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.

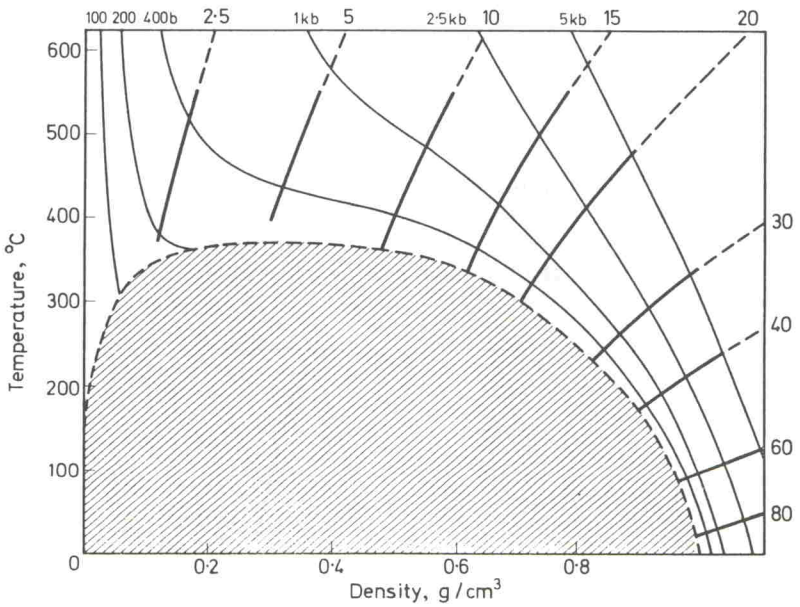

Figure 2. Dielectric constant of water as a function of temperature and density. ——: Measured. – – –: Calculated. ——: Isobars.

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

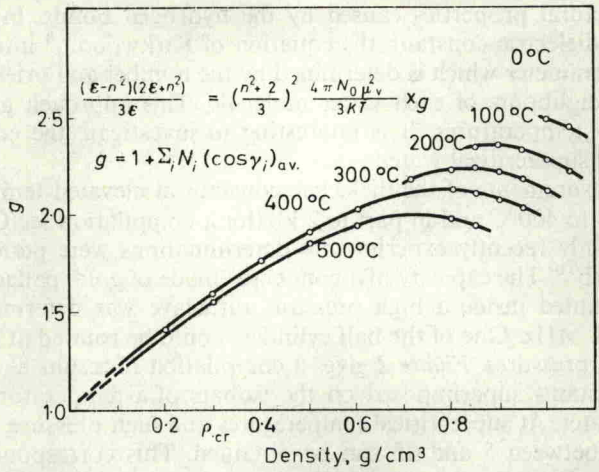

Figure 3. The Kirkwood correlation parameter from the experimental dielectric constant ε of water as a function of density and temperature (For a discussion of the inserted equation see ref. 8).

may indicate that a certain amount of structure still exists under these conditions. For a detailed discussion see ref. 8. It would be desirable to investigate dense supercritical hydrogen chloride in the same way for comparison.

More detailed information about the association of water by hydrogen bonds can be expected from the infra-red absorption spectrum. Particularly well suited for this purpose is the study of the absorption of the OD-vibration around 2500 cm^{-1} of HDO diluted in H_2O because of the absence of inter-

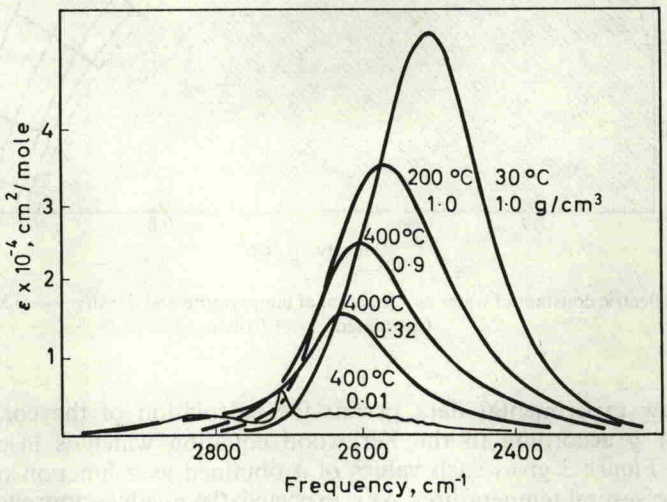

Figure 4. Infra-red OD absorption bands of 9·5 mole per cent HDO in H_2O for different temperatures and densities.