

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

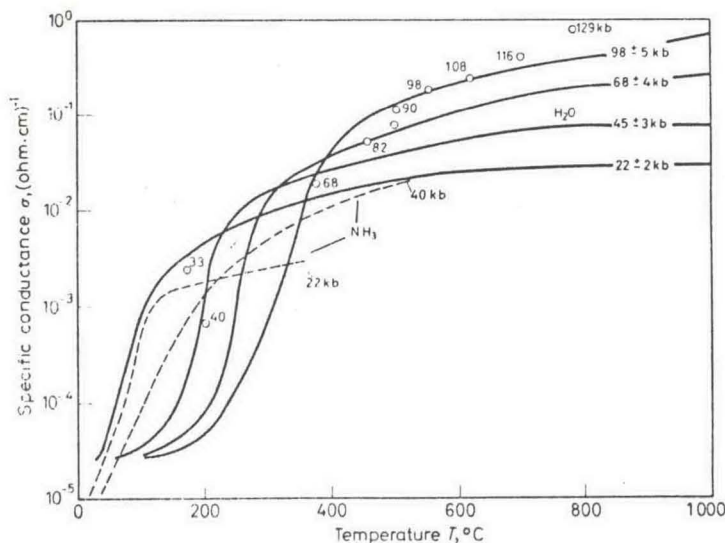


Figure 16. Specific conductance σ of pure water and pure ammonia at high temperatures and pressures. \circ denotes shock wave results of Hamann *et al.* The curves are results from static experiments.

AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

water was filled into a platinum-iridium cell placed between two opposed tungsten carbide anvils. The water was frozen to -30°C, compressed to the desired pressure and then heated by graphite resistance heaters while the conductance was recorded. Figure 16 gives isobars of the specific conductance as a function of temperature. The pressures have been calibrated by metal transition points and melting pressure curves of salts and ice. Starting from a low conductance the curves rise while the ice is melting. It is assumed that, after levelling off, that is for example above 500°C for the 98 kb isobar, the curves give the conductance of the fluid water.

The circles showing the earlier shock wave results of Hamann *et al.*⁴² are consistent with the static measurements considering the difficulties and differences of the two methods. This means that water at 1000°C and pressures between 100 and 120 kb has a specific conductance comparable to the conductance of a concentrated aqueous salt solution at 25°C.

The observed large increase of conductance is mainly due to an increase of the 'ionization product', that is of the product of the activities of hydrogen ions and hydroxyl ions in mole/l. Within the accuracy of this discussion the activities can be replaced by concentrations. It has been shown that the ion mobilities even at these extreme conditions can be relatively well estimated^{45,42} or derived from measurements with shocked salt solutions⁴⁶. The sum of the ion mobilities for hydrogen ions and hydroxyl ions at 670°C

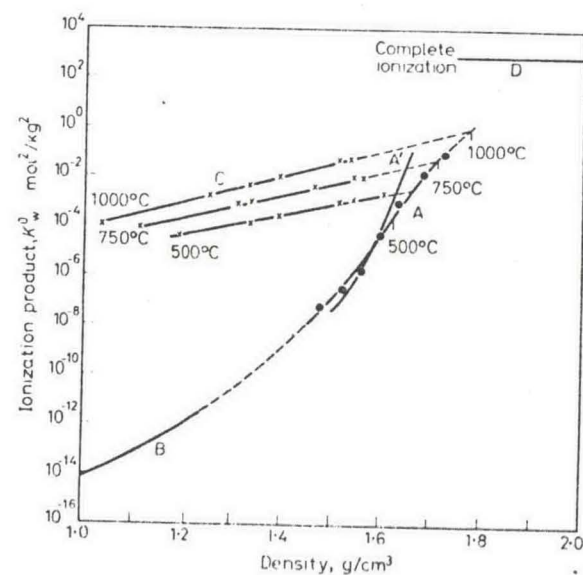


Figure 17. The ionization product K_w of water as a function of density according to Hamann and Linton. \bullet denotes shock wave results of Hamann and Linton, \times static measurements of Holzapfel and Franck⁴⁴.