities.

The data on ^{17}O and most of those on ^{18}O were obtained in a single laboratory, the Isotope Department of the Weizmann Institute of Science. This means that were data available from other laboratories the scatter would probably be larger. On the other hand it seems reasonable to accept that in the one laboratory the relations between the different waters have been found to about the precision claimed.

The measurements most urgently needed appear to be:[6] (i) the thermal expansion of D_2O over a wide temperature range; (ii) both the molar volume and the thermal expansion of a solution near $x_1 = 0.5, x_2 = 0.5, y_{16} = 0.5$, and $y_{18} = 0.5$, and its thermal expansion over a temperature range at least to 100°C; (iii) the effect of the oxygen isotopes on the isothermal compressibility.

As eq (45) shows, a power series is not fully satisfactory for representing volumes as a function of temperature, and the same weakness holds as a function of pressure. In the case of pressure, the volume decreases monotonically with increasing pressure, and a large number of isothermal compression equations have been proposed for various condensed phases. The application of several to water is considered in appendix II.

The temperature dependence is more difficult, as a power series has alternating signs and is poorly convergent, but it is difficult to think of anything better. The stable range of the isobaric curve ends at the boiling point, so it would be better from that view to make a correlation along the saturation curve where a wider temperature range is possible. Clearly, we would like a form of equation that deals adequately with the maximum densities and their pressure dependence, but it is not clear how to combine this with the requirement of mixtures made at constant temperature and pressure being nearly ideal, and eq (32) does not adequately provide for the latter feature.

Menaché [1] derived, and Millero and Emmet [3] confirmed, a relation between the change of density and $^2\delta$ and $^{18}\delta$. The simplest approximation to the dependence of ρ_w on the concentrations of the isotopes is obtained by writing

$$\rho_w = M_w/18.0, \qquad (47)$$

where M_w is given by eq (4) and 18.0 approximates the molar volume. The dependence is found by taking derivatives of this with respect to x_2, y_{17}, and y_{18} (neglecting tritium), which gives

$$d\rho_w/\mathrm{g\,cm}^{-3} = 0.1118\,dx_2 + 0.0558\,dy_{17} + 0.1113\,dy_{18}. \qquad (48)$$

If the more complete expression, $\rho_w = M_w/V_w$, is used, where V_w is given by eq (45), the coefficients are a function of temperature and composition. For the composition of SMOW at 4 °C there is obtained

$$d\rho_w/\mathrm{g\,cm}^{-3} = 0.1061\,dx_2 + 0.0541\,dy_{17} + 0.1126\,dy_{18}. \qquad (49)$$

The reference to y_{17} can be eliminated by eq (17). With this, eq (49) expressed in terms of δ, obtained from eqs (11) and (14), is

$$d\rho_w/\mathrm{g\,cm}^{-3} = 1.68\times10^{-8}\,d^2\delta‰ + 2.34\times10^{-7}\,d^{18}\delta‰. \qquad (50)$$

Starting from eq (47), Menaché obtained the coefficients 1.8 and 2.3. This expression has been shown to apply to the variations of natural waters, so in that sense it is useful. However, once again it is to be emphasized that the concentration of ^{17}O has been assumed rather than measured, and that it is inadequate for any precise purpose to assume that the density of water is specified by a number of parameters too small to specify it.

It is, in addition, possible to use eq (21) to eliminate one

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[6] Commission I.4 (Physicochemical Measurements and Standards) of the International Union of Pure and Applied Chemistry has issued a "Recommendation for the redetermination of the absolute density of water," calling for a redetermination of the absolute (i.e. massic) density, thermal expansion, and dissolved gases, at temperatures up to 40 °C. On the completion of this program knowledge of the density of ordinary water will greatly exceed that of other isotopic waters. As already remarked, the most serious unresolved problem in connection with ordinary water is how the density data below 40 °C join with those above that temperature.

of x_2 and y_{18}, in which case there is obtained for natural waters at 4 °C

$$d\rho_w/\mathrm{g\ cm^{-3}} = 0.1850\, dy_{18} = 0.2912\, dx_2$$

$$= 3.68\times10^{-7}\, d^{18}\delta‰ = 4.61\times10^{-7}\, d^{2}\delta‰, \qquad (51)$$

as given by Menaché [1]. These relations apply to natural waters from different sources, and are based on the coefficient 0.6355 of eq (21). However, on the basis of the numbers given in section 2.4, for laboratory conditions, which are better defined, the coefficient might be 0.7 at 0 °C, 0.6 at 20 °C, and 0.3 at 100 °C, which would produce substantial changes in the coefficients of eq (51).

4. Effect of Dissolved Atmospheric Gases on Density

4.1. Henry's-Law Relations for Dilute Gases in Water

It has long been known that saturation of ordinary water with air decreases the density, by perhaps a few parts per million, but the precise amount has been uncertain. Lauder [63] watched the buoyancy of a float change as gas dissolved and showed that the density decreases on the dissolution of nitrogen, increases with oxygen; saturation with air decreases the density by 4.7 p.p.m. at 0 °C, while carbon dioxide increases the density. The analysis below does not support his finding that the effects of oxygen and nitrogen are not additive for water in equilibrium with the atmosphere.

