

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.

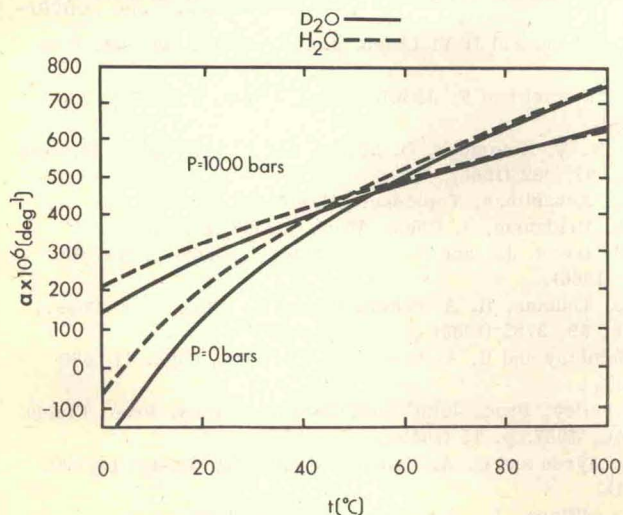


FIG. 5. The expansibilities of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

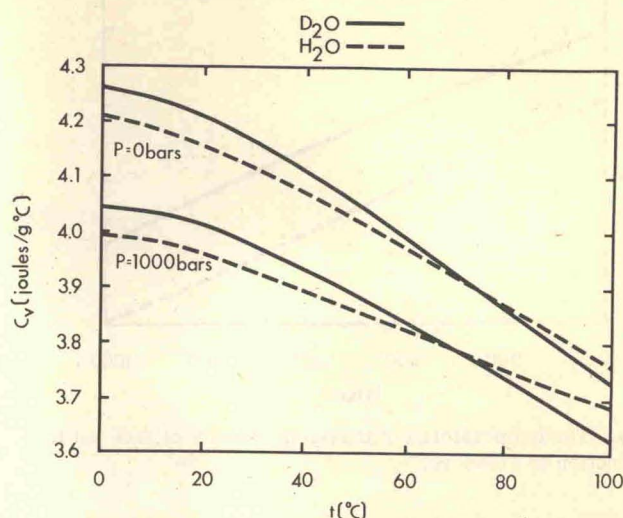


FIG. 6. The heat capacities at constant volume of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

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-

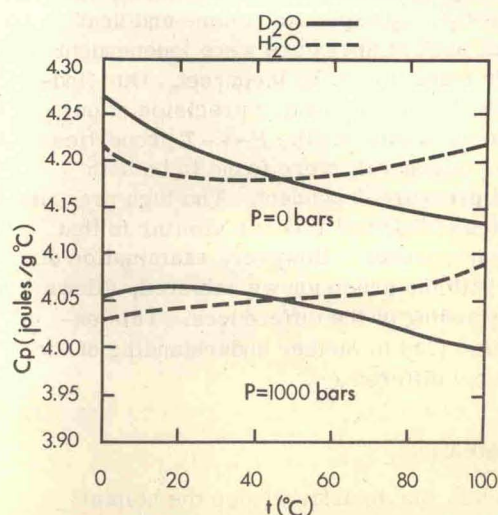


FIG. 7. The heat capacities at constant pressure of D_2O and H_2O as a function of temperature at 0 and 1000 bar pressure.

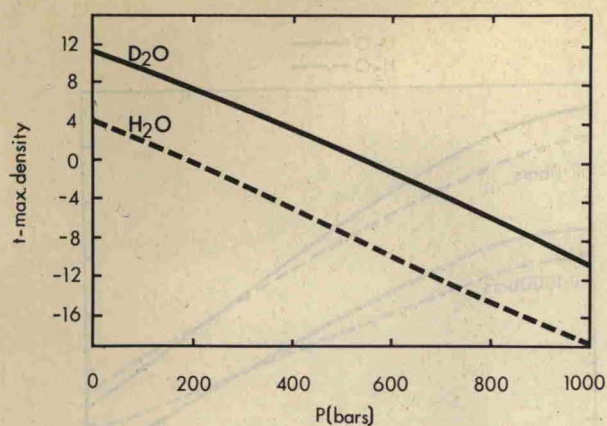


FIG. 8. The temperatures of maximum density of D_2O and H_2O as a function of pressure.

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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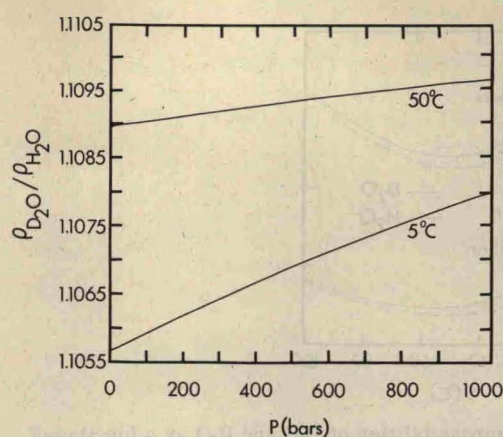


FIG. 9. The D_2O/H_2O density ratios as a function of pressure at 5 and 50 °C.

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