

The high pressure *PVT* properties of deuterium oxide

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The high pressure isothermal compressibilities of deuterium oxide from 5 to 100 °C and 0 to 1000 bars applied or gauge pressure were determined from sound speed data. These compressibilities were used to derive an equation of state of the form $V^0P/(V^0 - V^P) = B + A_1P + A_2P^2$, where V^0 and V^P are the specific volumes at an applied pressure of zero and P ; and B , A_1 , and A_2 are polynomial functions of temperature. The compressibilities derived from this equation of state are consistent with those derived from the sound speed data to $\pm 0.016 \times 10^{-6} \text{ bar}^{-1}$ over the entire pressure and temperature range (this is equivalent to $\sim 0.2 \text{ m sec}^{-1}$ in sound speed). The 1 atm sound-derived compressibilities agree on the average to $\pm 0.06 \times 10^{-6} \text{ bar}^{-1}$ with the direct measurements of Millero and Lepple. The P - V - T data from the sound-derived equation are compared with the high pressure work of Bridgman, Kesselman, Juza *et al.*, and Emmet and Millero. Good agreement (average deviation of $\pm 28 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) was found with the recent specific volume measurements of Emmet and Millero. The P - V - T properties of D_2O are compared to pure water. D_2O and H_2O are shown to follow similar trends. Contrary to previous reports, the $\text{D}_2\text{O}/\text{H}_2\text{O}$ ratios of the specific volumes and specific heats are shown to be functions of both temperature and pressure.

I. INTRODUCTION

Recently, using the computer technique developed by Wang and Millero,¹ we derived equations of state for pure water² and seawater.^{1,3} The same technique was used to derive an equation of state and the resulting P - V - T properties for a solution of 99.82% deuterium oxide (D_2O). Since Mathieson and Conway⁴ demonstrated that the change in sound speed with atomic fraction of D_2O is nearly linear in mole fraction, the results presented in this paper can easily be applied to any D_2O - H_2O mixture. Several investigators examined the V - T properties of D_2O at 1 atm.⁵⁻¹⁶ However, at pressures greater than 1 atm, few¹⁷⁻²⁰ examined either the P - V - T properties or the similarity of these properties to those of pure water.

There is both a practical and a theoretical significance for studying the similarities of the P - V - T properties of water (H_2O is used to denote normal water) and D_2O . On the practical side, the properties of D_2O can be estimated from H_2O on the basis of similarity. Comparison of the P - V - T properties of D_2O and H_2O is a method that is of use when studying the structural properties of water.²¹⁻²⁴ The most striking difference between D_2O and H_2O is the relationship to life processes. While H_2O is necessary for life, D_2O is poisonous to all but the lowest forms.²⁵ On the theoretical side, the results of most studies²¹⁻²⁴ indicated that at the same temperature, D_2O solutions are more structured than H_2O solutions. However, Nemathy and Scheraga²³ showed that the breakdown of this structural order, with an increase in temperature, was more rapid for D_2O than H_2O .

Since the excellent consistency of the high pressure sound data of Wilson^{26,27} was proven,² we consider our sound-derived equation of state for D_2O to be more reliable than any of the previous D_2O work. This work generally applies to both 100% D_2O and a D_2O - H_2O solution. Where specific numbers are used, an effort is made to identify the particular solution. In Sec. II we review the derivation of our equation, in Sec. III we

compare our results to previous D_2O work, and in Sec. IV we examine our results relative to H_2O .

II. EQUATION OF STATE

An equation of state for D_2O was derived directly from the velocity of sound c . The following thermodynamic relationship was used:

$$\beta = \frac{-1}{V^P} \left(\frac{\partial V^P}{\partial P} \right)_T = \frac{V^P}{c^2} + \frac{T\alpha^2 V^P}{C_P}, \quad (1)$$

in which β is the isothermal compressibility [$\beta = -1/V^P \times (\partial V^P/\partial P)_T$], V^P is the specific volume at pressure P , T is the absolute temperature, C_P is the heat capacity at constant pressure, and α is the expansibility [$\alpha = 1/V^P \times (\partial V^P/\partial T)_P$].