By direct measurement Marek [64] found the decrease of density on saturation with air to go through a maximum of 3.4 p.p.m. at 7 °C, while at 20 °C the decrease was 0.4 p.p.m. All other evidence shows his finding of a diminished effect below 7 °C to be in error. In a careful experiment, Chappuis [65] found that between 5 and 8 °C, a temperature range where measurements should be particularly reliable as variations of temperature have only a small effect on the density of water itself, saturation of water with air decreased the density by 3.0 p.p.m. Millero and Emmet [3] measured a lowering of 3.0±0.2 p.p.m. on saturation at 4 °C. Frivold [66] found a decrease of 1.9 p.p.m. at 15.6 °C. At 20 °C, Emeléus et al. [67] found a decrease of 2 p.p.m., but Richards and Harris [68] one of less than 0.2 p.p.m. These numbers have often been discussed, and combined in various ways. Bowman and Schoonover [69] chose a decrease of 2 p.p.m. at 0 °C and 1 p.p.m. at 20 °C. Brown and Lane [28], in their recent assessment, favor a decrease in density of 3 p.p.m. between 5 and 8 °C but of less than 1 p.p.m. above 20 °C. It is clearly a difficult metrological problem to improve on these numbers by direct measurement. An indirect method promises to be more illuminating.

If the presence of water vapor may be neglected for the moment, the earth's atmosphere has a compostion of about 0.78 mole fraction N_2, 0.21 O_2, 0.01 Ar, and 0.0004 CO_2, as well as traces of the other inert gases. The concentration of CO_2 varies by at least a factor of two from place to place, and is higher in cities than in the countryside. For nitrogen, oxygen, and argon, the assumption that at atmospheric pressure the atmosphere may be treated as an ideal mixture of ideal gases, and the aqueous solution as an ideal solution, is sufficiently accurate for calculating the density of the aqueous solution to 0.1 p.p.m., although other factors will be found to limit the precision to 1 p.p.m. Under these assumptions, if the total pressure of all the gases present except water is P_g then the partial pressures of the atmospheric gases are

$$P_{N_2} = 0.78\, P_g, \qquad (52)$$

$$P_{O_2} = 0.21\, P_g,$$

$$P_{Ar} = 0.01\, P_g,$$

$$P_{CO_2} = 0.0004\, P_g.$$

The partial pressure of water P_w is much more variable. It is usually determined from the saturation temperature or relative humidity, and often has a value about 17 mbar in the laboratory. When liquid water is present the partial pressure of water near the liquid will be close to the saturation pressure of water at that temperature, and gradients of P_w may exist. The total pressure P, the quantity that is determined with a barometer, is closely enough,

$$P = P_g + P_w, \qquad (53)$$

so that a determination of P and P_w permits the calculation of the partial pressures of the individual gases.

The evaluation of the effect of these dissolved gases on the density of liquid water will be made in two steps. The first is to obtain the Henry's law coefficient relating the concentration of the gas in solution to the partial pressure in the atmosphere above it. The second is to relate the volume of the solution to the concentration of gas in it. The system to be treated is that of a gas phase saturated with water in equilibrium with a liquid water solution saturated with the gases.

Henry's law relates the partial pressure of a gas, e.g. P_{N_2}, to its mole fraction, e.g. X_{N_2}, in the solution.

$$X_{N_2} = H_{N_2}^{-1}\, P_{N_2}, \qquad (54)$$

$$X_{O_2} = H_{O_2}^{-1}\, P_{O_2},$$

$$X_{Ar} = H_{Ar}^{-1}\, P_{Ar},$$

$$X_{CO_2} = H_{CO_2}^{-1}\, P_{CO_2},$$

where the Henry law coefficient $H_{N_2}^{-1}$ is written as a reciprocal to preserve the usual convention.

The presence of dissolved gases in the water gives a Raoult law lowering of the vapor pressure

$$P_w = (1 - X_{N_2} - X_{O_2} - X_{Ar} - X_{CO_2})\, P_w{}^\circ, \tag{55}$$

where $P_w{}^\circ$ is the vapor pressure of pure water at the temperature in question. As the term in parenthesis in eq. (55) is nearly unity at the concentrations considered, an iterative treatment of eqs (53), (54), and (55) converges quickly.

Solubility measurements are often reported as Bunsen coefficients which give the volume of gas/volume of solvent, or in terms of weight ratios. Furthermore, it is not always clear whether eqs (53) and (55) were applied in the reduction of the data. By working in mole fractions in the present paper we arrive at a treatment that we will hope does not vary much with change of isotopic composition of the water. For conversions of solubility data and for a review of the older data we follow Battino and Clever [70].

