TABLE II. The *P–V–T* properties of D_2O (99.82%).

P (bar)	V ($cm^3 g^{-1}$)	β (bar^{-1})$\times 10^6$	α (deg^{-1})$\times 10^6$
		$t = 5\,°C$	
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
		$t = 25\,°C$	
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
		$t = 50\,°C$	
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
		$t = 75\,°C$	
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

$$V^P = V^0 - V^0 P/(B + A_1 P + A_2 P^2) \; . \tag{4}$$

Differentiation of Eq. (4) with respect to pressure gives the compressibility (in bar^{-1}):

$$\beta = \frac{-1}{V^P}\left(\frac{\partial V^P}{\partial P}\right)_T = \frac{V^0(B - A_2P^2)}{V^P(B + A_1P + A_2P^2)^2} \quad . \tag{5}$$

Differentiation of Eq. (4) with respect to temperature gives the expansibility (in deg^{-1}):

$$\alpha = \frac{1}{V^P}\left(\frac{\partial V^P}{\partial T}\right)_P = \frac{1}{V^P}\left(\frac{\partial V^0}{\partial T}\right) - \frac{P(\partial V^0/\partial T)}{V^P(B + A_1P + A_2P^2)} + PV^0\,\frac{(\partial B/\partial T) + P(\partial A_1/\partial T) + P^2(\partial A_2/\partial T)}{V^P(B + A_1P + A_2P^2)^2} \quad . \tag{6}$$

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 $\pm 15 \times 10^{-6}$ $cm^3 g^{-1}$ 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 D_2O, 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 D_2O at 1 atm. We prefer the equation of Kell[28] 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 D_2O are from the work of Millero and Lepple.[6] Using a piezometric technique, they measured the compressibility of D_2O 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 Lepple[6] 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 workers[17–20] examined the high pressure *P-V-T* properties of D_2O. The most precise study at low temperatures is the work of Emmet and Millero.[17] They measured the specific volumes of (99.8%) D_2O (precise to within $\pm 10 \times 10^{-6}$ $cm^3 g^{-1}$) 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 Bridgman[20] provide few data points for comparison. In Fig. 2 we compare the differences in the specific volumes of D_2O 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 Lepple[6] at 1 atm.

t (°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

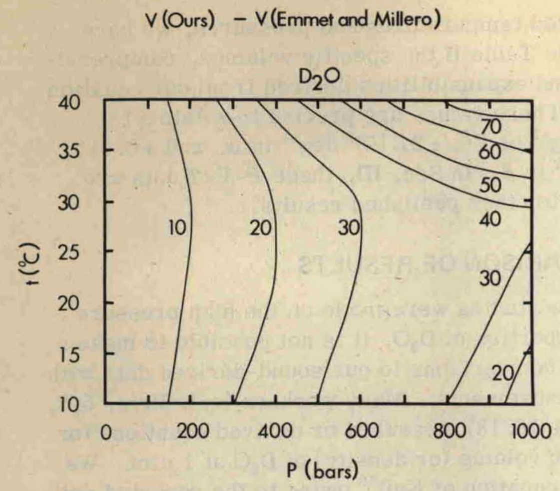

FIG. 2. A comparison of the differences in the specific volumes between the sound derived equation of state and the data of Emmet and Millero.[17] Unit of contour: 10×10^{-6} cm^3 g^{-1}.

the work of Emmet and Millero. The average deviation of the specific volume differences is 28×10^{-6}cm^{3}g^{-1}, and over 90% of the range (0–40 °C, 0-1000 bar) the deviations are within 40×10^{-6} cm^{3}g^{-1}. The maximum deviation is 75×10^{-6} cm^{3}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 sylphon method, Bridgman[20] 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 (~500×10^{-6} cm^{3}g^{-1}). Kesselman[19] 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 Bridgman[20] and Kirillin and Ulybin.[32] As a consequence, the agreement between Kesselman's and our equation of state is very poor (~1000×10^{-6} cm^{3}g^{-1} in specific volume). Poor agreement (1500×10^{-6} cm^{3}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 Scheraga[33] (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]

	$\Delta V\times10^6$ cm^3 g^{-1}		
t (°C)	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-

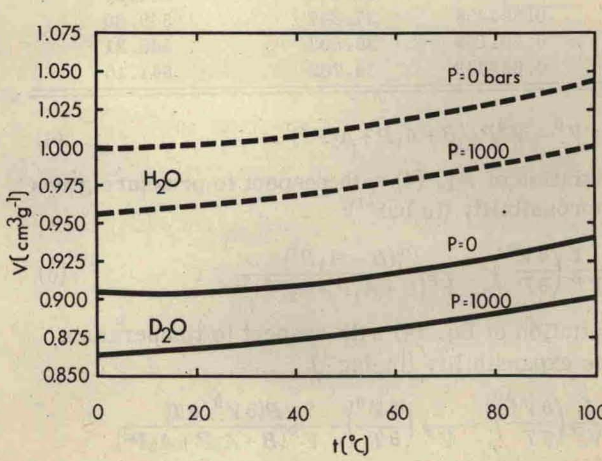

FIG. 3. The specific volumes of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.