and 114 kb for example should be 2090 ± 500 $cm^2\ ohm^{-1}\ mole^{-1}$. *Figure 17*, which is from Hamann and Linton[46], gives the ionization product of water derived from static and shock wave experiments as a function of density for several temperatures. At 1000°C and densities between 1·5 and 1·7 g/cm^3 the ionization product reaches values of 10^{-2} to 10^{-1} $mole^2\ l^{-2}$. 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 cm^3/mole. It has been suggested that water may become an ionic fluid if compressed to densities higher than about 1·8 g/cm^3 at high supercritical temperatures[46, 47]. 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°C and 40 kb using a similar method as in the water experiments[48]. 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°C and 40 kb has been estimated from these conductance data to be 4×10^{-4} $mole^2\ l^{-2}$. This would be an increase by about a factor of about 10^{18} over the value for 25°C at saturation pressure[49].

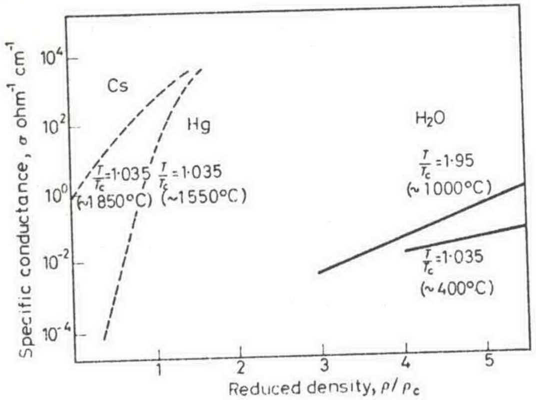

Figure 18. Specific conductance σ of supercritical caesium and mercury and of supercritical water as a function of reduced density ρ/ρ_c

As a conclusion it may be interesting to compare the electric conductance of dense supercritical water with the conductance of dense gaseous supercritical mercury[50] and caesium[51]. 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

of almost two is given. The difference in behaviour is very obvious. Mercury and caesium already attain a conductance of 1000 $ohm^{-1}\ cm^{-1}$ at less than twice the critical density. This has been shown as due to electronic conductance in the dense gas phase[50]. For water, as an ionic conductor, compression to more than five times the critical density and twice the critical temperature is necessary to reach a specific conductance of 1 $ohm^{-1}\ cm^{-1}$.

REFERENCES

1 S. Maier and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **70**, 639 (1969).
2 H. Köster and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **73**, 716 (1969).
3 C. W. Burnham, J. R. Holloway and N. F. Davis, *Amer. J. Sci., A*, **267**, 70 (1969).
4 H. M. Rice and I. M. Walsh, *J. Chem. Phys.* **26**, 815 (1957).
5 K. H. Dudziak and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **70**, 1120 (1966).
6 E. A. Bruges and M. R. Gibson, *J. Mech. Engng Sci.* **11**, 189 (1969).
7 J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).
8 D. Eisenberg and W. Kauzmann. *The Structure and Properties of Water*. Clarendon Press: Oxford (1969).
9 A. S. Quist and W. L. Marshall, *J. Phys. Chem.* **69**, 3165 (1965).
10 K. Heger, *Thesis, 1969*. Institute for Physical Chemistry, University of Karlsruhe, Germany.
11 J. A. Pople, *Proc. Roy. Soc. A*. **205**, 163 (1951).
12 E. U. Franck and K. Roth, *Disc. Faraday Soc.* **43**, 108 (1967).
13 W. F. J. Hare and H. L. Welsh, *Canad. J. Phys.* **36**, 88 (1958).
14 F. M. Buback, *Thesis, 1969*. Institute for Physical Chemistry, University of Karlstruhe, Germany.
15 H. Lindner, *Thesis, 1970*. Institute for Physical Chemistry, University of Karlsruhe, Germany.
16 G. E. Walrafen, in *Hydrogen-bonded Systems*, Taylor and Francis: London (1968).
17 H. C. Helgeson, *Amer. J. Sci.* **267**, 729 (1969).
18 H. D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **71**, 455 (1967).
19 H. D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **72**, 514 (1968).
20 D. Rykl and H. D. Lüdemann, *J. High Temp. High Press. Res.* **1**, 457 (1969).
21 J. S. Rowlinson, *Liquids and Liquid Mixtures*, 2nd ed. Butterworths: London (1969).
22 S. Sourirajan and G. C. Kennedy, *Amer. J. Sci.* **260**, 115 (1962).
23 G. C. Kennedy, G. J. Wasserburg, H. C. Heard and R. C. Newton. *Publ. No. 150*, Institute of Geophysics, UCLA (1960).
24 G. Schneider, *Ber. Bunsenges. Phys. Chem.* **70**, 497 (1966).
25 J. R. Krichevskii, *Acta Physicochimica, U.R.S.S.* **12**, 480 (1940).
26 D. S. Tsiklis, *Handbook of Techniques in High Pressure Research and Engineering*, Plenum: New York (1969).
27 J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria*. Prentice–Hall: New York (1969).
28 K. Tödheide and E. U. Franck, *Z. Phys. Chem. (Frankfurt)*. **37**, 387 (1963).
29 Z. Alwani, *Thesis, 1969*. Institute for Physical Chemistry, University of Karlsruhe, Germany.
30 A. Danneil, K. Tödheide and E. U. Franck, *Chem-Ing-Tech.* **39**, 816 (1967).
31 H. Lentz and E. U. Franck, *Ber. Bunsenges. Phys. Chem* **73**, 28 (1969).
32 M. Rigby, B. J. Alder, A. M. Lapse and C. E. Hecht, *J. Chem. Phys.* (1970) (in press).
33 S. D. Hamann, *Physicochemical Effects of Pressure*. Academic Press: New York (1957).
34 K. E. Weale, *Chemical Reactions at High Pressures*. Spon: London (1967).
35 F. Hensel and E. U. Franck, *Z. Naturforschung*, **19a**, 127 (1964).
36 E. U. Franck, D. Hartmann and F. Hensel, *Disc. Faraday Soc.* **39**, 200 (1965).
37 E. U. Franck, *Angew. Chem.* **73**, 309 (1961).
38 G. Ritzert and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **72**, 798 (1968).
39 W. L. Marshall, *Rev. Pure Appl. Chem.* **18**, 167 (1968).
40 K. Mangold and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **73**, 21 (1969).
41 S. D. Hamann, *J. Phys. Chem.* **67**, 2233 (1963).
42 H. G. David and S. D. Hamann, *Trans. Faraday Soc.* **55**, 72 (1959); **56**, 1043 (1960).
43 S. D. Hamann and S. D. Linton, *Trans. Faraday Soc.* **62**, 2234 (1966).
44 W. Holzapfel and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **70**, 1105 (1966).