The molar volume of a dilute solution in water is approximately

$$V = X_w V_w + \Sigma X_i V_i, \tag{56}$$

where X_w is the mole fraction of water, corresponding to the term in parenthesis in eq (55). As we are concerned only with the case where the dissolved gases are dilute, the partial molar volume of water V_w is just the molar volume of pure water given by eqs (34) or (45). The mole fraction X_i corresponds to that in eq (54), and the partial molar volume V_i of the dissolved component is the value for infinite dilution and is not considered to vary over the concentration range treated. These assumptions are reflected in the simple notation adopted. Millero and Emmet [3] measured the apparent molar volume as a function of concentration, but most of the work reviewed has large errors so that such refinements are not helpful.

The partial molar volume of solutes is an important quantity in the description of solutions, but the precision with which values are known is less than that for solubility. However, the precision is still more than adequate for calculating changes in the density of water to 0.001 kg m^{-3}. Two approaches to the determination of partial volumes have been used: In the first the density or volume of a solution is determined as a function of composition; this corresponds to the methods used with solutions of involatile solutes. The other makes use of the change of equilibrium constant with pressure as given by Krichevsky and Kasarnovsky [71] to give an extended version of eq (54)

$$\ln (f_i/X_i) = \ln H_i + \frac{V_i P}{RT}, \tag{57}$$

where f_i is the fugacity rather than the partial pressure, to indicate that non-ideality in the vapor phase has been taken into account, H_i the Henry law constant for low pressures defined by eq (54), R the gas constant, and T the absolute temperature.

The density of an aqueous solution is given by the quotient

$$\rho = M/V, \tag{58}$$

(cf. eq (30) for pure water), where V is given by eq (56) and M is the mean molecular weight

$$M = X_w M_w + \Sigma X_i M_i. \tag{59}$$

However, even without knowing the concentration of dissolved gas, we see that dissolution of the gas will increase/decrease the density as M_i/V_i is greater/less than M_w/V_w.

The results of calculations are most conveniently reported as the fractional change from the density of pure water. In the approximation that the amount of gas is small, there is obtained from eqs (56) and (59)

$$\frac{\rho - \rho_w}{\rho_w} = \frac{\Sigma X_i M_i\, (1 - \rho_w V_i/M_i)}{M_w}, \tag{60}$$

which is used in the calculations reported here.

4.2. Oxygen

Battino and Clever [70] recommend a Bunsen coefficient, for which the units are volume of gas at STP per volume of solvent at SP, for oxygen in water at 25 °C of 0.02847, based on 11 values obtained before 1965. Later work has been described by Murray and Riley [72] and a survey with an algebraic representation given by Weiss [73]. The latter paper tabulates the Bunsen coefficients for oxygen, nitrogen, and argon at 1 K intervals from 0 to 6 °C, and at 2 K intervals to 40 °C. The value for oxygen at 25 °C is 0.02844. The errors for that gas appear nowhere as much as 1%, so the data are adequate for present purposes. Bunsen coefficients α from that paper have been converted to Henry law coefficients by the relation given by Battino and Clever

$$H/\text{bar} = \frac{22709}{\alpha V_w} + 1.013, \tag{61}$$

where V_w is the molar volume of ordinary water. Molar volumes were obtained from eq (34) and the molecular weight from eq (4). The values of H obtained for oxygen, nitrogen, and argon are given in table 3.

TABLE 3. Henry law coefficients for O_2, N_2, and Ar in pure water. The Bunsen coefficients α/atm^{-1} are from Weiss [73], and conversion is by equation (61).

$t/{}^\circ$C	$10^3\alpha$/atm^{-1}	$10^{-3}H$/bar	$10^3\alpha$	$10^{-3}H$	$10^3\alpha$	$10^{-3}H$
	oxygen		nitrogen		argon	
0	49.10	25.67	23.74	53.09	53.63	23.50
4	44.13	28.56	21.50	58.63	48.29	26.10
10	38.16	33.03	18.81	67.00	41.84	30.12
20	31.05	40.53	15.59	80.71	34.12	36.88
30	26.30	47.72	13.45	93.31	28.93	43.38
40	23.10	54.15	12.02	104.06	25.38	49.28

The partial volumes of oxygen, nitrogen, and argon are surprisingly poorly known considering their importance in the thermodynamics of solutions. The available data for the three gases are shown in figure 2. The only gas for which sufficient data are available to give an idea of the error is nitrogen. For oxygen the dashed line shown in the figure has the equation

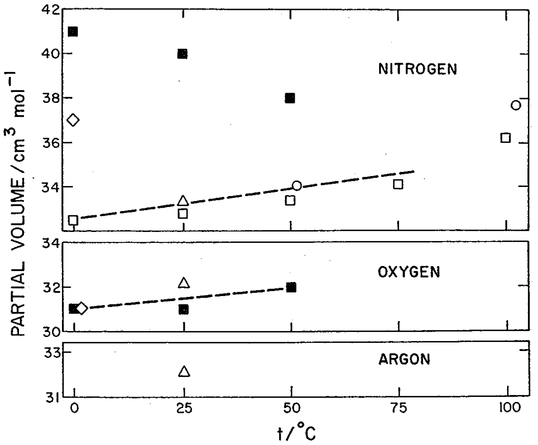

FIGURE 2. Molar volumes in water. □ Krichevsky and Kasarnovsky [71]; ■ Kritchevsky and Iliinskaya [75]; ◇ Lauder [63]; Δ Enns, Scholander, and Bradstreet [76]; o O'Sullivan and Smith [77].

