IONS IN AQUEOUS SOLUTIONS AT HIGH TEMPERATURES AND PRESSURES,

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SOMMAIRE

Aux hautes pressions l'eau est un bon solvant électrolytique même aux températures supercritiques. Les résultats de nouvelles mesures de la densité de l'eau à 600 °C et sous 10 kbar, de la constante diélectrique à 500 °C et sous 5 kbar et de l'absorption infrarouge à 400 °C et sous 4 kbar sont donnés et discutés.

On décrit la solubilité des gaz inertes, la formation de complexes du cobalt bivalent et du nickel et la conductivité électrolytique des sels dissous dans l'eau, aux températures super-critiques et à des pressions supérieures à 6 kbar.

On discute l'augmentation de la conductivité spécifique de l'eau pure qui est supérieure à 10^7 à 1 000 °C et sous 100 kbar.

SUMMARY

At high pressures water is a good electrolytic solvent even at supercritical temperatures. The results of new measurements of the water density to 600 °C and 10 kbar, of the dielectric constant to 500 °C and 5 kbar and of the infrared absorption to 400 °C and 4 kbar are given and discussed.

The solubility of inerts gases, the complex formation of bivalent cobalt and nickel and the electrolytic conductance of dissolvent salts in water at supercritical temperatures and pressures up to 6 kbar is described.

The increase of the specific conductance of pure water by more than 7 orders of magnitude at 1000 °C and 100 kbar is discussed.

ZUSAMMENFASSUNG

Unter hohem Druck ist Wasser auch bei überkritischen Temperaturen ein gutes elektrolytisches Lösungsmittel. Die Ergebnisse neuer Messungen der Wasserdichte bis 600 °C und 10 kbar, der Dielektrizitätskonstante bis 500 °C und 5 kbar und der Ultrarotabsorption bis 400 °C und 4 kbar werden mitgeteilt und diskutiert.

Die Löslichkeit von Inertgasen, die Komplexbildung von zweiwertigem Kobalt und Nickel sowie die elektrolytische Leitfähigkeit von gelösten Salzen in Wasser bei überkritischer Temperatur und Drucken bis zu 6 kbar wird beschrieben.

Die Zunahme der spezifischen Leitfähigkeit des reinen Wassers um mehr als 7 Grössenordnungen bis zu 1000 °C und 100 kbar wird diskutiert.

I. — Introduction.

Water as a solvent exhibits very different properties depending on the conditions of temperature and pressure. Although an extraordinary amount of information about aqueous solutions and mixtures is available for moderate temperatures and normal vapor pressures, the knowledge about such fluids at temperatures approaching and exceeding the critical temperature of water is still limited. The availability of new strong and noncorrosive materials, however, made physicochemical investigations with aqueous solutions at high temperatures and pressures possible, which have been pursued at several laboratories in recent years. Thus a comprehensive discussion of subcritical and dense supercritical aqueous phases may eventually be possible, and a qualitative survey appears to be feasible already at the present time.

The results of recent thermodynamic and electrochemical experiments performed in Karlsruhe will be presented. Dilute electrolyte solutions and even pure water at these conditions may assume certain properties which are normally observed in polar nonaqueous liquids, in concentrated aqueous solutions or in fused salts.

II. — Pure water.

Many properties of water are measured as functions of temperature and pressure, although the presentation of these properties as a function of temperature and density or specific volume is often preferable. Thus the knowledge of the PVT-relations for water is necessary. These relations for pure water can also be used to estimate the density of not too concentrated aqueous solutions at high temperatures and pressures. Fig. 1 gives a temperature-density diagram for water with isobars up to 100 kb, based on experimental results and calculations of
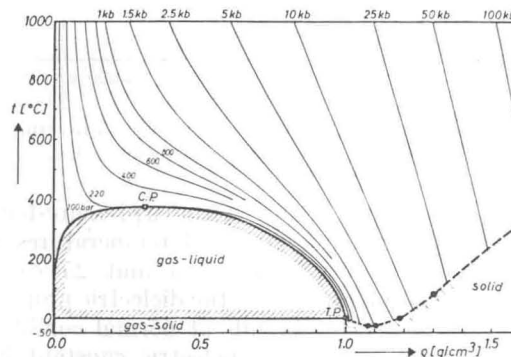

Fig. 1. — Temperature-density-(t-ρ)-diagram of water.

several authors. Between 200 and 850 °C and at pressures up to 6 kb recent results of static measurements are available [1]. These determinations have lately been extended to 10 kb at temperatures up to 600 °C [2]. From 25 to 250 kb shock wave data have been used [3]. The intermediate pressure range is covered by interpolations [for a survey of existing data and tables see MAIER and FRANCK [1]. In order to obtain the normal density of 1 g/cm³ in water at temperatures of 500 or 1 000 °C, pressures around 8 or 25 kb have to be applied.