Equation (1) was evaluated using an iterative computer technique developed by Wang and Millero.¹ To effect this technique for D_2O , the following data were used: the 1 atm densities of Kell²⁸ (estimated error of this equation is $\pm 3 \times 10^{-6} \text{ g cm}^{-3}$, estimated accuracy is $\pm 10 \times 10^{-6} \text{ g cm}^{-3}$); the 1 atm heat capacities of Eucken and Eigen¹²; and the velocity of sound data of Wilson.²⁹

Eucken and Eigen¹² measured the heat capacity at 1 atm of 100% D_2O from 20 to 130 °C. The error involved in using 100% D_2O heat capacity data in Eq. (1) is at least two orders of magnitude less than the claimed accuracy of Eucken and Eigen. Their claimed accuracy was $0.06 \text{ J g}^{-1} \cdot \text{deg}^{-1}$, which introduces an error of less than $0.005 \times 10^{-6} \text{ bar}^{-1}$ in compressibility.

The heat capacity data¹² below 60 °C were fitted to an equation and extrapolated down to get values for the range 5-20 °C. Since the heat capacity is such a minor contributor to the compressibility, extrapolation of the data to the lower temperatures where there are no data points of Eucken and Eigen is justified. This extrapolated data was then fitted, along with the data of Eucken and Eigen from 20 to 100 °C, to the following equation:

TABLE I. A comparison of the velocity of sound data (m sec^{-1}) of Wilson²⁹ and Millero *et al.*³⁰ at 1 atm for 99.82% D_2O .

t ($^{\circ}\text{C}$)	c (Wilson)	c (Millero <i>et al.</i>)	Δc (Wilson-Millero <i>et al.</i>)
4	1320.90	1320.67	0.23
10	1347.49	1347.32	0.17
15	1366.96	1366.75	0.21
20	1384.17	1383.87	0.30
25	1399.24	1398.86	0.38
30	1412.33	1411.88	0.45
35	1423.57	1423.09	0.48
40	1433.09	1432.63	0.46
45	1441.01	1440.63	0.38
50	1447.45	1447.20	0.25
55	1452.52	1452.46	0.06
60	1456.32	1456.49	-0.17
65	1458.97	1459.38	-0.41
70	1460.54	1461.18	-0.64
75	1461.14	1461.97	-0.83
80	1460.83	1461.78	-0.95
85	1459.70	1460.64	-0.94
90	1457.82	1458.57	-0.75

$$C_p^{\circ} = 4.2765 - 3.87183 \times 10^{-3} t + 6.6500 \times 10^{-5} t^2 - 7.1819 \times 10^{-7} t^3 + 2.973 \times 10^{-9} t^4 \quad (2)$$

The maximum deviation of the data of Eucken and Eigen (20–100 $^{\circ}\text{C}$) from Eq. (2) is $0.0015 \text{ J g}^{-1} \cdot \text{deg}^{-1}$.

Wilson²⁹ measured the velocity of sound in 99.82% D_2O from 4 to 98 $^{\circ}\text{C}$, and from 0 to ~ 1000 bar. He reported a probable experimental error of $\pm 0.16 \text{ m sec}^{-1}$. He fitted his data to a polynomial equation with a standard error of $\pm 0.20 \text{ m sec}^{-1}$. An error of $\pm 0.20 \text{ m sec}^{-1}$ in sound velocity will give an error of less than $0.016 \times 10^{-6} \text{ bar}^{-1}$ in compressibility. This resultant small error in compressibility is what enables us to derive a precise equation of state from sound velocities. Although a number of workers^{10,11,15} also measured the velocity of sound in D_2O at 1 atm, their results are in poor agreement with the work of Wilson. This is expected since these workers^{10,11,15} determined the sound speeds to only $\pm 1 \text{ m sec}^{-1}$. Recently, Millero *et al.*³⁰ determined the velocity of sound in D_2O relative to H_2O from 4 to 90 $^{\circ}\text{C}$ with a precision of $\pm 0.05 \text{ m sec}^{-1}$. A comparison of Wilson's²⁹ sound velocities with those of Millero *et al.*³⁰ is shown in Table I. This comparison shows that Wilson's sound velocities agree on the average to $\pm 0.45 \text{ m sec}^{-1}$ (which is equivalent to $\sim \pm 0.03 \times 10^{-6} \text{ bar}^{-1}$ in compressibility) with the more reliable work of Millero *et al.*³⁰ This good agreement at 1 atm, in addition to the proven consistency² of the high pressure sound data of Wilson,^{26,27} substantiates our use of Wilson's²⁹ sound velocities to derive an equation of state for D_2O .