$$V_{O_2}/\mathrm{cm^3\,mol^{-1}} = 31 + 0.02t \pm 1, 0 \leq t/°\mathrm{C} \leq 50. \quad (62)$$

The change of density of SMOW produced by equilibration with an atmosphere at a total pressure of 1.013 bar, and with oxygen comprising 0.21 mole fraction of the gases other than water, is shown in figure 3. The calculation was made by eq (60), and X_i was obtained from eq (54) using table 3. At temperatures below 50 °C the vapor pressure of water is small; at temperatures approaching 100 °C the contribution from atmospheric gases falls because the atmosphere is largely water vapor and the concentration of other gases is small. For oxygen, M/V is near the density of water, and at 50 °C, if the partial volume were at the upper limit of the error given, on dissolution oxygen would lower the density, while if it were at the lower limit the density would increase. In any event the density change is small, and even with one atmosphere of oxygen at 0 °C the density would only increase 2-3 p.p.m.

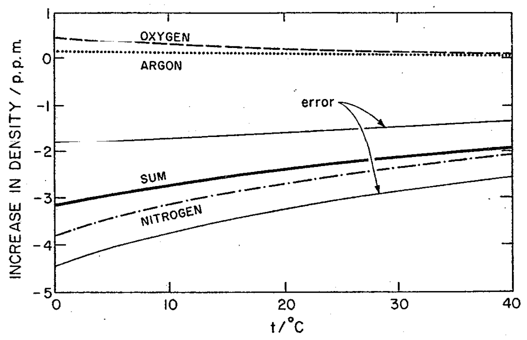

FIGURE 3. Increase of density of ordinary water in equilibrium with the nitrogen, oxygen, and argon of the atmosphere. Heavy solid line, sum of contributions from the three gases. Light solid lines, uncertainty of sum from uncertainty in partial volumes of the gases. If the effect of carbon dioxide were included the sum would be 0.3 p.p.m. upward at 0 °C.

4.3. Nitrogen

The solubility of nitrogen has been reviewed by Battino and Clever [70]. There are fewer data sets than for oxygen, but the agreement is adequate for the present calculation. Later work by Murray, Riley, and Wilson [74], and Weiss [73], whose table is the basis of table 3, is in agreement.

The partial molar volumes are shown in figure 2. Only for nitrogen are there enough data to form an idea of their accuracy. The values of Kritchevsky and Iliinskaya [75], near 40 cm³ mol⁻¹, are both very high relative to other values and show a negative temperature coefficient where all other data sets show a positive one. These data have, therefore, been ignored. The single value by Lauder [63] at 0 °C is also high. A straight line through the remaining low-temperature data gives

$$V_{N_2}/\mathrm{cm^3\,mol^{-1}} = 32.6 + 0.027t \pm 1, 0 \leq t/°\mathrm{C} \leq 75, \quad (63)$$

where the error is approximate as the data do not warrant any precise statistical treatment. The same error was deemed appropriate for oxygen as well. The calculated effect on the density is shown in figure 3.

4.4. Argon

Once again the solubility has been taken from Weiss [73], and the values used in the calculations are given in table 3. The only value of the partial molar volume is from Enns et al. [76] who obtained the value of 32.2 cm³ mol⁻¹ shown in figure 2. Because the ratio M_{Ar}/V_{Ar} is 25% greater than M_w/V_w, this gas increases the density of water by an amount great enough to show in figure 3, even at the low concentration present in air.

4.5. Discussion on O_2, N_2, and Ar

Figure 3 also shows the combined effect on the density of normal water saturated with nitrogen, oxygen, and argon, present in the proportions given by eq (52) at a total pressure (water vapor plus the three gases) of 1 atm. As the partial volumes of the three gases have been determined by similar methods, the errors are expected to be in the same direction in the three cases; this gives the error band shown for the sum of the effects of the three gases. A larger partial volume gives a lesser (more negative) increase in density. We see on comparing figures 2 and 3 that Lauder's values for the density of air and oxygen are about right, but that his value for nitrogen is in error. There is, accordingly, no evidence that the effects are non-additive.

No data are available on the solubility of these gases in waters of other isotopic compositions. However, as the present description of the aqueous solution has been in terms of molar quantities, the same solubility and partial volumes may be used to estimate the change of density produced by the dissolution of these three gases in waters of other isotopic compositions. For example, $D_2{}^{18}O$ has a molecular weight of 22 and a density of 1.22 g cm^{-3}. A calculation using eq (60) then shows equilibration with the nitrogen in the atmosphere to lower the density by 5.4 p.p.m. Oxygen lowers it 1.5 p.p.m., rather than the small positive effect in ordinary water, and argon has a near-zero effect. The sum gives a total lowering of the density of 7 p.p.m.