The dielectric constant is significant of the properties of water as an electrolytic solvent. Earlier measurements of this quantity at elevated temperatures were made up to 400 °C and in part to 2 kb [for a compilation of these data see QUIST and MARSHALL [4]]. Only recently determinations were performed up to 500 °C and 5 kb [5]. The capacity of a condenser made of gold-palladium semi-cylinders mounted inside a high pressure autoclave was determined at a frequency of one megacycle. One of the semi-cylinders could be rotated at high pressures and temperatures. The capacity passes through a maximum and a minimum with one full rotation. Thus the elimination of the capacity of the leads is possible. Fig. 2 gives a compilation of results as
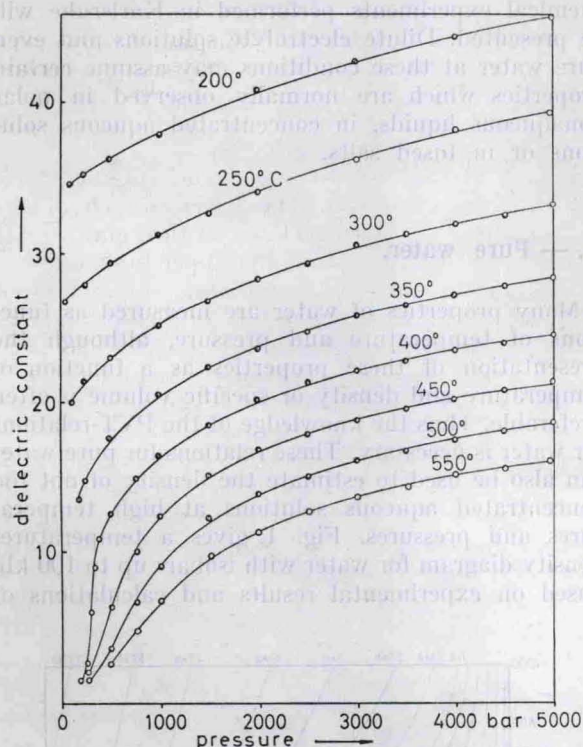
after having adjusted the orientation factor of this equation to the available experimental data. Beyond 500 b the new experimental data are somewhat higher than the calculated ones, but the deviation does not exceed five percent.

For a better understanding of dense supercritical water, knowledge about molecular interaction or association in the fluid is desirable. Liquid water is largely composed of associates formed by hydrogen bonding. As a consequence the absorption of the hydrogen-oxygen vibration in the infrared assumes the shape of one very intense broad band. The maximum absorption of this band is shifted by 300 wave numbers to lower frequencies as compared with the center of the absorption band of isolated gaseous molecules because of the action of hydrogen bonding. Particularly well suited for the study of this effect is the absorption of the OD-vibration around 2 500 cm⁻¹ of HDO diluted in H_2O, because of the absence of interference of other vibrations [8].

Recently this HDO absorption has been studied over a wide range of densities at the supercritical temperature of 400 °C [9]. A special cell had to be designed which could be used to 4 kb at this temperature [10] (fig. 3). It is of the reflection type, similar
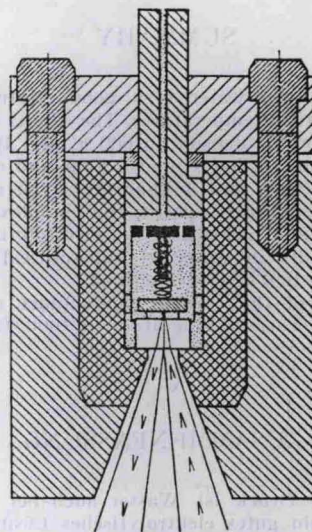

Fig. 3. — High temperature-high pressure infrared absorption cell ([9], [10]) with single window of colourless synthetic sapphire.

Fig. 2. — Dielectric constant of water as a function of pressure for several temperatures [5].

curves of dielectric constants within a pressure-temperature diagram. At supercritical temperatures and high pressure values between 5 and 25 can be obtained. This corresponds to the dielectric properties of some polar organic liquids at normal conditions. Previous estimates of the dielectric constant have been made [4, 6] using the KIRKWOOD equation [7]

in some respect to the cell described by WELSH [11]. The cell has a single window of colourless synthetic sapphire. Attached to the inner surface of the sapphire is a platinum-iridium mirror. Spacers of gold foil determine the distance between mirror and sapphire. Thus a path length of twice the distance between mirror and sapphire surface is provided, which is independent of the applied pressure. The aperture of the sapphire is 8 mm. The body of the cell is made from a noncorrosive nickel alloy and can heated from outside. This high temperature-high pressure cell was attached to a PERKIN-ELMER 521 grating spectrometer using a modified « Micro Specular Reflectance Assessory ».

Figure 4 shows the variation of absorption at 400 °C between densities of 0.01 and 0.9 g/cm³ or pressures from 50 to 4 000 b. At the highest density the absorption band is similar to the one observed in liquid water at room temperature. An indication of rotational structure appears only at densities lower than 0.1 g/cm³. Thus the infrared spectrum of the OD-vibration of HDO diluted in H_2O gives no evidence for freely rotating water molecules at densities higher than 0.1 g/cm³. This may imply that dipole-dipole interaction and remaining hydrogen bonding at densities higher than one tenth of the density of normal liquid water are sufficient to impede water molecules from rotating freely long enough to produce a discernible rotational structure in the spectrum. This apparent strong intermolecular interaction which is retained in supercritical water is of consequence for the electrolytic solvent properties of this fluid.
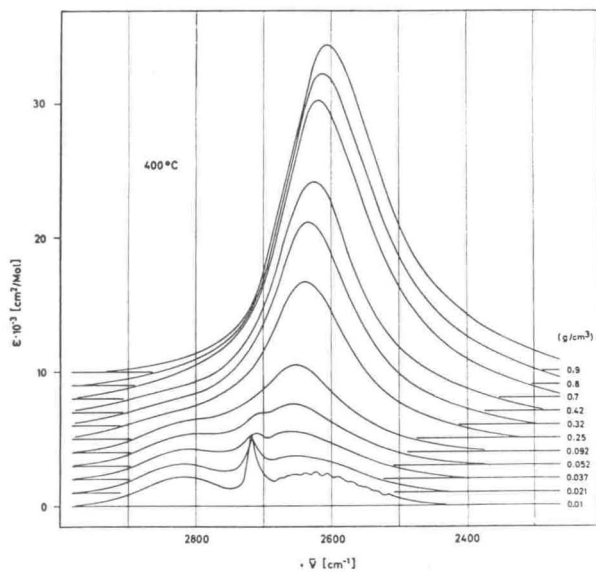

