

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

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

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 $\text{cm}^3 \text{ g}^{-1}$):

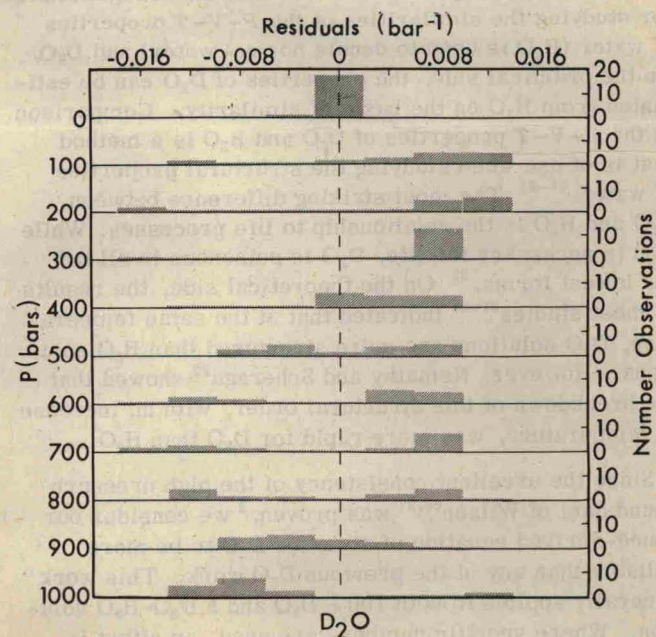


FIG. 1. The residuals between compressibilities from Eq. (2) and the sound derived data for each pressure.

TABLE II. The *P-V-T* properties of D₂O (99.82%).

<i>P</i> (bar)	<i>V</i> (cm ³ g ⁻¹)	β (bar ⁻¹) $\times 10^6$	α (deg ⁻¹) $\times 10^6$
<i>t</i> = 5 °C			
0	0.904468	51.547	-114.14
100	0.899880	50.177	-76.14
200	0.895436	48.846	-40.21
300	0.891130	47.553	-6.27
400	0.886959	46.297	25.75
500	0.882916	45.077	55.91
600	0.878997	43.891	84.29
700	0.875199	42.738	110.93
800	0.871515	41.618	135.91
900	0.867943	40.529	159.28
1000	0.864478	39.470	181.10
<i>t</i> = 25 °C			
0	0.905429	46.480	191.74
100	0.901282	45.326	206.31
200	0.897257	44.213	220.47
300	0.893347	43.137	234.19
400	0.889548	42.099	247.42
500	0.885856	41.095	260.13
600	0.882266	40.124	272.28
700	0.878774	39.185	283.85
800	0.875378	38.277	294.81
900	0.872072	37.397	305.14
1000	0.868854	36.546	314.83
<i>t</i> = 50 °C			
0	0.912656	44.859	428.72
100	0.908625	43.685	428.71
200	0.904715	42.569	429.08
300	0.900921	41.506	429.75
400	0.897235	40.494	430.66
500	0.893652	39.529	431.74
600	0.890168	38.608	432.95
700	0.886777	37.730	434.22
800	0.883475	36.890	435.52
900	0.880257	36.089	436.80
1000	0.877120	35.322	438.02
<i>t</i> = 75 °C			
0	0.924576	46.121	602.54
100	0.920384	44.789	593.65
200	0.916329	43.534	585.55
300	0.912403	42.351	578.16
400	0.908598	41.234	571.40
500	0.904907	40.179	565.22
600	0.901324	39.183	559.56
700	0.897842	38.240	554.37
800	0.894456	37.347	549.60
900	0.891159	36.503	545.21
1000	0.887948	35.702	541.16

$$V^P = V^0 - V^0 P / (B + A_1 P + A_2 P^2) \quad (4)$$

Differentiation of Eq. (4) with respect to pressure gives the compressibility (in bar⁻¹):

$$\beta = \frac{-1}{V^P} \left(\frac{\partial V^P}{\partial P} \right)_T = \frac{V^0 (B - A_2 P^2)}{V^P (B + A_1 P + A_2 P^2)^2} \quad (5)$$

Differentiation of Eq. (4) with respect to temperature gives the expansibility (in deg⁻¹):

$$\alpha = \frac{1}{V^P} \left(\frac{\partial V^P}{\partial T} \right)_P = \frac{1}{V^P} \left(\frac{\partial V^0}{\partial T} \right) - \frac{P(\partial V^0 / \partial T)}{V^P (B + A_1 P + A_2 P^2)} + P V^0 \frac{(\partial B / \partial T) + P(\partial A_1 / \partial T) + P^2(\partial A_2 / \partial T)}{V^P (B + A_1 P + A_2 P^2)^2} \quad (6)$$

