

THE BEHAVIOR OF WATER IN THE GIANT PLANETS. D.J. Stevenson, California Institute of Technology, Pasadena, CA 91125 and E. Fishbein, UCLA, Los Angeles, CA 90024.

Water is the third most abundant constituent in the planets, after hydrogen and helium. It is probably the most abundant constituent in Uranus and Neptune, comparable (by mass) to the abundance of helium in Saturn and might be enhanced relative to solar abundance in Jupiter. Despite its undoubted importance, little is known about its behavior at the temperatures and pressures relevant to the interiors of these planets. The current procedure for constructing models of these planets uses existing water Hugoniot data to define an equation of state which is both consistent with laboratory data and yet merges smoothly with Thomas-Fermi-Dirac calculations at  $P \sim 10$  Mbar (e.g., see ref. 1). Although this approach cannot be faulted from an empirical point of view, given the present data base, it provides no insight into the structural, electronic and mixing properties of water. It is of great importance to know, for example, whether water is soluble in hydrogen at the temperatures, pressures and mixture ratios relevant to the giant planets. This has implications for the internal structure, thermal evolution and atmospheres of these bodies. The work reported here represents the first tentative steps towards understanding these problems. Laboratory data must provide the final answers.

Ionic water: It has been known for many years that the electrical conductivity of water rises dramatically during shock compression. Hamann and Linton (2) advanced a number of arguments to support the conjecture that this can be understood as a pressure dissociation/ionization of the form  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \text{OH}^-$  with the left hand side being overwhelmingly predominant at low pressure and temperature, while the RHS predominates for shock pressures exceeding 150-200 kbar (shock temperatures  $\sim 1500$  K). Recent conductivity measurements (3) show that the conductivity  $\sigma$  reaches a plateau value  $\approx 20$  (ohm-cm) $^{-1}$  for  $P \geq 200$  kbar, consistent with a fluid in which mobility rather than ion concentration is the limiting process for conduction (as in an ionic melt, e.g., liquid  $\text{NH}_4^+ \text{F}^-$  which is "isoelectronic" with  $\text{H}_3\text{O}^+ \text{OH}^-$ ).

The hypothetical ionic state has been tested further by construction of a model equation of state. The model assumes that  $E$ , the static ( $T = 0$ ) energy per ion pair ( $\text{H}_3\text{O}^+ \text{OH}^-$ ), consists of a nearest neighbor repulsive Born-Mayer interaction plus a long-range coulombic (Madelung) term. Accordingly,

$$E = \frac{-\alpha e^2}{R} + 8 B e^{-KR}$$

where a CsCl structure is assumed,  $\alpha$  is the Madelung constant ( $\approx 1.763$ ),  $R$  is the nearest neighbor distance and  $B, K$  are constants to be determined. Thermal corrections were evaluated using free-volume theory (4). This model is obviously approximate since it does not directly model the fluid state (for which  $\alpha$  and the coefficient 8 in  $E$  would change slightly). However, Fig. 1 shows that the model is capable of reproducing the water Hugoniot at high pressures for the parameter choices  $B = 6.45 \times 10^4$  eV and  $K = 2.507 a_0^{-1}$  (where  $a_0$  is the first Bohr radius). The model also correctly reproduces the shock temperatures (5,6) and predicts a zero pressure ( $\rho = 1.64 \text{ g cm}^{-3}$ ) binding energy of ionic water (relative to infinitely dispersed  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions) of -8.2 eV, only slightly higher than the binding energy of ordinary ice I (relative to the same energy zero), consistent with the requirement that only modest temperature ( $\sim 10^3$  K) and/or pressure ( $\sim 10^2$  kbar) rises are needed to shift the equilibrium  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \text{OH}^-$  predominantly to the right. This result for the binding energy inspires confidence in the physical reality of the model. Furthermore, this model does not require that the Hugoniot behave differently

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at high pressures from its low pressure behavior, consistent with the data (3). Notice that the model is intended to explain water at high pressures and temperatures; in particular, the  $T = 0$  K state of crystalline  $\text{H}_3\text{O}^+\text{OH}^-$  analogous to crystalline CsCl is not likely to be correct. (This is not a serious deficiency for the temperatures relevant to the giant planets.) Hard sphere fluid perturbation theory (8) is being used with the above interaction energy to obtain the thermodynamic properties of the fluid state.

Mixture Properties: The  $\text{H}_2$ - $\text{H}_2\text{O}$  phase diagram is obviously of most importance. No direct experimental evidence appears to exist for this phase diagram in the fluid phase but a number of constraints can be imposed on it:

(i) The solubility of  $\text{H}_2$  in water at  $T = 298$  K and  $P = 1$  bar is  $1.5 \times 10^{-5}$  mole fraction. This is insensitive to temperature but approximately obeys Henry's Law (9). This suggests that low solubility persists as water approaches its critical point (218 bars, 647 K).

(ii) Existing systematics on the solubility of water in hydrocarbons can be understood using the solubility parameter approach (9). Application of this theory suggests that the mole fraction  $x$  of fluid water soluble in fluid hydrogen obeys  $x \approx \exp(-T_1/T)$ , where  $T_1 \approx 4000$  K, provided  $x \ll 1$  and the pressure is much greater than 200 bars but small compared to 50 kbar.

