

Fig. 12 shows curves of the equivalent conductance of KCl obtained for these mixtures as a function of the mean molar volume \bar{V} of the water-argon-mixtures. Λ is highest in pure water around $\bar{V} = 30 \text{ cm}^3 \cdot \text{mole}^{-1}$ and decreases considerably with increasing argon mole fraction, which is primarily due to lowering of the dielectric constant of the mixture.

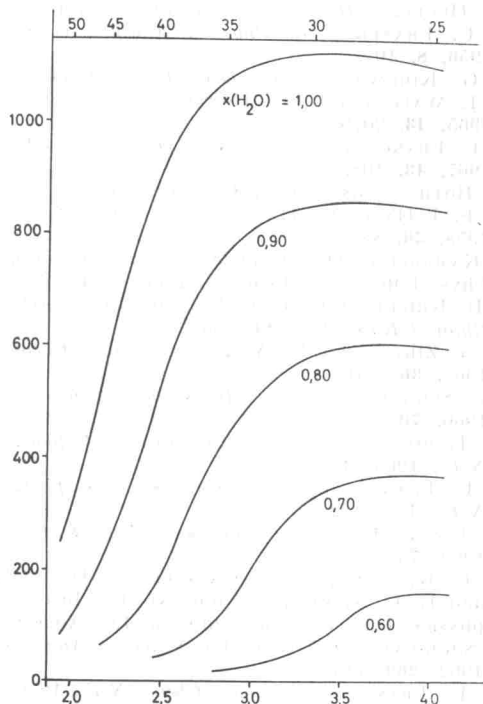


Fig. 12. — Observed equivalent conductance Λ of KCl at 440 °C in water-argon mixtures of several compositions as a function of mean density (in mole/cm³) or of mean molar volume (in cm³/mole) (31). $x(\text{H}_2\text{O})$: mole fraction of water in the mixture.

When proper estimates are made for the viscosity of the mixtures one obtains the plausible result that the admixed argon does not appreciably affect the dissociation of KCl if the amount of water per total volume remains constant. In fig. 13 the logarithm of the association constant K_A has been plotted as a function of $(\epsilon \cdot T)^{-1}$. The upper curve is for water-argon mixtures of different compositions at 713 °K. The lower curve is for water-dioxane mixtures, determined by FUOSS and LIND (32). According to the approximation by FUOSS (33) these curves should be linear if the effective ion radii were constant. If these radii had constant values for all temperatures and solvents, within the validity of this approximation K_A would be a function of ϵ and T only and the two curves should coincide. The curvature is not very pronounced. Coincidence of the two curves, however, could only be achieved if one choose to adapt the ion radii: A detailed discussion (31) suggests smaller effective ion radii for the high temperature argon-water mixtures than for the low temperature dioxane-water solvents. This, however, is based on the assumption of the validity of the macroscopic dielectric constant even in the vicinity of the ions.

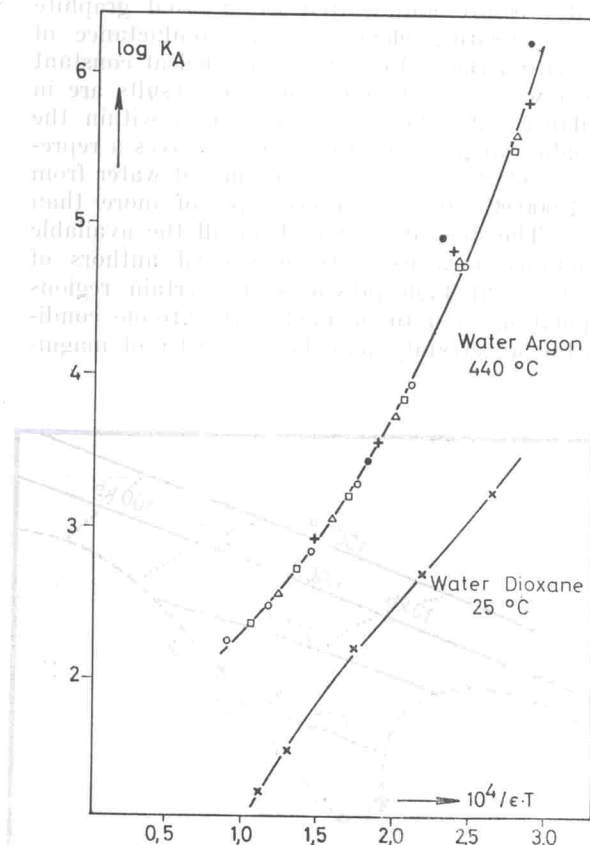


Fig. 13. — Logarithms of the association constant K_A of KCl in water-argon mixtures at 440 °C and in water-dioxane mixtures at 25 °C as a function of the reciprocal product of dielectric constant ϵ and temperature. $x(\text{H}_2\text{O})$: mole fraction of water in the water-argon mixtures (31).

