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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 H₂O 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/cm³, 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 work¹⁻³. At pressures above about 25 kb, water densities at high temperatures have been derived from shock wave experiments⁴.