Fig. 4. — Molar extinction coefficient ε of the OD-stretching vibration as a function of frequency $\bar{\nu}$ in cm⁻¹ at 400 °C and at different densities of water (g/cm³) [9]. Note the different base lines of the individual curves.

III. — Solubility.

The miscibility of gases at low pressures can be expected to exist also at high pressures and elevated temperatures if the components are not too different. It has to be examined, however, whether complete miscibility is also possible if dense, gaseous supercritical water is combined with a nonpolar fluid or a solid. The discussion of these phenomena requires the knowledge of the phase boundaries in the pressure-temperature-composition (P — T — x) diagram of such two-component systems.

A system of two components has a critical curve which in simple cases connects the critical points of the pure components in the P-T-x-diagram without interruption. If the components are more different the critical curve is divided into two branches origi-

nating at the two critical points. The branch which begins at the higher critical point may eventually extend to temperatures and pressures which are higher than the respective values of that critical point. This behavior has been predicted by KAMERLINGH ONNES [12] and first demostrated experimentally by KRICHEVSKII and al. [13]. A detailed discussion is given by SCHNEIDER and by ZIKLIS [14, 14a].

A typical example is the system $CO_2 — H_2O$, the phase behavior of which is qualitatively represented in fig. 5. The dimensions are distorted in
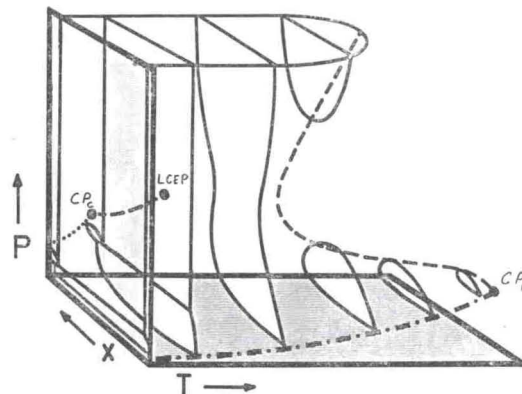

Fig. 5. — Schematic pressure-composition-temperature (P, T, x)-diagram of the system water-carbon dioxide. CP_c = critical point of CO_2; CP_w = critical point of water. - - - : critical curve.

this figure in order to show the characteristic properties more clearly. The lower branch of the critical curve ends at the « lower critical end point », LCEP at 31.5 °C and 74 b. The upper branch of the critical curve passes a minimum temperature of 266 °C and 2.45 kb and proceeds to higher temperatures with increasing pressure. This curve has been determined up to 268 °C and 3.6 kb. An upper critical end point, UCEP, has not been found in this range. To the left of the critical curve is the two phase region indicated by isotherms which have the shape of two separate loops above the minimum temperature. Above 266 °C and at pressures of one kb and more, mixtures of CO_2 and H_2O of all compositions can exist with a total density approaching that of normal liquid water. Earlier measurements of PVT-data of the homogeneous phase gave no conclusive information about possible chemical association between the CO_2 and H_2O molecules [16]. The electric conductance of such mixtures is not appreciably higher than that of pure water at similar conditions.

It would be inferred from the behavior of $CO_2 — H_2O$ — mixtures that beyond about 400 °C dense homogeneous mixtures could also be prepared of water with inert second components such as argon or simple hydrocarbons. With the addition of argon for example one should be able to alter continuously the electrolytic properties of dense supercritical water.

The phase equilibria of the argon-water system have recently been determined experimentally [17].

This was accomplished with a new method by which registration of PT-curves at constant volumes could be combined with visual observation of the fluid content of a high pressure cell. No extraction of samples from an autoclave was necessary. The cell had an observation window of synthetic sapphire. Its volume of a few cm³ could be varied by changing the position of a piston. Thus not only phase separations but also the PVT-relation in the homogeneous state could be determined. The results are shown in fig. 6 as isotherms. No separated isotherms with two loops occur.
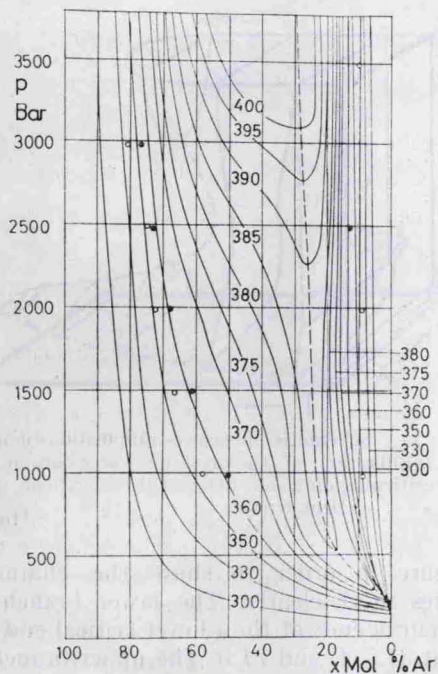

Fig. 6. — Isotherms of the two-phase boundary of the water-argon system. The heterogeneous state is within the isotherms. - - -: critical curve ([17]).