Nitrogen and argon have no atom in common with water, so there is no exchange effect. While oxygen is present in water the rate of exchange with gaseous oxygen is sufficiently small that it is possible to make measurements on a sample of water that is not in isotopic equilibrium with the oxygen in the atmosphere over it.

4.6. Carbon Dioxide

Although it was the solubility of carbon dioxide that led Henry to the law bearing his name, viz. eq. [54], the law does not in fact describe the behavior of dilute solutions of carbon dioxide well because of the equilibria

$$\begin{aligned} CO_2 + H_2O &\rightleftharpoons H^+ + HCO_3^- \\ &\rightleftharpoons 2H^+ + CO_3^=. \end{aligned} \tag{64}$$

This reaction produces a rapid interchange of oxygen between CO_2 and H_2O, and indeed is used for the normalization of the composition of the oxygen isotopes. In normalization the composition of oxygen in the two components becomes substantially the same, but not exactly, as fractionation causes an enrichment of ^{18}O in CO_2 relative to the water with which it is in contact [78]. Atmospheric carbon dioxide interchanges with atmospheric oxygen by photosynthesis and combustion. The net result is that atmospheric oxygen is richer in ^{18}O than is sea water, which in turn is richer than fresh water, facts already alluded to in section 2.1.

The equilibrium constant for the first ionization of eq (64) is conventionally defined as

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}, \tag{65}$$

and that for the second ionization as

$$K_2 = \frac{[H^+][CO_3^=]}{[HCO_3^-]},$$

where the square brackets should denote activities for systems at finite concentrations, but as we are concerned with dissolved substances at high dilution the activity coefficients may be taken as unity and the square brackets then denote the concentrations of the species indicated. The total or stoichiometric mole fraction of carbon dioxide in solution is

$$[\Sigma CO_2] = [CO_2] + [HCO_3^-] + [CO_3^=]. \tag{67}$$

The preceding sections on oxygen, nitrogen, and argon gave a complete specification of the algebra and an adequate summary of the data, and the results calculated there are reliable. On the other hand, for carbon dioxide, and ammonia to be treated in the next section, the algebra is more complicated, the experimental data are inconsistent and ambiguous, and data on the second ionization of carbon dioxide are scanty. In view of the difficulties, particularly of the molar volumes, we treat only the effect on the density at 0 °C. Effects will be less at higher temperatures. To preserve the algebra used for the preceding gases, concentrations are expressed as mole fractions, though these are not the usual units for expressing equilibria in solution.

Edwards, Newman, and Prausnitz [79] give the Henry law relation between the partial pressure of CO_2 and the mole fraction of the dissolved species CO_2 as 676 bar at 0 °C. For a partial pressure of 0.0004 bar, this gives the mole fraction of species CO_2 in solution as 5.9×10^{-7}. The same authors give the first dissociation constant as 4.7×10^{-9} (mole fractions). The ionization of a weak acid in dilute solution is a standard problem [80]. Denoting the ionization product of water as K_w,

$$K_w = [H^+][OH^-], \tag{68}$$

the hydrogen ion concentration in a carbon dioxide solution is given by

$$[H^+]^2 = K_w + K_1[CO_2]\{1 + 2K_2/[H^+]\}, \tag{69}$$

which may be solved iteratively. At 0 °C K_w has the value 3.65×10^{-19}, and K_2 for carbon dioxide is about $3. \times 10^{-11}$. These values yield a mole fraction of H^+ of 5.3×10^{-8}, and hence by eqs (65) concentrations of species HCO_3^- of 5.2×10^{-8}, effectively equal to that of H^+, and of $CO_3^=$ of $3. \times 10^{-11}$, a negligible amount. Only if the partial pressure of carbon dioxide were three orders of magnitude smaller would K_w and K_2 make significant contributions to eq (69), but in that case the dissolved carbon dioxide would make a negligible contribution to the density of the solution.

There is considerable uncertainty about the partial molar volume of carbon dioxide. At 0 °C Lauder [63] found a value of 44 cm^3 mol^{-1} at low pressures, and 28 cm^3 mol^{-1} at 7 mbar, Kritchevsky and Iliinskaya [75] found 32 cm^3 mol^{-1}, while Enns et al. [76] found 34.8 cm^3 mol^{-1} at 25 °C. Parkinson and de Nevers [81] found 37.6 cm^3 mol^{-1}, which Gibbs and Van Ness [82] reanalyzed to obtain 38 cm^3 mol^{-1} at 0 °C. If 38 cm^3 mol^{-1} is taken as a tentative value for 0 °C, then eq (60) gives an increase in density of 0.20 p.p.m. for the species CO_2. The only other species abundant enough to affect the density is HCO_3^-. Millero [83] gives the partial molar volume of that ion at 25 °C as 23.4 cm^3 mol^{-1}. Equation (60) shows that this species increases the density by 0.06 p.p.m. The two species together increase it by 0.26 p.p.m.

The solubility of CO_2 in D_2O was measured by Curry and Hazelton [84] as 0.9, on a molar basis, of that of H_2O. The same authors [85] found the ratio of the first ionization constants $K_{1,H}/K_{1,D}$ to be 2.7 at 25 °C. Thus the argument given in section 4.1, that by working in molar quantities the results will give approximate answers on isotopic substitution is of limited value for carbon dioxide solutions.

