

AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

fact that water molecules within the hydration spheres of the produced ions are more densely arranged than in the free fluid. This effect is particularly evident in supercritical aqueous solutions where the compressibility of the fluid is high. A number of electrolytes, simple acids, alkali hydroxides and halides have been investigated in recent years to about 700°C and 6 kb^{37, 38, 39}. Maximum equivalent conductances have been observed at water densities between 0.4 and 0.8 g/cm³ which are up to one order of magnitude greater than at room temperature. The conductivity of dilute aqueous potassium chloride solutions could be measured to 1000°C and 12 kb⁴⁰. A piston-cylinder type apparatus with internal heating has been used. The electrolyte solution was compressed by a uniaxial press within a micro conductance cell which could be heated in a few minutes to the desired temperature, thus reducing contamination by corrosion. A platinum-sheathed thermocouple served as one of the conductance electrodes. Results are shown in *Figure 15*. The equivalent conductance is plotted as a function of temperature for

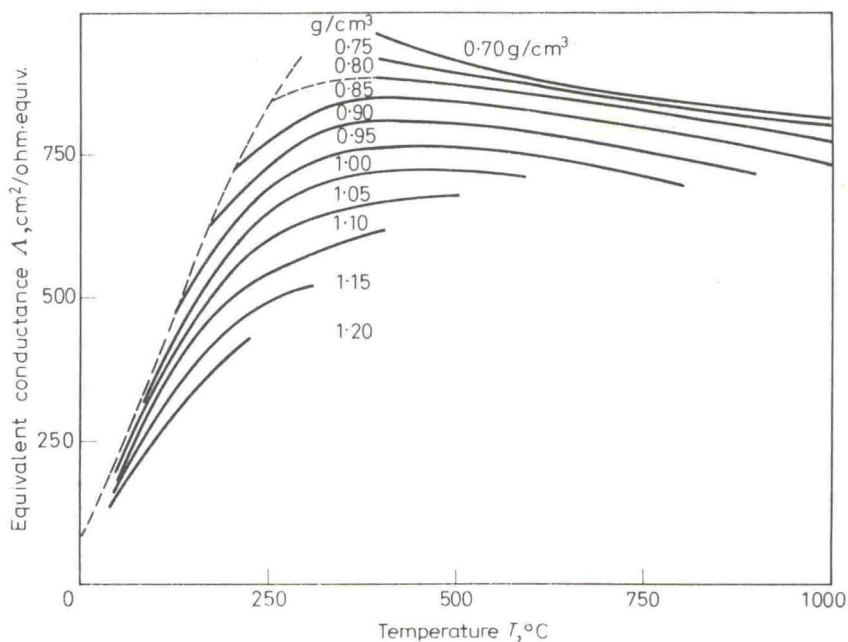


Figure 15. Equivalent conductance Λ of 0.01 M KCl in water as a function of temperature at high densities. Dashed line denotes boundary of two-phase region.

different densities of the solution. Since the salt concentrations were low, the densities were assumed to be equal to the density of pure water under the same conditions. At the normal density of 1.0 g/cm³, for example, the conductance increases with temperature as expected. Above 400°C, however, the curve levels off and may even have a flat maximum. The other constant density curves show similar behaviour at conductances which are seven to

eight times higher than at zero degrees. This phenomenon is explained by assuming ion pair formation which leads to effective degrees of dissociation of 0.7 to 0.9 at densities between 0.7 and 1.0 g/cm³ and temperatures higher than 400°C. The ion pair association constant above 400°C appears to be remarkably independent of temperature at constant density, probably because the product of dielectric constant and temperature varies only very little under these conditions⁴⁰. Also, the viscosity does not change very much with temperature at these densities above 400°C.

VI. IONIC DISSOCIATION OF PURE WATER

The enthalpy of the ionic dissociation of water is +13.4 kcal/mole at standard conditions. The volume decrease connected with the dissociation is -21 cm³/mole⁴¹. Thus a combination of temperature increase and pressure increase should produce very high values of the ion product in water. Hamann *et al.*^{42,43} reported shock wave measurements of the electrical conductivity of water at shock pressures between 20 and 130 kb with temperatures extending to about 800°C. While the specific conductance of pure liquid water at 20°C and atmospheric pressure is 4×10^{-8} ohm⁻¹ cm⁻¹, a value of 1.2 ohm⁻¹ cm⁻¹ was observed at 133 kb and 804°C. This increase in conductance by more than seven orders of magnitude was confirmed by static conductance measurements⁴⁴, where more combinations of pressure and temperature are possible than in the shock wave experiments. A very small amount of

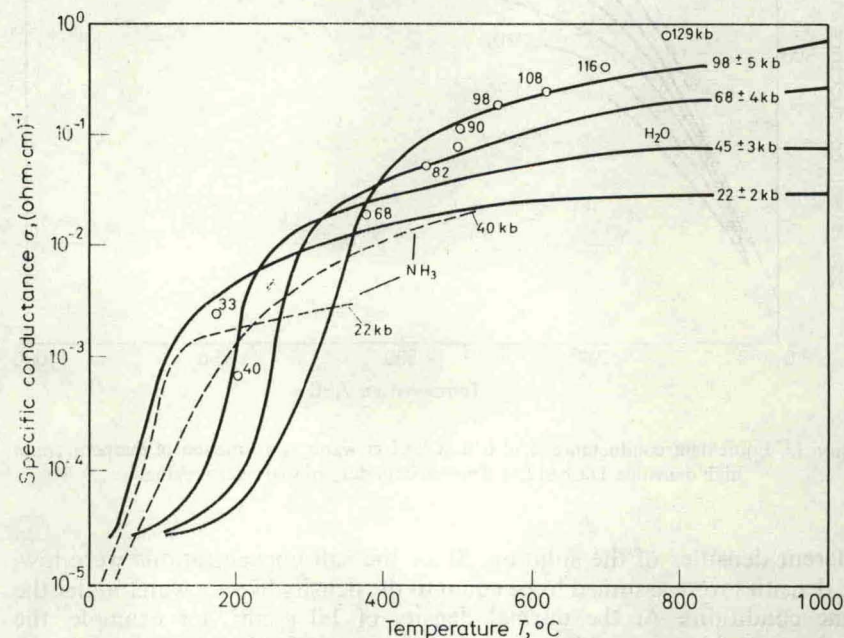


Figure 16. Specific conductance σ of pure water and pure ammonia at high temperatures and pressures. \circ denotes shock wave results of Hamann *et al.* The curves are results from static experiments.