Of special interest is the formation of hydrogen ions and hydroxyl ions by dissociation in pure water. The logarithm of the « ion product », $\log K_m$, in the liquid at the triple point is -14.95 . It must increase with rising temperature and pressure. This follows from the positive enthalpy of dissociation and from the fact, that the water molecules in the hydration shells of ions are more densely packed than in the free liquid. Thus at very high temperatures and pressures pure water should be very conductive. This has been confirmed by HAMANN and coworkers (34) who made conductance measurements in water compressed by shock waves to temperatures of about 800 °C and to maximum pressures of about 120 kb. Specific conductances in the vicinity of $1 \text{ ohm}^{-1} \text{ cm}^{-1}$ have been observed. This is comparable to the specific conductance of concentrated aqueous salt solutions at room temperature.

It was desirable to repeat conductance measurements in this range using a static method, which permits a more direct determination of temperature and pressure and enough time for the establishment of the dissociation equilibrium. Such measurements have been made up to 1 000 °C and 100 kb using a platinum-iridium micro cell which was placed into an « opposed anvil » arrangement (35). The water in the cell was frozen at -30 °C , subjected to the

desired pressure and heated by internal graphite resistance heating elements. The conductance of water within the cell could be recorded at constant pressure with rising temperature. The results are in accordance with the shock wave data within the reasonable range of accuracy. Fig. 14 gives a representation of the specific conductance of water from 0 to 1000 °C and up to pressures of more than 100 kb. The diagram is based on all the available conductance measurements of several authors of pure water at high pressures. In certain regions interpolations had to be made. At extreme conditions the uncertainty may be one order of magnitude.

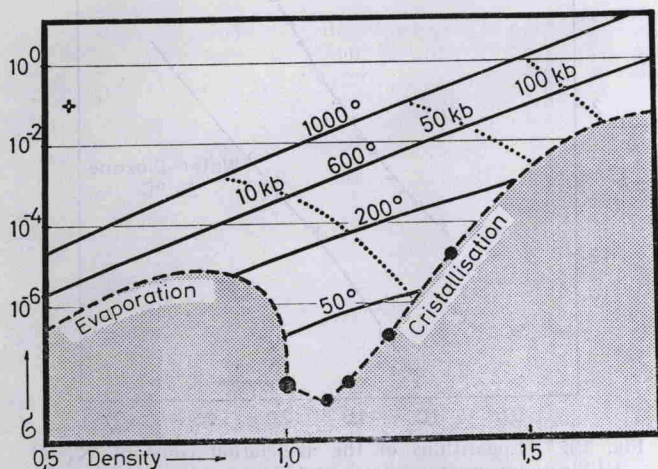


Fig. 14. — Specific conductance σ of water between 0 °C and 1000 °C and at pressures up to 100 kb as a function of water density.

— : isotherms,
 : isobars,
 - - - - : boundary of homogeneous one-phase region.

Both types of experiment — dynamic and static — demonstrate, however, that at very high temperatures and pressures above 100 kb the ion product of water can reach values of 10^{-2} (mol/l)² or even of 1 (mol/l)² and that the degree of ion formation may become several percent or more. Thus water assumes the properties of a concentrated ionic solution. Very recent analogous static measurements seem to indicate a similar behavior of dense supercritical ammonia.

V. — Conclusion.

The investigation of water and aqueous solutions within a very wide range of temperatures and densities, especially at supercritical conditions offers a very useful possibility to study the basic properties of ionic solutions. Parameters can be varied within wide limits without change of chemical compositions. The transport properties of dense gases can be combined with the electrolytic properties of liquid water. The high miscibility permits unusual combinations of components.