4.7. Ammonia

Ammonia is not an important component of the normal atmosphere. It is mentioned here solely because it is a contaminant of sloppily distilled water. Further, as the sloppy technique that permits the presence of ammonia is likely to permit the presence of carbon dioxide as well, a more complicated system of equilibria prevails than that described in the preceding section. In particular, the ionization equilibrium of water, eq (68), permits a considerable concentration of NH_4^+ with HCO_3^- or $CO_3^=$. There is a rapid interchange of hydrogen between ammonia and water, so the hydrogen isotopes in the ammonia and water become substantially the same.

For pure ammonia solutions, Edwards et al. [79] give a Henry coefficient of 0.26 bar at 0 °C. Ammonia solutions are significantly less dense than pure water. The analysis of Efremova and Sokolova [86] shows that the partial volume of the species NH_3 must be near 37 cm^3 mol^{-1} at 0 °C.

The case where both ammonia and carbon dioxide are present has been studied extensively at higher temperatures in connection with the water-carbon dioxide-ammonia-urea system. At the lower temperatures of interest here, equilibria and the abundances of the species can be evaluated by the algorithm of Edwards et al. Millero [83] gives the partial volume of NH_4^+ as 17.9 cm^3 mol^{-1} at 25 °C, which combines with the 23.4 cm^3 mol^{-1} for HCO_3^- to give $\rho_w V_i/M_i$, the quantity in eq (60), as 0.52, leading to an increase in density of the solution. If NH_4^+ and $CO_3^=$ are the dominant species, as CO_3^- has a conventional partial molar volume of -4.3 cm^3 mol^{-1}, the ratio $\rho_w V_i/M_i$ is 0.33, again producing an increase in density.

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Appendix I

Isotopic Uncertainties in Practical Density Measurements

Interest in the density of water comes from two, essentially unrelated directions. Density values are needed for a description of water itself and as a standard for calibration or for measurements on other materials. The main paper has treated water itself, and devoted considerable attention to uncertainties in our knowledge. This appendix treats errors arising in the use of water as a calibrating substance, and particularly errors arising from the choice of a density table. In such calibrations the maximum precision is not always sought.

Increased awareness of the importance of isotopic composition means that a worker wishing to calibrate a volume by finding the weight of ordinary water contained can no longer uncritically accept that his water has an isotopic composition matching that appropriate for the table of densities he is using. If he is calibrating a pycnometer, the isotopic variations of the fluids to be measured in it must be taken into account as well in arriving at the uncertainties of the final result.

In the past, handbooks have given density tables for (ordinary) water at atmospheric pressure without comment about their limits of validity, and indeed, the present author has produced one such table [87]. It is now clear that such handbooks must henceforth be used more critically if densities are to be measured more precisely than corresponds to the normal range of variation of atomic weights from isotope fractionation. Most density tables give one or two figures beyond that point, and these extra figures are usually considered to have physical meaning, rather than existing solely to aid interpolation. Girard and Menaché [88] have compared tables for atmospheric pressure up to 40 °C. In another paper [2] they gave an approach only feasible for precise work; there appear to be no modern guidelines for work of lower precision.

I.1. Precision in Density Measurements

If p*n* is used to denote a precision (and, we hope, accuracy) of 1 in 10^n, then the care needed for work of various precisions is approximately as follows:

p3: This precision is adequate for many engineering applications. At this precision ordinary water is water, isotopic composition can be ignored, and temperature, pressure, and purity need not be controlled too closely.

p4: Again at this precision the isotopic composition of ordinary water need not be considered, and all modern tables of the density of water at atmospheric pressure are equivalent.

p5: For this precision the density of laboratory water should be checked at one temperature and pressure against a known standard, and the density table at all temperatures and pressures multiplied by a factor ϕ defined as $\rho_{sample}/\rho_{table}$. Most tables of the density of water are equivalent at this precision. If the water is being used as a calibration material for density determinations, the uncertainty of the isotopic composition of the material to be measured is important also.

p6: To attain this, one of the methods of water purification that is strict in its control of isotopic composition must be adopted, and the water so purified must be shown to be controlled on an hourly, daily, and seasonal basis. The adoption of the 1968 International Practical Temperature Scale changes tables by up to 5 p.p.m. Even the best tables may differ by several units in the sixth place; the uncertainty of the experimental work on which they are based is somewhat larger. The table used must be specified in reporting the results. It is quite possible that future work will produce changes of 1 or 2 in the sixth place at temperatures between 0 and 40 °C, while larger changes are almost certain above 40 °C. Pressures must be measured to 20 mbar.

p7: This range is only within the competence of metrological laboratories that have specialized in this direction, and at present work only deals with water between 0 and 40 °C and at atmospheric pressure. The isotopic composition of each water sample must be measured, and particular attention must be paid to thermometry. Any density table given now has only an interim value. As the values adopted will need future correction, experimental details must be given clearly.