This means that here the upper branch of the critical curve has no minimum. From the critical point of pure water it proceeds monotonously to
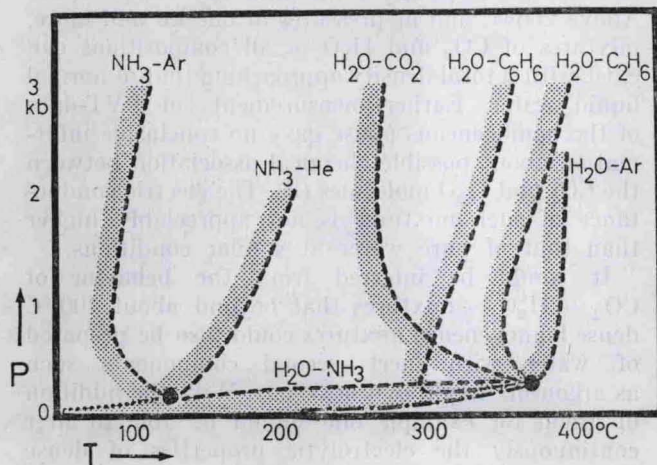

Fig. 7. — Experimentally determined critical curves for binary systems with ammonia or water combined with several nonpolar second components ([17]).

400 °C and 3.1 kb, the limit of these measurements. Thus high density argon-water mixtures of all compositions can be prepared beyond 400 °C. They have been used in electrolytic experiments described below.

Critical curves resembling those of the $CO_2 - H_2O$ and $Ar - H_2O$ systems have also recently been observed with systems of several hydrocarbons and water. A compilation of such curves is given in fig. 7.

Obviously, very concentrated aqueous solutions of these hydrocarbons can be made between 300 and 400 °C at not too high pressures. Applications of such solutions can be imagined.

IV. — Spectroscopic Investigation of Complexes.

Not only volatile compounds but also inorganic salts, oxides and similar substances have a considerable solubility in dense supercritical water. According to KENNEDY and al. ([18]), the system $SiO_2 - H_2O$ has an UCEP at 1080 °C and 9.8 kb. A considerable part of the phase diagram for $NaCl - H_2O$ has also been investigated ([19]). It may well be typical for other systems containing similar salts and water. At 600 °C and 1 kb for example, fluid mixtures appear to be possible with NaCl contents between zero and more than fifty weight percent NaCl. Accordingly concentrated aqueous electrolyte solutions can be prepared in a wide range of supercritical temperatures and pressures. Unfortunately little or nothing is known at present of the densities of such solutions. A discussion of the causes of solubility of electrolytes in supercritical water has been given earlier ([20]). Compilations of data and references are presented by several authors ([21, 22]).

Not only alkali halides and other compounds with small molecules can be dissolved in supercritical water. Several heavy metals can from complex compounds which are stable enough to exist in the aqueous fluid at high temperatures. In some cases the stability of such complexes can be increased by the addition of high concentrations of alkali halides to the fluid. Some of these « hydrothermal » solutions are considered in geochemistry as having been important for the transport of heavy metals in the earth's crust. Lead chloride complexes for example have been discussed extensively from this point of view ([23]).

Recently the range of existence of complexes of bivalent cobalt and nickel has been investigated spectroscopically in the visible and near ultraviolet regions ([24]). For this purpose an absorption double cell was constructed, which could be used with aqueous solutions up to 500 °C and 6 kb. The windows were cylindrical rods from synthetic sapphire of 60 mm length. The high temperature inside the cell decreased along the length of these windows. The body of the cell was of noncorrosive stell alloy and the solutions could be pumped through the cell at high temperatures and pressures.

Dilute solutions of bivalent cobalt chloride were

investigated to 500 °C ([25]). The pink solution at 25 °C has a maximum of absorption at 515 nm. At 500 °C and relatively low pressure (0.5 kb) a blue solution with a much stronger absorption having a maximum around 700 nm is formed. Increasing the pressure to 6 kb reduces the absorption and shifts the maximum to about 600 nm. This is explained assuming an equilibrium between hexagonal and tetrahedral cobalt complexes. At room temperature the hexagonal form with six water ligands prevails. With increasing temperature, however, the tetrahedral form with four ligands is favoured and predominates at 500 °C. Electrolytic conductance measurements indicate, that these tetrahedral complexes are mainly neutral diaquo-dichloro-complexes. Increasing pressure at constant high temperature is displacing the equilibrium again towards the hexagonal arrangement with more water attached to the cobalt atom.