For selected temperatures and pressures, we have tabulated in Table II the specific volumes, compressibilities, and expansibilities derived from our equation of state. These values are precise to within $\pm 15 \times 10^{-6}$ cm³g⁻¹ in *V*^{*P*}, $\pm 2 \times 10^{-6}$ deg⁻¹ in α , and $\pm 0.016 \times 10^{-6}$ bar⁻¹ in β . In Sec. III, these *P-V-T* data are compared to other published results.

III. COMPARISON OF RESULTS

Since few studies were made on the high pressure *P-V-T* properties of D₂O, it is not possible to make a number of comparisons to our sound-derived data with direct measurements. Many workers (c.f. Refs. 5, 7, 8, 10, 13, 14, 16, 18) measured or derived equations for the specific volume (or density) of D₂O at 1 atm. We prefer the equation of Kell²⁸ owing to the reported estimated error of $\pm 3 \times 10^{-6}$ g cm⁻³ and established accuracy of $\pm 10 \times 10^{-6}$ g cm⁻³. Also, many of the above mentioned studies do not cover as comprehensive a temperature range.

The most reliable 1 atm compressibilities for D₂O are from the work of Millero and Lepple.⁶ Using a piezometric technique, they measured the compressibility of D₂O from 5 to 65 °C near 1 atm to within $\pm 0.1 \times 10^{-6}$ bar⁻¹. Comparisons of the 1 atm compressibilities determined from our equation of state and the work of Millero and Lepple⁶ are shown in Table III. The comparisons show that except at 65 °C our results are in excellent agreement (average deviation $\pm 0.05_5 \times 10^{-6}$ bar⁻¹) with those of Millero and Lepple.

A number of workers¹⁷⁻²⁰ examined the high pressure *P-V-T* properties of D₂O. The most precise study at low temperatures is the work of Emmet and Millero.¹⁷ They measured the specific volumes of (99.8%) D₂O (precise to within $\pm 10 \times 10^{-6}$ cm³g⁻¹) from 2 to 40 °C with a high pressure magnetic float densimeter. In the range of our equation of state (5-100 °C and 0-1000 bar), the measurements of Juza *et al.*,¹⁸ Kesselman,¹⁹ and Bridgman²⁰ provide few data points for comparison. In Fig. 2 we compare the differences in the specific volumes of D₂O obtained from our equation of state and

TABLE III. A comparison of the compressibility data (bar⁻¹) from the equation of state and Millero and Lepple⁶ at 1 atm.

<i>t</i> (°C)	$\beta \times 10^6$	$\beta \times 10^6$ (Millero and Lepple)	$\Delta\beta \times 10^6$ [Eq. (5)-Millero and Lepple]
5	51.54 ₇	51.49	0.06
10	49.80 ₂	49.74	0.06
15	48.41 ₇	48.38	0.04
20	47.32 ₆	47.37	-0.04
25	46.48	46.52	-0.04
30	45.84 ₁	45.88	-0.04
35	45.37 ₉	45.37	0.01
40	45.07 ₃	45.10	-0.03
45	44.90 ₅	44.97	-0.06
50	44.85 ₉	44.91	-0.05
55	44.92 ₄	44.98	-0.06
60	45.09	45.16	-0.07
65	45.34 ₉	45.51	-0.16

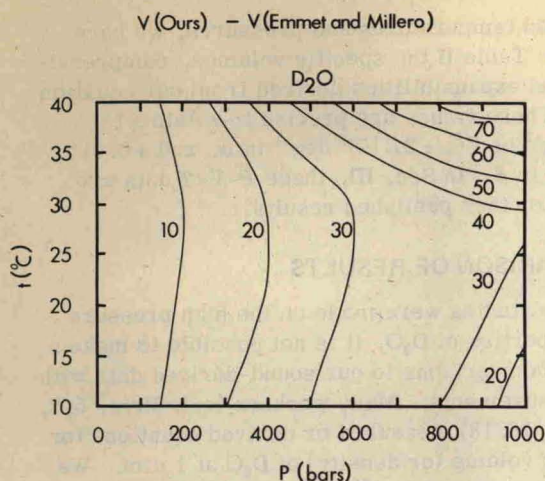


FIG. 2. A comparison of the differences in the specific volumes between the sound derived equation of state and the data of Emmet and Millero.¹⁷ Unit of contour: $10 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

the work of Emmet and Millero. The average deviation of the specific volume differences is $28 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, and over 90% of the range (0–40°C, 0–1000 bar) the deviations are within $40 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. The maximum deviation is $75 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ at 40°C and 1000 bar. The larger deviations at the high temperatures and pressures are probably a result of errors in the direct measurements due to the nonequilibrium of the magnetic float.³¹ The overall agreement is good and provides support for the validity of our equation of state.