I.2. Isotopic Contributions to Density Errors

In calibrating a volume by using water as a standard substance, the usual isotopic error comes from the use of a density table that relates to a different isotopic composition from the water used, and, as indicated in the previous section, such an error would become significant only at the p5 level. If a calibration of the highest precision were attempted, and isotopic abundances were measured, then errors would arise only from uncertainties in eq (45) or whatever source of densities was used. Work of such a level represents the present limit of calibrations based on water.

If the volume calibrated is a pycnometer to be used in determining the density of other substances, then the isotopic variation of the latter is important too. In particular, because of isotopic variations, the atomic weight of carbon [4] is given only to 1/12000 so, for example, without measurement of the isotopic composition the molecular weight of methanol, to take a definite example, is given at best to 1/30000, although density measurements on this compound are often reported to 1 in 10^5. There are relatively few substances which can be purified sufficiently to justify so much precision. Indeed, the separation procedures commonly used in purification also produce isotopic fractionation. Accordingly, if different laboratories purify the same material by different methods they may arrive at different massic volumes even if the molar volumes are equal.

Formerly, when atomic weights were poorly known, there was value in making massic volume measurements more accurately than molar volumes could be given. Today, for the many elements whose atomic weights are known to the precision set by isotopic variation, it is necessary to measure the isotopic composition if increased precison is wanted.

A third case was referred to in section 3.2 in the discussion of eq (35) and the velocity of sound. The adiabatic compressibility κ_S is given by

$$\kappa_S = (\partial \ln \rho/\partial P)_S = \rho^{-1}u^{-2},$$

where κ_S, ρ, and u (the velocity of sound) are functions of isotopic composition as well as of temperature and pressure. As u can be measured to a few parts per million, an important error of κ_S is the choice of an inappropriate table for the determination of ρ.

The composition of most samples of water used for calibration purposes in the past, or indeed at present, is not known. For precisions of p6 or less it need not be known provided the density is tied to a well defined standard, which at present is SMOW. If we consider two samples of water of approximately natural composition, then the ratio of densities ϕ will vary much less with changes of temperature and pressure than will density itself. This same approximation was made earlier in a treatment of the thermal expansion of water at atmospheric pressure [26]. What we wish here is a series of density measurements leading back to SMOW. That is, we write

$$\rho_{(\text{sample})} = \phi\rho_{(\text{SMOW})}, \tag{I-1}$$

where, when ϕ has been found for one temperature and pressure it will be assumed to hold for other temperatures and pressures. The measurement of differences of a few p.p.m. or less in density of water samples has long been possible. While large samples of SMOW are not available, there should be no difficulty in each laboratory obtaining a reference sample whose density relative to SMOW is known with sufficient precision.

As ϕ is unlikely to differ from unity by more than 10 or 20 p.p.m., eq (I-1) is unlikely to produce errors at the p6 level, but it must be realized that experimental data to permit a firm statement are lacking. The quantity ϕ, recommended here only as a way to deal with small variations in density, is not a parameter to allow for the effect of small variations of isotopic composition on other thermodynamic or transport properties.

Appendix II

Equation of State of Water Under Pressure

Conflicting ideals involving accuracy, simplicity, elegance, and generality must be reconciled in the construction of an equation of state. Accordingly, as one or other of these factors is given greater weight, different equations will be arrived at. The question considered in this appendix is how the equation of state of water can be represented beyond the very limited pressure range for which eq (45) applies. As the data available relate only to ordinary and heavy water, the results are suggestive only and do not provide a firm basis for the description of the isotopic waters.

The data that may be considered reliable to 1 kbar and 100 °C are those of Fine and Millero [89] and Kell and Whalley [90] for ordinary water, and Fine and Millero [54] for heavy water. It is not clear whether the treatment that is to show the least dependence on isotopic composition should follow eq (45) and treat $\partial V/\partial p$, whether $\partial \rho/\partial p$ is better behaved, or whether it is best to treat the isothermal compressibility

$$\kappa = (\partial \ln \rho/\partial p)_T = -(\partial \ln V/\partial p)_T. \qquad \text{(II-1)}$$

As the latter quantity is the one usually reported, the analysis has been based on putting a surface exactly through the density ρ_0 at atmospheric pressure and exactly through the compressibility κ_0 at that pressure, seeking a relation that holds over a useful range of pressure. We seek an equation that will permit the calculations of densities at the p6 level. The one-atmosphere values on which the analysis is based are: for ρ_0(SMOW), eq (31) with coefficients from table 2; for κ_0, ref. 26; for D_2O, ref. 54.

We dismiss without serious consideration polynomial representations. It is true that the volume of a fluid may be represented by a power series in the pressure

$$V = V_0 + a_1 p + a_2 p^2 + \ldots, \qquad \text{(II-2)}$$

and that such a polynomial with a suitable number of terms is good for representing data over a narrow range. If, however, the coefficients are to be obtained by least squares from data covering a great range, uncertainties in the individual coefficients become large, and an unphysical waviness may appear in the derivatives. Such equations also extrapolate poorly.