In fig. 8 some of the observed absorption spectra for dilute cobalt (II) chloride solutions are shown for 0.5 and 6 kb and for 300 and 500 °C. The strong
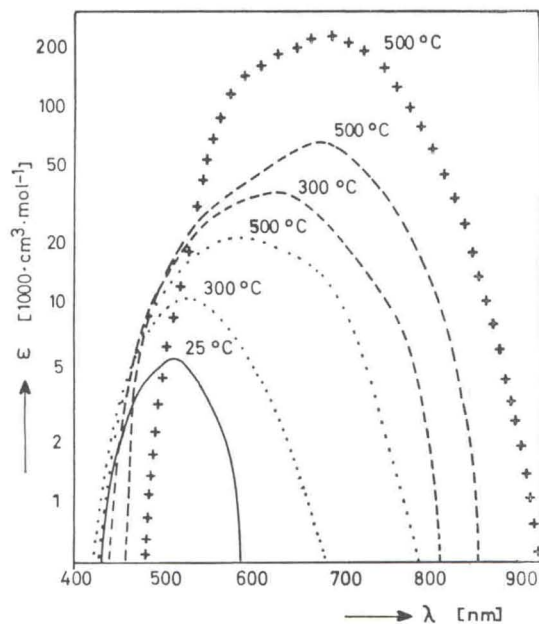
concentrations of chloride ions can be added by using lithium chloride. It appears, as if in a 10-molal lithium chloride solution even nickel(II)chloride can exist as tetragonal chloro-aquo-complex at high temperatures. This is suggested by fig. 9, where several absorption curves at 0.5 kb are shown. Making use of investigations of tetrahedral nickel-complexes in other solvents at lower temperature, the broad absorption around 680 nm in fig. 9 is ascribed to trichloro-monoaquo or dichloro-
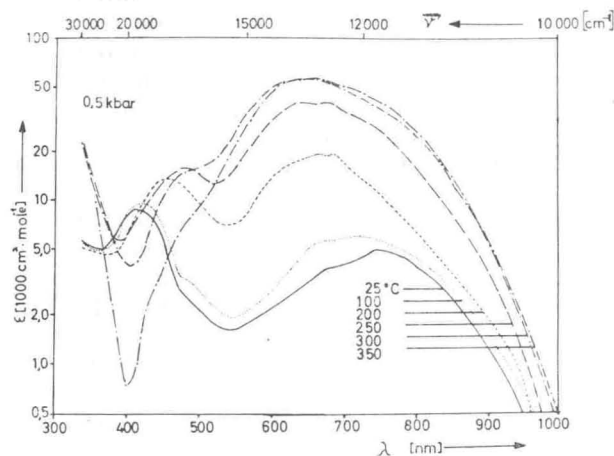

Fig. 9. — Observed absorption spectra for nickel(II)chloride in aqueous solution with addition of 10 molar LiCl. ($NiCl_2$: 0.01 molar) ([25]).

diaquo nickel complexes. The similarity of the curves for 300 and 350 °C in this range suggests that the formation of tetrahedral complexes is almost complete. Tetrahedral halogeno-aquo-nickel(II)complexes had so far not been observed. Apparently they can be stabilized sufficiently by very high chloride concentrations conbined with high temperatures and pressures.

Fig. 8. — Observed absorption spectra
for dilute cobalt(II)chloride solutions.

——————— : 25 °C, 1b;
- - - - - - - : 0.5 kb.
· · · · · · · · : 6 kb.
+ + + + : 1.0 kb and addition of 4.0 molar NaCl. ([24]).

absorption of the tetrahedral cobalt complexes at 0.5 kb and high temperature is evident. Increasing pressure reduces the absorption towards the curve observed at room temperature. The addition of sodium chloride to 4.0-molal concentration causes a very considerable increase of absorption with a maximum at 680 nm, which is attributed to a tetrahedral trichloro-monoaquo complex.

Calculations of the concentrations of these complexes as a function of temperature and total density of the solutions have been made. Very high

V. — Electrolytic Conductance.

Measurements of the electrolytic conductance are particularly well suited to give information about water at high temperatures as an electrolytic solvent. At supercritical conditions the dielectric constant can be varied continuously within a wide range simply by changing the pressure without altering the chemical composition and this constant can still be maintained high enough to permit ionic dissociation of dissolved electrolytes (see fig. 2). In the same region, however, the viscosity is reduced considerably, for instance to one tenth of the value for normal liquid water, thus producing high ion mobilities. The viscosity of water has been measured to 560 °C and 3.5 kb ([26]).

Equivalent conductances for a number of alkali salts, alkali hydroxides and inorganic acids have been determined experimentally using different designs at temperatures up to about 700 °C and pressures up to about 5 kb ([27], [28], [29], [30]). Many of these solutes dissociate either completely or to

a high extent if the water density is higher than about 0.5 g/cm³. The maximum equivalent conductances observed are between five and ten times higher than in normal liquid solutions. Dissociation constants have been derived for several compounds. Three more recent examples of conductance measurements shall be discussed in detail.

The conductance of a 0.01 molal potassium chloride solution was measured up to 1000 °C and 12 kb with an estimated accuracy better than ± 5 % in the greater part of this range of conditions (³⁰). This was done to investigate the conductance and ion formation of a typical simple electrolyte over several hundred degrees at constant high solvent densities. While in most of the earlier high temperature conductance experiments externally heated cylindrical high pressure cells of special superalloys were used, an arrangement with internal resistence heating was used here. The solution was contained in a cylindrical stainless steel cell mounted in an uniaxial press. The solution could be pressurized by this press with a tightly fitting piston. The two platinum electrodes were concentric cylinders of 2 mm outer diameter, insulated by sintered corundum. They were mounted to the piston and inserted into the fluid, so that the geometry of the electrodes remained constant. The inner electrode was a sheathed thermocouple, so that the temperature was always determined in the region where the conductance was measured. A KANTHAL resistance heater was placed outside the cell proper but inside the pressurized region. Thus all the temperatures desired could be attained in less than two minutes, which limits contamination of the solution by corrosion. Fig. 10 gives an impression of the cell arrangement. Details are described elsewhere (³⁰).
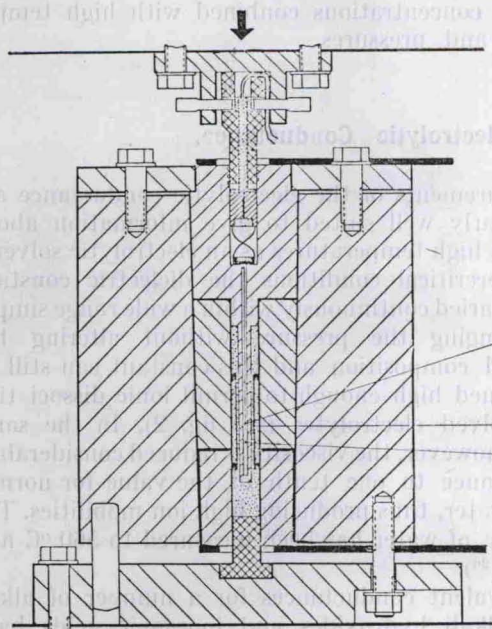