Using a siphon method, Bridgman²⁰ measured the specific volume of 99.9% D_2O from –20 to 100°C and 0 to ~12 000 bar. A comparison of our results (adjusted to 99.9% D_2O) with those of Bridgman are shown in Table IV. The agreement is not very good; however, over most of the range the differences are within the experimental error of Bridgman's direct measurements ($\sim 500 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$). Kesselman¹⁹ derived an equation of state for D_2O for the range 20–380°C and 0–500 bar. He states that the average deviations of his equation do not exceed the experimental error of Bridgman²⁰ and Kirillin and Ulybin.³² As a consequence, the agreement between Kesselman's and our equation of state is very poor ($\sim 1000 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in specific volume). Poor agreement ($1500 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) was also found with the data of Juza *et al.*¹⁸ They measured the specific volume of D_2O at 80 and 100°C, 499 and 999 bar.

IV. COMPARISONS OF THE P - V - T PROPERTIES OF D_2O AND H_2O

Since the viscosity, melting point, temperature of maximum density, and heat capacity are all higher in D_2O than in H_2O , Nemethy and Scheraga³³ (and others) proposed that there is more structural order in D_2O than in H_2O , or that the degree of hydrogen bonding is higher in D_2O than in H_2O . In recent years a number of workers^{21–23} have examined the structural properties of D_2O relative to H_2O . Although the high pressure P - V - T properties of D_2O and H_2O are similar, the small differences that do occur can be very useful in

TABLE IV. A comparison of the specific volume data from the equation of state and Bridgman.²⁰

t (°C)	$\Delta V \times 10^6 \text{ cm}^3 \text{ g}^{-1}$		
	0 bar	499 bar	999 bar
20	–455	–1045	–1569
40	226	–562	–1027
50	262	270	–1037
60	–113	–350	–990
80	62	–40	–993
100	...	272	–176

the examination of the structure of H_2O . It is not the purpose of this paper to discuss these differences in great detail; however, it is useful to examine some of them. Above the temperature of maximum density the P - V - T properties of D_2O and H_2O are similar. For example, the specific volumes increase as the temperature is increased, and decrease as the pressure is increased; the expansibilities increase as the temperature is increased and increase as the pressure is increased; the compressibilities decrease as the pressure is increased, and go through a minimum when plotted versus temperature. In this section we examine the effect of temperature and pressure on the P - V - T properties of D_2O and H_2O . The P - V - T properties for D_2O are from the equation of state (3), and the properties for H_2O are from the equation derived by Fine and Millero.²

The effect of temperature on the specific volume, compressibility, expansibility, and specific heats at constant volume and pressure of D_2O and H_2O are examined graphically. In Fig. 3 the specific volumes of D_2O and H_2O are plotted versus temperature at two pressures ($P=0$ and 1000 bar). The curves are similar for D_2O and H_2O with H_2O having the larger volumes. The compressibilities of D_2O and H_2O (Fig. 4) show the minimum in the middle temperature range at both pressures (0 and 1000 bar).

The expansibilities of D_2O and H_2O (Fig. 5) plotted versus temperature are also graphically similar. For both liquids the expansibility values at 0 and 1000 bar converge in the middle temperature range. The conver-

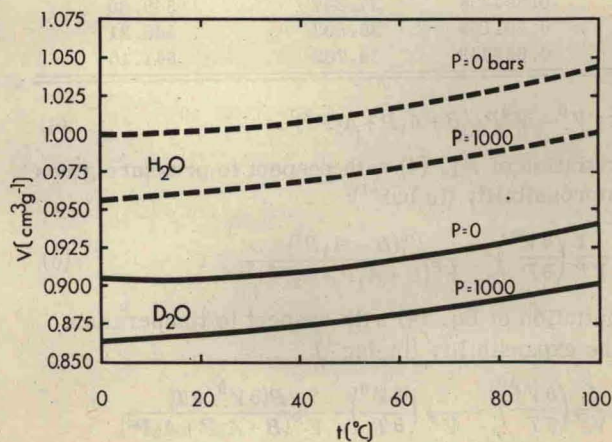


FIG. 3. The specific volumes of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