(iii) The measured argon-water supercritical phase diagram (10) exhibits "gas-gas immiscibility of the first kind" (11). This can be understood using the Hildebrand solubility parameter approach (12,13). Since the solubility parameters of water and hydrogen are even more different than those for water and argon, this immiscibility should be further enhanced in  $\text{H}_2$ - $\text{H}_2\text{O}$ . Quantitatively, the Ar- $\text{H}_2\text{O}$  phase diagram can be scaled to  $\text{H}_2$ - $\text{H}_2\text{O}$ , with the result that  $T_1 \approx 3200$  K in the above solubility formula. However, the critical temperature in the  $\text{H}_2$ - $\text{H}_2\text{O}$  system at  $3 \text{ kbar} \leq P \leq 50 \text{ kbar}$  is probably about 1200 K (composition  $\sim 20\%$   $\text{H}_2$  mole fraction). These results when applied to existing planetary models immediately imply that outermost regions of Uranus and Neptune cannot be uniformly mixed  $\text{H}_2$ - $\text{H}_2\text{O}$ -He. Existing interior models assume layering; these calculations provide partial support for this assumption.

In the pressure range  $50 \text{ kbar} \leq P \leq 200 \text{ kbar}$ , extrapolations of existing data are unreliable and theoretical modeling of water is difficult. At  $P \gg 200 \text{ kbar}$ , water prefers the "ionic melt" state, essentially because of the long-range electrostatic  $R^{-1}$  term. A water molecule surrounded by hydrogen molecules is unable to take advantage of this ionic state because the proton affinity of  $\text{H}_2$  is much less than that of  $\text{H}_2\text{O}$ . The mole fraction  $x$  of water soluble in hydrogen will then be given by  $x \approx \exp(-\Delta E/kT)$ , where  $\Delta E \approx (24/R - 24/R_0)eV$  is the increase in electrostatic energy that results when a water molecule is immersed in  $\text{H}_2$ , and  $R_0$  is the nearest neighbor distance for the pressure at which ionic and non-ionic water states are equally favorable energetically.

The model described above is crude. However, preliminary results from a detailed calculation using liquid perturbation theory involving all of the intermolecular interactions confirm its essential features. The hydrogen-rich end of the  $\text{H}_2$ - $\text{H}_2\text{O}$  system is found to exhibit positive volume of mixing ( $\text{H}_2\text{O}$  occupies more volume when it is non-ionic). In Jupiter and Saturn, the high temperatures and low water mixing ratios in the hydrogen envelope lead to the prediction of complete miscibility. In Uranus and Neptune, the lower temperatures and expected higher mixing ratios (these planets have much less hydrogen) lead to the prediction of partial separation: a water ocean beneath a primarily hydrogen-helium envelope. The interface between "ocean" and atmosphere will be sharp even though the pressure is several hundred kilobars and the temperature is a few thousand degrees.

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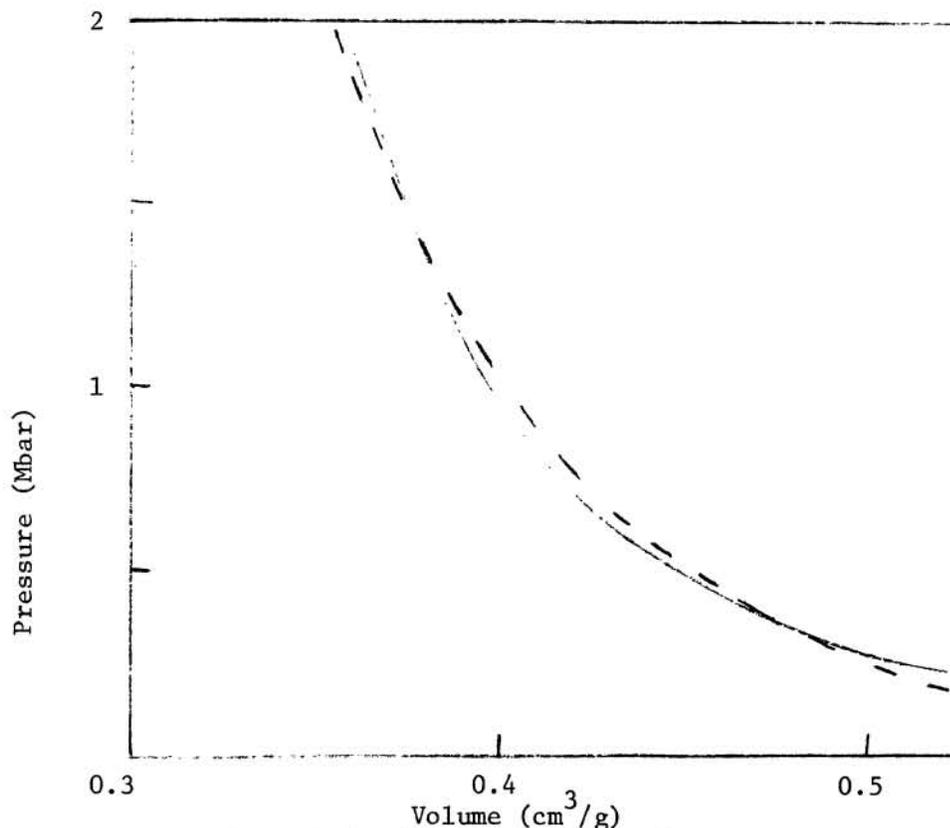


Figure 1: Solid line is principal Hugoniot (7) and dashed line shows best fitting ionic model.