Fig. 10. — High pressure-high temperature conductance cell (³⁰).

a: space filled with electrolyte solution.
b: small cylindrical electrode arrangement.
c: internal resistance heater.

A compilation of results is shown in fig. 11. The equivalent conductance Λ of KCl is plotted as a function of temperature for constant solution densities between 0.7 and 1.2 g/cm³. Because of the small salt concentration the solution density was assumed as equal to the density of pure water at the same conditions. Up to 400 °C the conductance increases at all densities and attains maximum values of about 900 cm².ohm⁻¹.mole⁻¹. Above this temperature, however, the conductance appears to decrease at all densities. Discussion of the data shows, that the product of the dielectric constant and the temperature varies relatively little in this range and consequently the estimated degree of dissociation for the KCl molecules shows only a small variation, for instance from 0.87 to 0.75 between 300 and 1 000 °C at a density of 0.80 g/cm³. Triple ion formation appears to be unimportant in this region. LiCl and CsCl have been investigated in the same region and it is suggested that the behavior of KCl is typical for other monovalent salts.
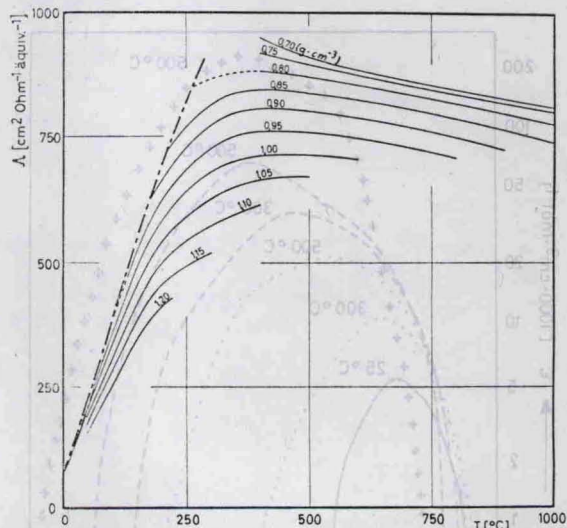

Fig. 11. — Equivalent conductance Λ of a dilute aqueous solution of potassium chloride as a function of temperature for constant high densities (³⁰).

—·—·—: liquid-gas coexistence curve.

In section III it has been shown that dense homogeneous mixtures of argon and water at all compositions can exist beyond 400 °C. Such fluid mixtures can be used as electrolytic solvents the dielectric constant of which can be varied at constant temperature and molar volume by changing the mole fraction of water. This is comparable to the well-known experiments at normal temperature with binary mixtures of water and dioxane or a similar polar compound with low dielectric constant. Argon, however, is a completely inert compound which will certainly not participate in any kind of ion solvation. Thus conductance measurements have been made at 440 °C up to about 4 kb with aqueous mixtures containing between 0 and 40 mole percent argon (³¹). KCl was dissolved in this supercritical fluid to a concentration of 5×10^{-4} mole.l⁻¹.

Fig. 12 shows curves of the equivalent conductance of KCl obtained for these mixtures as a function of the mean molar volume $\overline{V}$ of the water-argon-mixtures. Λ is highest in pure water around $\overline{V} = 30$ cm³ . mole⁻¹ and decreases considerably with increasing argon mole fraction, which is primarily due to lowering of the dielectric constant of the mixture.
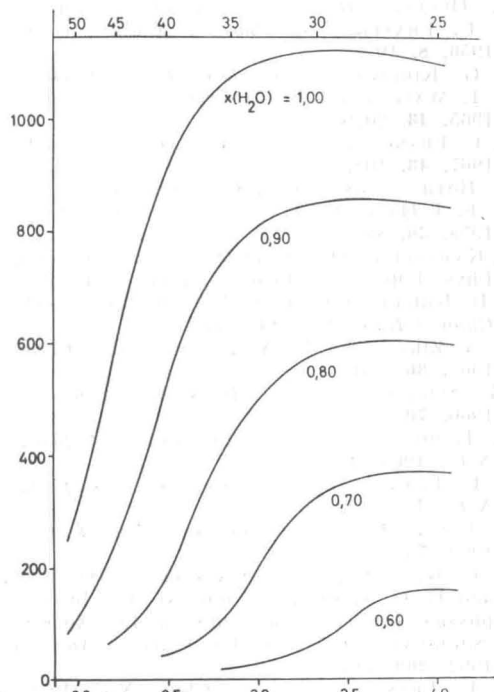

Fig. 12. — Observed equivalent conductance Λ of KCl at 440 ºC in water-argon mixtures of several compositions as a function of mean density (in mole/cm³) or of mean molar volume (in cm³/mole) [31]. $x(H_2O)$: mole fraction of water in the mixture.