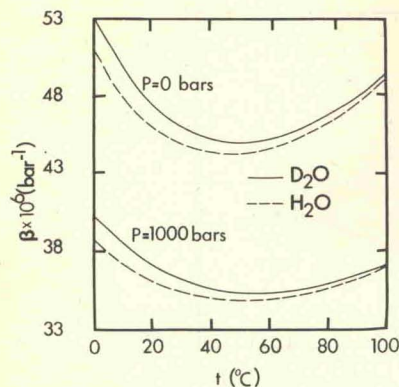


FIG. 4. The compressibilities of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

gence is at approximately $50^\circ C$ for H_2O and D_2O .

The heat capacities at constant volume (C_V) plotted versus temperature show fairly similar patterns for D_2O and H_2O (Fig. 6). For the C_V of D_2O at pressures of 0 and 1000 bar, there is a stronger negative slope—especially at higher temperatures—than for H_2O . The differences between the slopes of the C_V for H_2O and for D_2O may be due to structural differences between the two liquids. We may be seeing the more rapid breakdown of the structural order in D_2O than H_2O as the temperature is increased. This was previously shown by Nemethy and Scheraga.³³ In Fig. 7 we see similar curves for the C_P of H_2O and D_2O at 0 and 1000 bar pressure.

Figure 8 is a plot of the temperatures of maximum density of D_2O and of H_2O versus pressure. We note the similar decrease in the temperatures of maximum density as the pressure is increased for both liquids. The slope of the fitted D_2O temperatures is slightly weaker than that of H_2O . This may be another indication of a D_2O - H_2O structural difference, and a less rapid breakdown of the D_2O structural order as the pressure is increased.

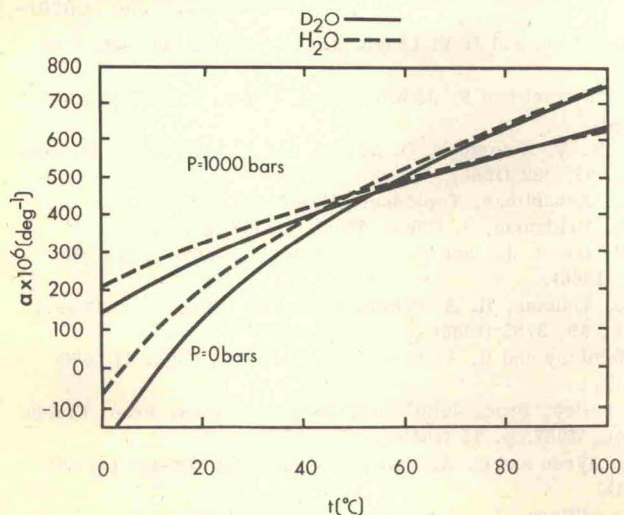


FIG. 5. The expansibilities of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

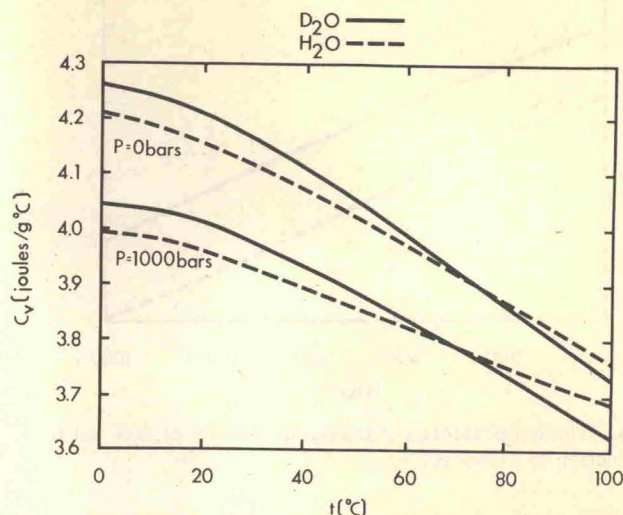


FIG. 6. The heat capacities at constant volume of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

We also examined the effect of pressure on the P - V - T properties of D_2O and H_2O . Once again we looked at the specific volume, compressibility, expansibility, and specific heats at constant volume and pressure. Over the range of both equations we found that the P - V - T properties of D_2O and H_2O followed the same patterns when plotted versus pressure.

