

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  $-30^{\circ}\text{C}$ , 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  $500^{\circ}\text{C}$  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.*<sup>42</sup> are consistent with the static measurements considering the difficulties and differences of the two methods. This means that water at  $1000^{\circ}\text{C}$  and pressures between 100 and 120 kb has a specific conductance comparable to the conductance of a concentrated aqueous salt solution at  $25^{\circ}\text{C}$ .

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<sup>45,42</sup> or derived from measurements with shocked salt solutions<sup>46</sup>. The sum of the ion mobilities for hydrogen ions and hydroxyl ions at  $670^{\circ}\text{C}$

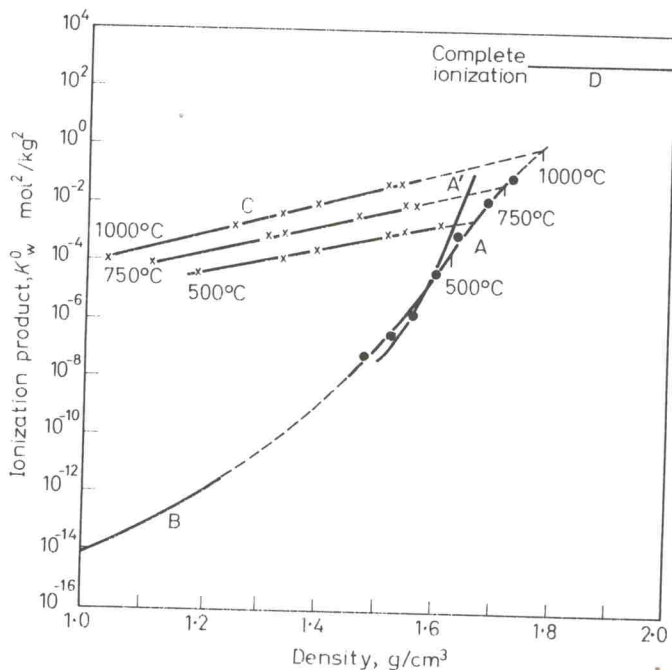
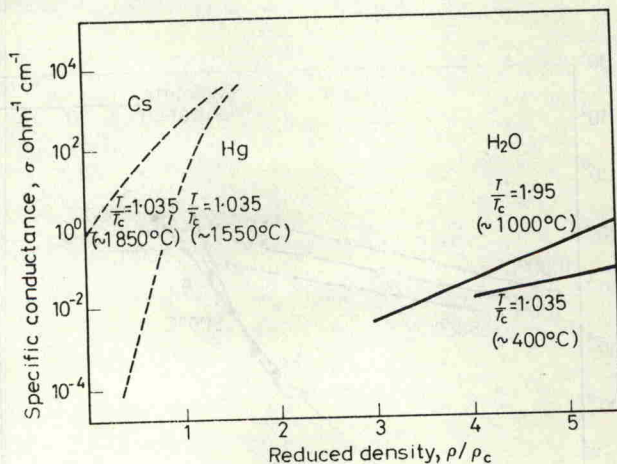


Figure 17. The ionization product  $K_w$  of water as a function of density according to Hamann and Linton. ● denotes shock wave results of Hamann and Linton, × static measurements of Holzapfel and Franck<sup>44</sup>.

and 114 kb for example should be  $2090 \pm 500 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ . *Figure 17*, which is from Hamann and Linton<sup>46</sup>, gives the ionization product of water derived from static and shock wave experiments as a function of density for several temperatures. At  $1000^\circ\text{C}$  and densities between 1.5 and  $1.7 \text{ g/cm}^3$  the ionization product reaches values of  $10^{-2}$  to  $10^{-1} \text{ mole}^2 \text{ l}^{-2}$ . This increase of the product by more than twelve orders of magnitude over the value for standard conditions is not unreasonable if one assumes a constant energy of dissociation and an average reaction volume change for the pressure range between 7 and  $10 \text{ cm}^3/\text{mole}$ . It has been suggested that water may become an ionic fluid if compressed to densities higher than about  $1.8 \text{ g/cm}^3$  at high supercritical temperatures<sup>46,47</sup>. This plausible suggestion means that water at these conditions would behave similarly to fused sodium hydroxide. It is indicated in the upper right corner of *Figure 17*.

Recently conductance measurement with pure fluid ammonia have been made to  $600^\circ\text{C}$  and 40 kb using a similar method as in the water experiments<sup>48</sup>. The two broken curves in *Figure 16* give the results. It appears as if the ionization would also be increased substantially by raising temperature and pressure. The ionization product for ammonia at  $500^\circ\text{C}$  and 40 kb has been estimated from these conductance data to be  $4 \times 10^{-4} \text{ mole}^2 \text{ l}^{-2}$ . This would be an increase by about a factor of about  $10^{18}$  over the value for  $25^\circ\text{C}$  at saturation pressure<sup>49</sup>.



*Figure 18.* Specific conductance  $\sigma$  of supercritical caesium and mercury and of supercritical water as a function of reduced density  $\rho/\rho_c$ .

As a conclusion it may be interesting to compare the electric conductance of dense supercritical water with the conductance of dense gaseous supercritical mercury<sup>50</sup> and caesium<sup>51</sup>. This is done in *Figure 18*. The logarithm of the specific conductance is plotted as a function of reduced density. The actual density is divided by the critical density of each substance. The comparison is made at a reduced temperature of 1.035—slightly above the critical point. For water, however, a second curve for a reduced temperature