BIBLIOGRAPHY

- (1) S. MAIER and E. U. FRANCK. — *Ber. d. Bunsenges.*, 1966, **70**, 639.
- (2) H. KÖSTER and E. U. FRANCK. — In press, *Ber. Bunsenges.*, 1969, **73**.
- (3) H. M. RICE and J. M. WALSH. — *J. chem. Phys.*, 1957, **26**, 815.
- (4) A. S. QUIST and W. L. MARSHALL. — *J. phys. Chem.*, 1965, **69**, 3165.
- (5) K. HEGER. — *Dissertation*, Karlsruhe, 1969.
- (6) E. U. FRANCK. — *Z. Physikal. Chemie*, (Frankfurt), 1956, **8**, 107.
- (7) J. G. KIRKWOOD. — *J. chem. Phys.*, 1939, **7**, 911.
- (8) T. T. WALL and D. F. HORNIG. — *J. chem. Phys.*, 1965, **43**, 2079.
- (9) E. U. FRANCK and K. ROTH. — *Discuss. Faraday Soc.*, 1967, **43**, 108.
- (10) K. ROTH. — *Dissertation*, Karlsruhe, 1968.
- (11) W. F. J. HARE and H. L. WELSH. — *Canad. J. Phys.*, 1958, **36**, 88.
- (12) H. KAMERLINGH ONNES and W. H. KEESOM. — *Commun. Phys. Lab. Univ. Leiden*, Suppl. n° 15, 1907.
- (13) I. R. KRICHEVSKII and P. BOLSCHAKOV. — *Acta Phys. Chim. URSS*, 1941, **14**, 353.
- (14) D. S. ZIKLIS and L. A. ROTT. — *Russ. Chem. Rev.*, 1967, **36**, 351.
- (14a) G. SCHNEIDER. — *Ber. Bunsenges. physik. Chem.*, 1966, **70**, 497.
- (15) K. TÖDHEIDE and E. U. FRANCK. — *Z. phys. Chem. N.F.*, 1963, **37**, 387.
- (16) E. U. FRANCK and K. TÖDHEIDE. — *Z. phys. Chem. N.F.*, 1959, **22**, 232.
- (17) H. LENTZ and E. U. FRANCK. — *Ber. d. Bunsenges*, 1969, **73**, 28.
- (18) G. C. KENNEDY, G. J. WASSERBURG, H. C. HEARD and R. C. NEWTON. — *Publ. Nr. 150 Inst. of Geophysics, University of California, Los Angeles* 1960.
- (19) S. SOURIRAJAN and G. C. KENNEDY. — *Amer. J. Sci.*, 1962, **260**, 115.
- (20) E. U. FRANCK. — *Z. phys. Chem. N.F.*, 1956, **6**, 23.
- (21) G. M. MOREY and J. M. HESSELGESSER. — *Trans. Amer. Soc. mech. Eng.*, 1951, **73**, 865.
- (22) H. L. BARNES (Editor). — *Geochemistry of Hydrothermal Ore Deposits*, Holt, Rinehart and Winston, Inc., New York, 1967.
- (23) H. C. HELGESON. — *Complexing and Hydrothermal Ore Deposition*, Pergamon Press, 1964.
- (24) H. D. LÜDEMANN and E. U. FRANCK. — *Ber. d. Bunsenges*, 1967, **71**, 455.
- (25) H. D. LÜDEMANN and E. U. FRANCK. — *Ber. d. Bunsenges*, 1968, **72**, 514.
- (26) K. H. DUDZIAK and E. U. FRANCK. — *Ber. d. Bunsenges.*, 1966, **70**, 1120.
- (27) E. U. FRANCK. — *Z. phys. Chem. N.F.*, 1956, **8**, 92.
- (28) A. S. QUIST, W. MARSHALL and H. R. JOLLEY. — *J. phys. Chem.*, 1965, **69**, 2726.
- (29) G. RITZERT and E. U. FRANCK. — *Ber. d. Bunsenges.*, 1968, **72**, 798.
- (30) K. MANGOLD and E. U. FRANCK. — *Ber. d. Bunsenges*, 1969, **73**, 21.
- (31) D. HARTMANN and E. U. FRANCK. — In press *Ber. Bunsenges*, 1969, **73**.
- (32) J. E. LIND Jr and R. M. FUOSS. — *J. phys. Chem.*, 1961, **65**, 999.
- (33) R. M. FUOSS and F. ACCASCINA. — *Electrolytic Conductance*, New York, 1959.
see also G. B. MONK. — *Electrolytic Dissociation*, London, 1961.
- (34) H. D. DAVID and G. D. HAMANN. — *Trans. Faraday Soc.*, 1959, **55**, 72; 1960, **56**, 1043.
- (35) W. HOLZAPFEL and E. U. FRANCK. — *Ber. d. Bunsenges*, 1966, **70**, 1105.

DISCUSSION

L. Onsager. — Last week in Munich at a symposium on the properties of ice, E. WHALLEY reported a complete experimental