Some workers tried to show that at each temperature the D_2O/H_2O ratios of certain P - V - T properties are independent of pressure. Rivkin⁸ showed that from 50 to $100^\circ C$ and from 0 to 100 bar the D_2O/H_2O density ratios were independent of pressure to within 510×10^{-6} . We found that for 50 and $75^\circ C$, from 0 to 1000 bar the ratios were within 674×10^{-6} and 481×10^{-6} , respectively.

Figure 9 examines the D_2O/H_2O ratios of the densities versus pressure at 5 and $50^\circ C$. The figure shows the linearity of the ratios versus pressure, with larger slopes at lower temperatures. In view of recent work (this paper, Emmet and Millero,¹⁷ and Fine and Mil-

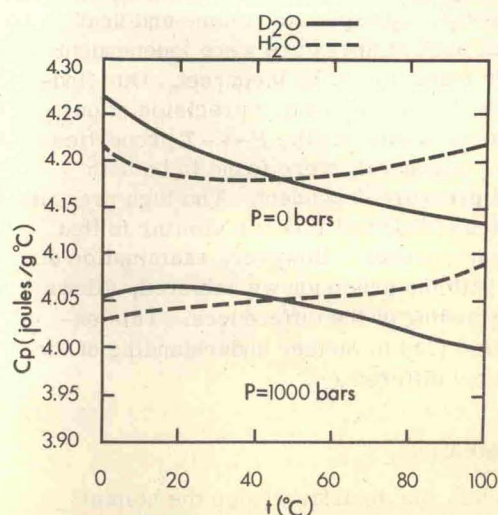


FIG. 7. The heat capacities at constant pressure of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

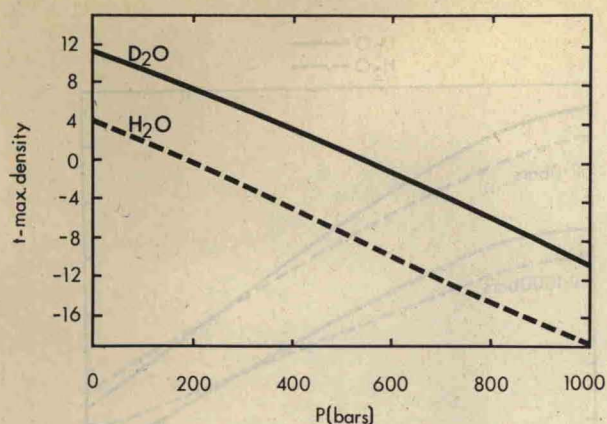


FIG. 8. The temperatures of maximum density of D_2O and H_2O as a function of pressure.

l ero^2), we do not consider that these ratio differences for the densities (or specific volumes) are independent of pressure.

Rivkin and Egorov⁹ also examined the D_2O/H_2O ratios. They examined them for heat capacities from 20 to 100 °C and 0 to 100 bar pressure. They concluded that the ratios of the heat capacities were independent of pressure to within 0.014. Our results showed similar ratios from 0 to 1000 bar. However, considering the reported accuracy of recent heat capacity measurements, for example on seawater by Millero *et al.*³⁴ ($\pm 0.0005 \text{ J g}^{-1} \cdot \text{deg}^{-1}$), the D_2O/H_2O heat capacity ratios are not independent of pressure. We assert that neither the D_2O/H_2O ratios of the densities nor the heat capacities are independent of pressure (or temperature).

We conclude that the most precise high pressure P - V - T properties can be derived from our equation of state for D_2O . This equation was derived from the velocity of sound data of Wilson.²⁹ There is good agreement of the P - V - T properties from this sound-derived equation with the recent direct experimental work of Emmet and Millero.¹⁷ We found a similarity in the D_2O and H_2O curves plotted versus temperature and pressure for all the P - V - T properties. It was previously reported^{8,9} that the D_2O/H_2O specific volume and heat capacity ratios at each temperature were independent of pressure. We found this to be incorrect. Our finding was primarily due to the greater precision of our data. The differences between the P - V - T properties for D_2O and H_2O , in general, were found to be both temperature and pressure dependent. The high pressure P - V - T properties of D_2O and H_2O are similar in that they follow the same trends. However, examination of the properties, with the precision we achieved, allows a clearer understanding of the differences. This examination may also lead to further understanding of the D_2O - H_2O structural differences.

