

investigated to 500 °C<sup>(25)</sup>. 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

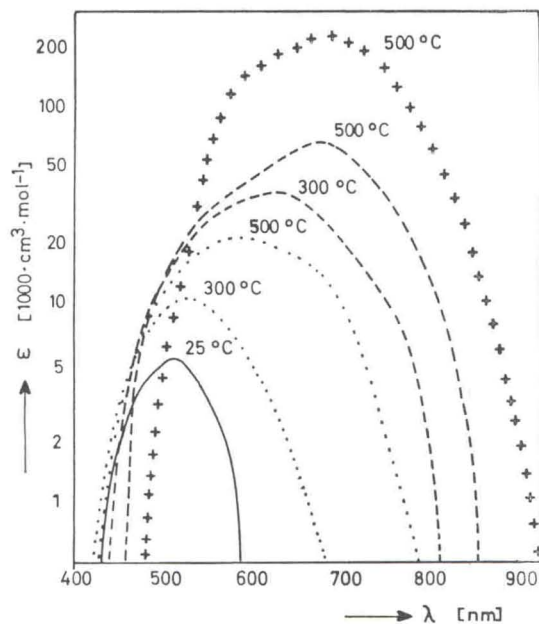


Fig. 8. — Observed absorption spectra for dilute cobalt(II)chloride solutions.

- : 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-molar 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

concentrations of chloride ions can be added by using lithium chloride. It appears, as if in a 10-molar 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-

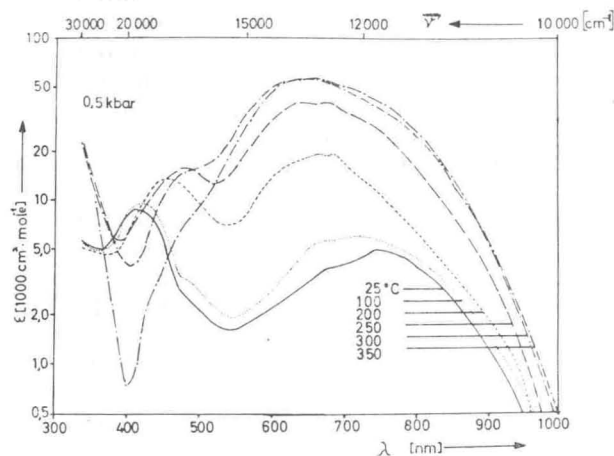


Fig. 9. — Observed absorption spectra for nickel(II)chloride in aqueous solution with addition of 10 molar LiCl. ( $\text{NiCl}_2$ : 0.01 molar) (25).

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 combined with high temperatures and pressures.

## 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  $0.5 \text{ g/cm}^3$ . 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  $1000^\circ\text{C}$  and 12 kb with an estimated accuracy better than  $\pm 5\%$  in the greater part of this range of conditions<sup>(30)</sup>. 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 resistance 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<sup>(30)</sup>.

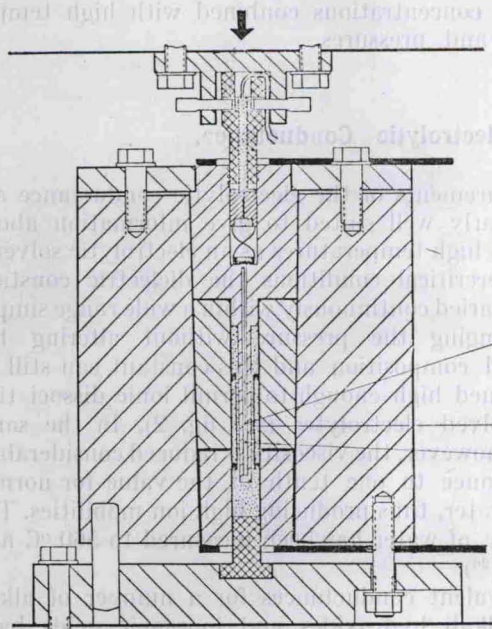


Fig. 10. — High pressure-high temperature conductance cell<sup>(30)</sup>.

- 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  $\Lambda$  of KCl is plotted as a function of temperature for constant solution densities between  $0.7$  and  $1.2 \text{ g/cm}^3$ . 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  $400^\circ\text{C}$  the conductance increases at all densities and attains maximum values of about  $900 \text{ cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mole}^{-1}$ . 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  $1000^\circ\text{C}$  at a density of  $0.80 \text{ g/cm}^3$ . 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.

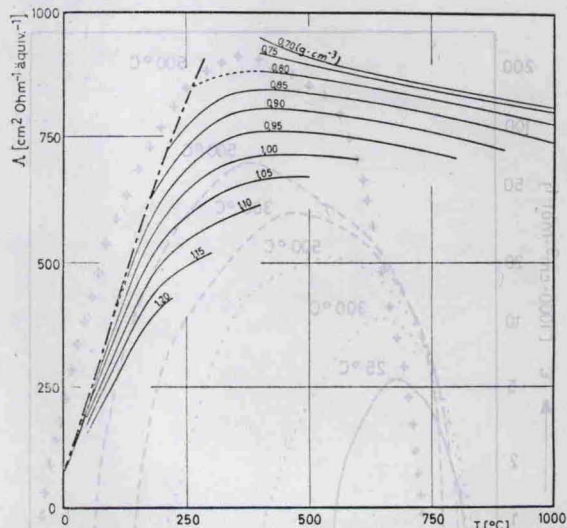


Fig. 11. — Equivalent conductance  $\Lambda$  of a dilute aqueous solution of potassium chloride as a function of temperature for constant high densities<sup>(30)</sup>.

— — —: 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  $400^\circ\text{C}$ . 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 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  $440^\circ\text{C}$  up to about 4 kb with aqueous mixtures containing between 0 and 40 mole percent argon<sup>(31)</sup>. KCl was dissolved in this supercritical fluid to a concentration of  $5 \times 10^{-4} \text{ mole.l}^{-1}$ .