Fig. 13. — Logarithms of the association constant K_A of KCl in water-argon mixtures at 440 ºC and in water-dioxane mixtures at 25 ºC as a function of the reciprocal product of dielectric constant ε and temperature. $X(H_2O)$: mole fraction of water in the water-argon mixtures [31].

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 $(\varepsilon.T)^{-1}$. The upper curve is for water argon mixtures of different compositions at 713 ºK. 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.
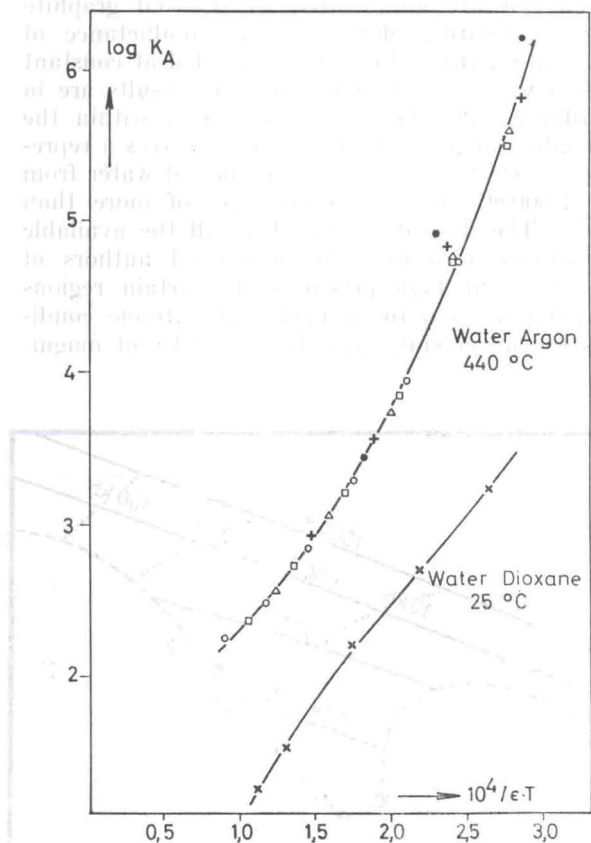
Of special interest is the formation of hydrogen ions and hydroxyl ions by dissociation in pure water. The logarithm of the « ion product », log K_w, in the liquid at the triple point is — 14.95. It must increase with rising temperature and pressure. This follows from the positive enthalpy of dissociation 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 ºC and to maximum pressures of about 120 kb. Specific conductances in the vicinity of 1 ohm⁻¹ 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 ºC 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 ºC, 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 1 000 °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.
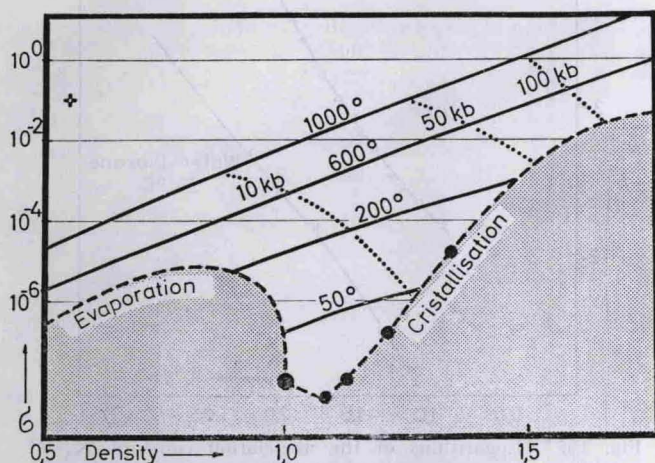

Fig. 14. — Specific conductance σ of water between 0 °C and 1 000 °C and at pressures up to 100 kb as a function of water density.

—— : 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 combin d 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. nᵒ 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 pressBer. 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. — Elektrolytic 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

study and KRAMERS-KRONIG analysis of the infrared absorption spectrum. He arrived at the remarkable conclusion that 3/4 of the difference between the optical and microwave refractive indices, respectively 1.31 and 1.18, arises from vibrations of frequency less than 10^{13} (325 cm^{-1}). This means that a change in the length of a hydrogen bond (0 — 0 distance) produces a large electric moment, with proportionality constant of about 0.3 electronic charges, as WHALLEY observed. Some of us may have suspected such an effect, but hardly anybody realized how big it was. The molecular models which underly present theories of dielectric constants do not incorporate this important property of the hydrogen bonds. In a realistic theory we must recognize it: on the whole it seems easier now to understand the large dielectric constant of water.

A. R. Ubbelohde. — To what extent does the abnormal mobility of protons and OH$^-$ ions, found in water under ordinary conditions, persist to higher temperatures and pressures? As is well known, this mobility gives important information about the cluster structure of water, and about other cooperative effects between H$_2$O molecules in assemblies. of high density, whether liquid or gaseous. The frequencies at which these mobilities begin to show relaxation dependence may likewise give significant information. Has any frequency dependence been observed at higher temperatures and pressures?