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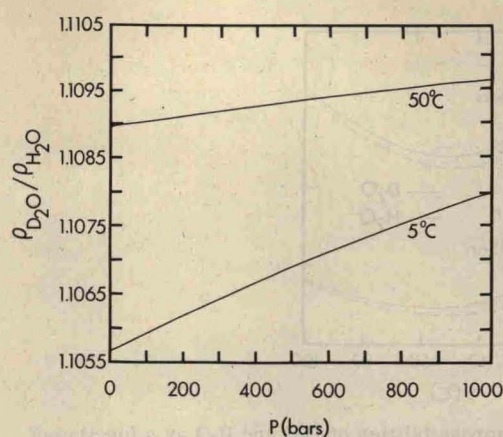


FIG. 9. The D_2O/H_2O density ratios as a function of pressure at 5 and 50 °C.

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- ¹D. P. Wang and F. J. Millero, *J. Geophys. Res.* **78**, 7122 (1973).
- ²R. A. Fine and F. J. Millero, *J. Chem. Phys.* **59**, 5529 (1973).
- ³R. A. Fine, D. P. Wang, and F. J. Millero, *J. Mar. Res.* **32**, 433 (1974).
- ⁴J. G. Mathieson and B. E. Conway, *J. Anal. Chem.* **44**, 1517 (1972).
- ⁵F. J. Millero, E. V. Hoff, and R. Dexter, *J. Chem. Eng. Data* **16**, 85 (1971).
- ⁶F. J. Millero and F. K. Lepple, *J. Chem. Phys.* **54**, 946 (1971).
- ⁷F. Steckel and S. Szapiro, *Trans. Faraday Soc.* **59**, 331 (1963).
- ⁸S. L. Rivkin, *At. Energ.* **7**, 457 (1959).
- ⁹S. L. Rivkin and B. N. Egorov, *At. Energ.* **7**, 462 (1959).
- ¹⁰R. T. Lagemann, L. W. Gilley, and E. G. McLeroy, *J. Chem. Phys.* **21**, 819 (1953).
- ¹¹M. Pancholy, *J. Acoust. Soc. Am.* **25**, 1003 (1953).
- ¹²V. A. Eucken and M. Eigen, *Z. Elektrochem.* **55**, 343 (1951).
- ¹³V. S. Krauchenko, *At. Energ.* **20**, 212 (1966).
- ¹⁴T. L. Chang and L.-H. Tung, *Nature* **143**, 737 (1949).
- ¹⁵D. R. McMillan, Jr. and R. T. Lagemann, *J. Acoust. Soc. Am.* **19**, 957 (1947).
- ¹⁶T. L. Chang and J. Y. Chien, *J. Am. Chem. Soc.* **63**, 1709 (1941).
- ¹⁷R. T. Emmet and F. J. Millero, *J. Chem. Eng. Data* (in press).
- ¹⁸J. Juza, V. Kmonicek, O. Sifner, and K. Schovanec, *Physica (Utr.)* **32**, 362 (1966).
- ¹⁹P. M. Kesselman, *Teploenergetika* **4**, 72 (1960).
- ²⁰P. W. Bridgman, *J. Chem. Phys.* **3**, 597 (1935).
- ²¹C. M. Davis, Jr. and D. L. Bradley, *J. Chem. Phys.* **45**, 2461 (1966).
- ²²M. R. Thomas, H. A. Scheraga, and E. Schreer, *J. Phys. Chem.* **69**, 3722 (1965).
- ²³G. Nemethy and H. A. Scheraga, *J. Chem. Phys.* **41**, 680 (1961).
- ²⁴E. Whalley, *Proc. Joint Conf. Thermo. Trans. Prop. Fluids IUPAC*, 1957, p. 15 (1959).
- ²⁵J. A. Ayres and C. A. Trilling, *Nucl. Eng. Design* **14**, 363 (1971).
- ²⁶W. D. Wilson, *J. Acoust. Soc. Am.* **31**, 1067 (1959).
- ²⁷W. D. Wilson, *J. Acoust. Soc. Am.* **32**, 1357 (1960).
- ²⁸G. S. Kell, *J. Chem. Eng. Data* **12**, 66 (1967).

²⁹W. D. Wilson, J. Acoust. Soc. Am. **33**, 314 (1961).

³⁰F. J. Millero, P. Cheturkin, T. Kubinski (in preparation).

³¹R. T. Emmet, Ph.D. thesis, University of Miami, 1973.

³²V. A. Kirillin and S. A. Ulybin, Teploenergetika **4**, 67 (1959).

³³G. Nemethy and H. A. Scheraga, J. Chem. Phys. **41**, 680 (1964).

³⁴F. J. Millero, G. Perron, and J. E. Desnoyers, J. Geophys. Res. **78**, 4499 (1973).