WATER AND AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

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ABSTRACT

A survey is given of recent results on properties of water and aqueous solutions at high pressures and high temperatures with emphasis on supercritical conditions. New *PVT*-data for water from static measurements are available to 1000°C and 10 kb. Dielectric constants and viscosity have been measured to 550°C and 5 kb. Infra-red and Raman spectra of OD-vibrations of HDO in H_2O to 400°C and 5 kb give information about the extent of hydrogen bonded structure. Critical curves of binary aqueous systems with one inert component, for example argon, extending to 3 kb and 400°C are discussed. Absorption spectra of bivalent cobalt and nickel chlorides are measured to 500°C and 6 kb and conclusions about the stability of octahedral and tetrahedral complexes are drawn. Shock wave and static conductance measurements to 1000°C and more than 100 kb demonstrate the increase of the ion product of water by twelve orders of magnitude or more at these conditions.

I. INTRODUCTION

WATER and aqueous solutions are, very probably, the most thoroughly investigated class of fluids. An extraordinary amount of information is available for moderate temperatures and for pressures close to the normal vapour pressures. The knowledge of such fluids at temperatures approaching and exceeding the critical temperature of water, however, is much more limited. This is particularly true for those properties which are of interest for chemistry, as for example the electrolytic behaviour of water, solubility and miscibility at high temperatures and chemical equilibria at supercritical conditions. In recent years, work in this field has increased considerably, however, partly as a consequence of the advent of many new strong and non-corrosive construction materials. A survey of some selected results of this new work will be presented.

As an introduction a temperature/density diagram for pure water is given in *Figure 1*. The non-shaded area is the range of existence for a homogeneous fluid. At density 1 g/cm^3, near the abscissa is the triple point (T.P.). The points on the heavy (dashed) line extending to the right denote the transitions between the different modifications of ice. A number of isobars are shown. Up to about 10 kb data from static experiments for the density of water are available from recent work[1–3]. At pressures above about 25 kb, water densities at high temperatures have been derived from shock wave experiments[4].

The intermediate range has to be covered by interpolation. In order to retain the normal density at 1 g/cm^3 to 500°C a pressure of about 8 kb is necessary. At 1 000°C pressures of about 20 kb have to be applied for the same purpose.

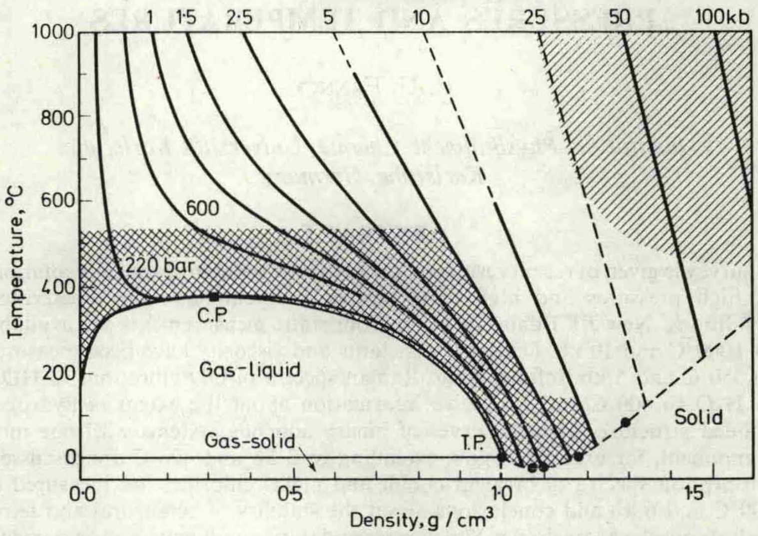

Figure 1. Temperature/density diagram of water. Full lines: measured isobars. Dashed lines: interpolated isobars. Cross-hatched zone: viscosity and dielectric constants determined. Single shading: ionic conductance determined.

In order to evaluate the possibilities of water at high pressures and elevated temperatures as a chemical solvent, knowledge of the dielectric constant and of the viscosity are particularly useful. The cross-hatched area up to about 500°C and 5 kb in *Figure 1* denotes the conditions at which the static dielectric constant[5] and the viscosity[5, 6] have been determined experimentally. At supercritical temperatures, for example at 500°C, the viscosity varies much less with the density of the fluid than at low temperatures. At 0·2 g/cm^3 and 0·8 g/cm^3 and at 500°C the viscosity has been found to be $3{\cdot}8 \times 10^{-4}$ poise (P) and $10{\cdot}5 \times 10^{-4}$ P respectively. This means that the viscosity is lower than that of liquid water at room temperature by a factor of 10 or 20. Dense supercritical water is a medium of very high fluidity and, consequently, dissolved neutral or ionic particles have high diffusion coefficients and ion mobilities in this medium.

In the upper right part of *Figure 1* the region has been approximately indicated in which direct determinations of the conductance and ionic product of water have been made with shock wave and static experiments. It appears as if at 1000°C and pressures beyond 100 kb water approaches the state of an ionic fluid.

II. DIELECTRIC AND SPECTROSCOPIC PROPERTIES

The static dielectric constant of water is to a large extent determined by the