A restricted form of the polynomial equation is, however, useful for the evaluation of densities near atmospheric pressure. Using the gage pressure p as defined by eq (26), the density is then approximately

$$\rho = \rho_0 (1 + \kappa_0 p), \qquad \text{(II-3)}$$

which produces an error of less than 1 p.p.m. at pressures less than 10 bar, and the same range applies to eq (45).

As we know κ_0 we will write

$$\kappa = \kappa_0 f(p), \qquad \text{(II-4)}$$

where $f(0) = 1$. The value of ρ_0 will then appear as a constant of integration when eq (II-1) is integrated to give volumes or densities.

A simple equation of state can be derived by assuming that $f = 1$. This gives

$$V = V_0 \exp(-\kappa_0 p), \qquad \text{(II-5)}$$

an equation used by Guggenheim [91]. This equation correctly describes the volume as falling off at high pressure. If, however, the reciprocal is taken we see that the equation corresponds to the density rising exponentially with pressure. This is much too fast, and comes from the assumed constancy of f. Accordingly, the useful range of this equation is limited. Rather, f should fall toward zero with increasing pressure.

A general way to treat the data is to combine equations (II-1) and (II-4), and then to integrate to give

$$\ln(\rho/\rho_0)/\kappa_0 = \int_0^p f\,dp = F(p). \qquad \text{(II-6)}$$

A suitable representation of $F(p)$ may then be sought, subject to the restriction that its derivative is unity at $p = 0$. However, the difficulty with such an approach is that there seems to be no systematic way to seek suitable functions to represent F.

Understandably then, the procedure actually followed has been more exploratory. It consisted, first, in guessing that κ might fall away according to

$$\kappa = \kappa_0/(1 + \lambda p)^2, \qquad \text{(II-7)}$$

where λ is a positive coefficient whose value is to be found; $\lambda = 0$ corresponds to eq (II-5). Combining this with eq (II-1) gives

$$\rho = \rho_0 \exp\{\kappa_0 p/(1 + \lambda p)\}. \qquad \text{(II-8)}$$

This equation has an algebraic advantage over the two other equations to be discussed that the parameter λ only occurs once, so that the values may be found directly rather than by an iterative method. Its value is a slowly varying function of temperature and pressure, with a minimum value near 30 °C, with the parameter increasing with pressure at lower temperatures, and decreasing at higher temperatures. For both ordinary and heavy water the value is near 130 Mbar^{-1}.

Assuming that ρ_0 and κ_0 are correct, the error of equation (II-8) arising from an error in λ increases with pressure. If the value λ was used, and the value $\lambda+\delta$ is correct, then the leading term for the fractional error is

$$\epsilon = -\tfrac{1}{2}\kappa_0 \delta p^2, \qquad \text{(II-9)}$$

or, as $\kappa_0 \sim 50\ \text{Mbar}^{-1}$, the pressure to give an error of 1 in 10^6 is

$$p/\text{bar} = \frac{1}{\sqrt{25\delta}}, \qquad \text{(II-10)}$$

and δ may be as large as 25 Mbar^{-1} at pressures less than 1 Kbar.

In a search for a better equation, a second guess was that κ might fall according to

$$\kappa = \frac{\kappa_0}{1 + \mu p}, \qquad \text{(II-11)}$$

and in the limit of small values of p, $\mu = 2\lambda$. Combining this with eq (II-1) gives

$$\rho = \rho_0 (1 + \mu p)^{\kappa_0/\mu}, \qquad \text{(II-12)}$$

which was apparently first given, with μ constant, by Kirkwood [92], but is usually ascribed to Murnaghan [93, 94] who gave it for an isotropic elastic solid. Evaluation of μ for ordinary water shows it to increase with pressure at temperatures below 40 °C, and to decrease at higher temperatures. This equation seems worse at higher pressures than eq (II-8).

A third equation was obtained by guessing that κ might fall away exponentially on any isotherm

$$\kappa = \kappa_0 \exp(-\nu p), \qquad \text{(II-13)}$$

and as $p \to 0$, $\nu = \mu = 2\lambda$. Combining this with eq (II-1) gives

$$\rho = \rho_0 \exp\left\{\frac{\kappa_0}{\nu}[1 - \exp(-\nu p)]\right\}. \qquad \text{(II-14)}$$

Parameter ν falls with increasing pressure.

A number of approximations to the equation of state of water, particularly of SMOW and heavy water, have been discussed in this appendix. For computational errors not to exceed 1 p.p.m., eq (II-3) may be used for $p<10$ bar. For eq (II-5) the range is 15 bar. For eqs (II-8), (II-12) or (II-14) with a fixed value of the parameters $2\lambda = \mu = \nu = 260$ Mbar^{-1}, the range is 40 bar. By allowing for the temperature and pressure variation of λ, a satisfactorily small number of parameters are sufficient to extend the range of (II-8) to 1 kbar with less than the uncertainty of the data, which for SMOW is approximately $40\times10^{-12}p^2$ p.p.m. However, pursuit of the description of one isotopic composition only would be alien to the main interest of this paper and is not reported.

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