The intermediate range has to be covered by interpolation. In order to retain the normal density at 1 g/cm³ to 500°C a pressure of about 8 kb is necessary. At 1000°C pressures of about 20 kb have to be applied for the same purpose.
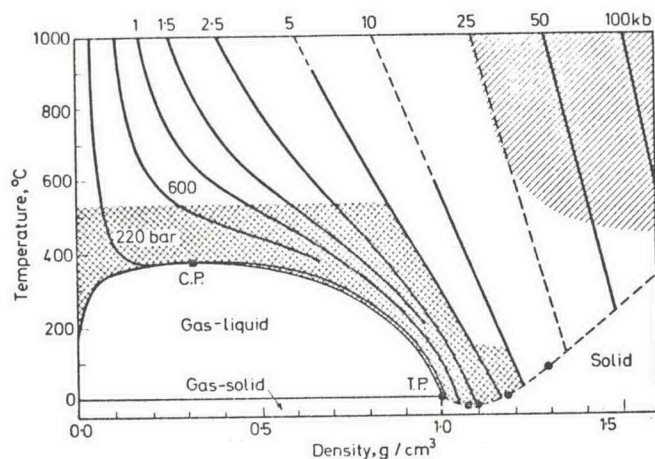

Figure 1. Temperature/density diagram of water. Full lines: measured isobars. Dashed lines: interpolated isobars. Cross-hatched zone: viscosity and dielectric constants determined. Single shading: ionic conductance determined.

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/cm³ and 0·8 g/cm³ and at 500°C the viscosity has been found to be $3·8 \times 10^{-4}$ poise (P) and $10·5 \times 10^{-4}$ 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

14

peculiar structural properties caused by the hydrogen bonds. In order to calculate the dielectric constant, the equation of Kirkwood[7, 8] introduces a correlation parameter which is determined by the number and orientation of the nearest neighbours of each water molecule. This approach gave good results at low temperatures. It is interesting to investigate the correlation parameter for supercritical water.

Earlier measurements of the dielectric constant at elevated temperatures were made up to 400°C and in part to 2 kb (for a compilation see Quist and Marshall[9]). Only recently experimental determinations were performed to 550°C and 5 kb[10]. The capacity of a condenser made of gold–palladium half cylinders mounted inside a high pressure autoclave was determined at a frequency of 1 MHz. One of the half cylinders could be rotated at high temperatures and pressures. *Figure 2* gives a compilation of results as curves of dielectric constants superimposed on the isobars of a temperature/density diagram of water. At supercritical temperatures and high pressure, values of the constant between 5 and 25 can be obtained. This corresponds to the dielectric properties of polar organic liquids under normal conditions.
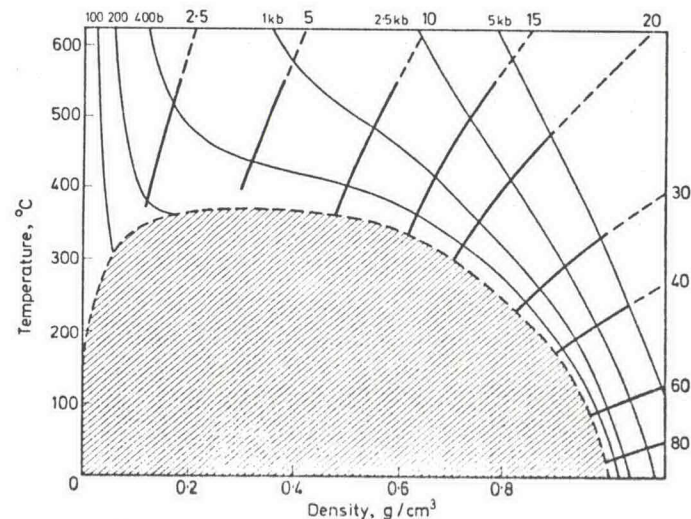

Figure 2. Dielectric constant of water as a function of temperature and density. ——: Measured. – – –: Calculated. ——: Isobars.

The new experimental data permit the calculation of the correlation parameter g according to the Kirkwood equation which is inserted in *Figure 3*. *Figure 3* gives such values of g obtained as a function of water density for several temperatures. As is expected, the g-values approach unity with decreasing density. It is interesting that even at 400°C and around the critical density of 0·32 g/cm³ the g-parameter is still about 1·5 or 1·6, which

15