Our equation of state is of the form of a second degree secant bulk modulus¹⁻³:

$$K = PV^0 / (V^0 - V^P) = B + A_1 P + A_2 P^2, \quad (3)$$

where K is the secant bulk modulus (at 1 atm absolute pressure or $P=0$ bar applied pressure, $K=1/\beta$); V^P and V^0 are, respectively, the specific volumes at

pressure P and 1 atm (0 bar); B , A_1 , and A_2 are polynomial functions of temperature (t in $^{\circ}\text{C}$). The specific volume at 1 atm ($P=0$), V^0 ($\text{cm}^3 \text{g}^{-1}$), is taken from Kell²⁸:

$$V^0 = (1 + 17.96190 \times 10^{-3} t) / (1.104690 + 20.09315 \times 10^{-3} t - 9.24227 \times 10^{-6} t^2 - 55.9509 \times 10^{-9} t^3 + 79.9512 \times 10^{-12} t^4). \quad (3a)$$

The coefficient B (in bar), which is the reciprocal of the 1 atm compressibility, is given by

$$B = 1.8607370 \times 10^4 + 1.7026 \times 10^2 t - 2.40556 t^2 + 1.02703 \times 10^{-2} t^3 - 1.5680 \times 10^{-5} t^4. \quad (3b)$$

The pressure coefficients A_1 and A_2 are given by

$$A_1 = 3.129069 - 4.53919 \times 10^{-3} t + 4.3252 \times 10^{-4} t^2 - 4.7659 \times 10^{-6} t^3 + 1.6244 \times 10^{-8} t^4 \quad (3c)$$

$$A_2 = 1.07903 \times 10^{-4} - 5.5471 \times 10^{-7} t - 1.6758 \times 10^{-7} t^2 + 2.384 \times 10^{-9} t^3 - 9.301 \times 10^{-12} t^4 \quad (3d)$$

Figure 1 is a pictorial representation of the residuals or deviations (in bar^{-1}) of the pressure derivative of the fitted equation (3) from the original sound data. We note that the residuals are apparently random: At zero bar, they are clustered around zero. From 100 to 400 and, not as pronounced, from 600 to 700 bar, they are more heavily weighted on the negative side, whereas at 500 and 800 bar they appear to be more evenly distributed around zero.

The choice of a second degree secant bulk modulus was discussed by Wang and Millero,¹ Fine and Millero,² and Fine, Wang, and Millero.³ When deriving the P - V - T properties, Eq. (3) is convenient to use. Equation (3) can be rearranged to give the specific volume (in $\text{cm}^3 \text{g}^{-1}$):

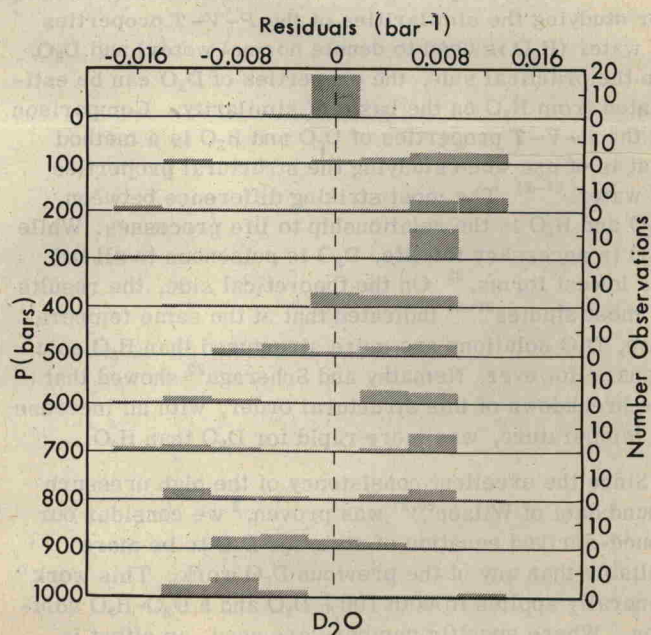


FIG. 1. The residuals between compressibilities from Eq. (2) and the sound derived data for each pressure.