E. U. Franck. — We have tried to measure the abnormal mobility of protons in aqueous solutions up to about 300 ºC and up to about 5 kbars. Beginning with normal conditions, the increase of temperature as well as the increase of pressure cause an increase of the abnormal mobility, which may perhaps be ascribed to a facilitation of structural diffusion of clustered areas because at elevated temperatures and pressures more simple water molecules are available.

(This would be in accordance with the assumption that high pressure breaks up voluminous clusters).

The increase of extra mobility of protons however appears to level off at temperatures beyond 200 or 300 ºC and also at pressures beyond several kbars. Thus it is likely that the proton mobility in aqueous solutions cannot be increased by more than perhaps a factor of about three by an elevation of temperature and pressure only.

The abnormal proton mobility has so far at high temperatures and pressures ony been investigated up to about 100 kilocycles. As could be expected no relaxation has been observed in this range. An extension of such measurements to higher frequencies at elevated temperatures and pressures would be very difficult but very interesting and rewarding.

T. Ackerman. — I wander whether Dr ROTH has made an attempt to observe an additional continuous absorption due to « excess » or « defect » protons in the IR spectra of solutions of acids and bases in the high pressures region at elevated temperatures.

What is the meaning at the term « freely rotating water molecules » used in the discussion of the infrared spectra shown in slide Nº 2.

E. U. Franck. — So far Dr ROTH in our Laboratory has only investigated the infrared absorption of pure water and of several alcohols at wave numbers not smaller than about 2 500. Mr BUBACK has used the same cell to investigate the absorption of pure HCl up to 150 ºC and 1 000 bars in the range of absorption of the HCl vibrations. Extension of measurements to lower wave numbers than about 2 200 cm^{-1} was not possible because of the absorption of the sapphire windows with about 10 mm thickness. Also the corrosion of acidic solutions at high temperatures would cause considerable difficulties in the all-metal cell. It may, however, be possible to do such measurements in the future using silicon windows.

In this presentation the term « freely rotating » molecules has only been used to describe molecules which because of their rotation give rise to an observable rotational structure of the vibrational absorption band. It is not exclued that there may be rotating molecules which because of certain interactions with neighbours cannot be detected specifically by such spectra.

H. Friedman. — With regard to the very interesting data on conductivity of aqueous KCl on isochores of nearly constant viscosity, it would be of interest to compare with the theory of the effect of dielectric relaxation on ionic mobility. This is the theory to which a number of people have contributed, but most recently R. W. ZWANZIG. I wonder whether you have considered this problem?

E. U. Franck. — Whe should like very muchto follow your suggestions to try to study experimentally the effect of dielectric relaxation on ionic mobility in a region of conditions where the density of the fluid is high and where the viscosity of the fluid varies only slightly with density and temperature. The results of such measurements would certainly be very rewarding.

As is demonstrated by the diagram shown, however, such relaxation experiments should be made at temperatures of 400 ºC and higher and at pressures of several kilobars (unfortunately). At the present time the experimental difficulties seem to be very high or even prohibitive. Corrosion is one of the major obstacles. We should, however, think about it again.

J. C. Justice. — Professor FRANCK has shown experimental results for association constants for KCl in argon — water mixtures indicating the rare gas component in the solvent was « inert » in opposition to dioxane — water mixtures studied by FUOSS and al. where dioxane, being a structure breaker, led to further complications.

In fact, though simple as may look argon atoms, it is known that in water they lead to a reinforcement of the water structure. In that respect they cannot be considered as inert; their influence though opposite to that of dioxane in water leads also to further complications. A really « inert » second component that would not affect at all water structure seems even inaccessible since the mere fact to introduce (in imagination) « vacuum cavities » in water would tend to reinforce water structure in the immediate outer vicinity of the surface of such cavities. To what extent this consideration may be of negligeable consequences?

E. U. Franck. — I agree that argon atoms in water may well be not an inert component and may well influence the structure of the surrounding water considerably. Such effects, however, ave very probably restricted to relatively low temperatures. We assume that at the temperature applied here (440 ºC) and at the applied densities which were somewhat below 1 g/cm³ any effects of the argon on the structure of the surrounding water are too small to be detected. This would certainly be different in the range of gas hydrate formation.

A. R. Ubbelohde. — If the density of the system is fairly high one might expect the different space requirements for the insertion of different inert gas atoms into the mixture to result in notable differences in certain physical effects. For example the breaking up of clusters of water molecules by different inert gases at the same concentrations should show same effects of atomic size. Have any comparisons been made say, between neon, argon, and xenon in these respects? In the case of molten salts, insertion of inert gases involves considerable work to displace the ions. One might expect the additional space requirements for xenon, say compared with argon, to outweigh the higher polarisability of xenon; its solubility at the same temperatures should be smaller than that of argon. Unfortunately experimental tests do not yet appear to have been made.

E. U. Franck. — I am very happy about the encouragement which we receive from your suggestion to investigate mixed aqueous solvents, which contain larger atoms than argon as the second component. We shall try to do it.

Before using such mixed solvents for conductance experiments we have to know the two-phase range and critical curve of such a system. For that purpose we have started to make these thermodynamic measurements with the system xenon-water. Since Dr LENTZ in our Laboratory has developed a very small apparatus for simultaneous visual observation and determination of PVT-data of such mixtures we need only

small quantities of the expensive xenon. Since the sample space mounted is horizontally and because of the continuous control by observation through a sapphire window. we believe to be able to avoid errors caused by gravitational forces.

The apparatus of Dr LENTZ is described in a paper of LENTZ and myself. [17]).