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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

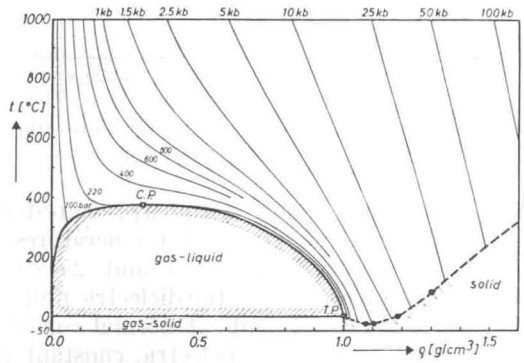

Fig. 1. — Temperature-density-(t-ϱ)-diagram of water.

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

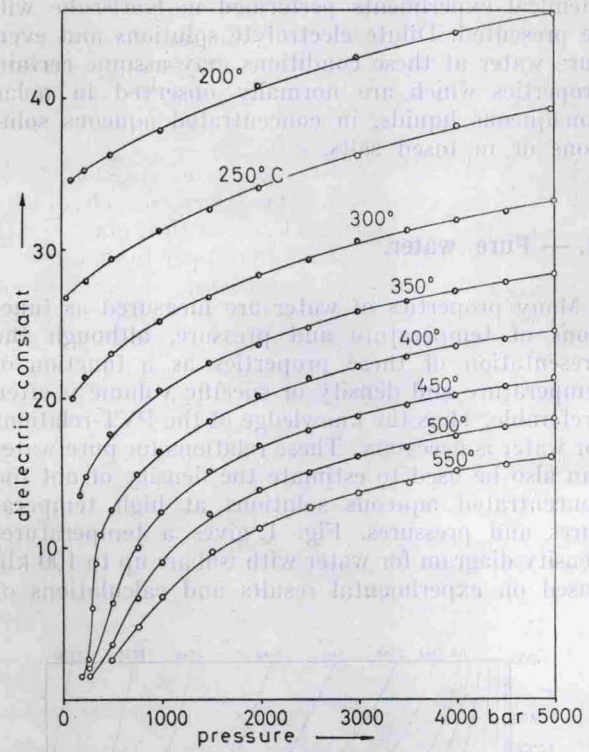

Fig. 2. — Dielectric constant of water as a function of pressure for several temperatures (5).

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) 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

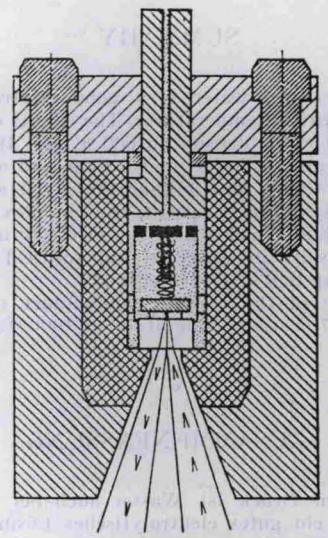

Fig. 3. — High temperature-high pressure infrared absorption cell (9, 10) with single window of colourless synthetic sapphire.

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 ».