

these windows. The cells were of a non-corrosive high strength alloy and in some cases lined with gold-palladium or platinum.

Dilute solutions of bivalent cobalt chloride were investigated to 500°C. The pink solution at 25°C has a maximum of absorption at 515 nm. At 300°C and the relatively low pressure of 350 bar a blue solution with a much

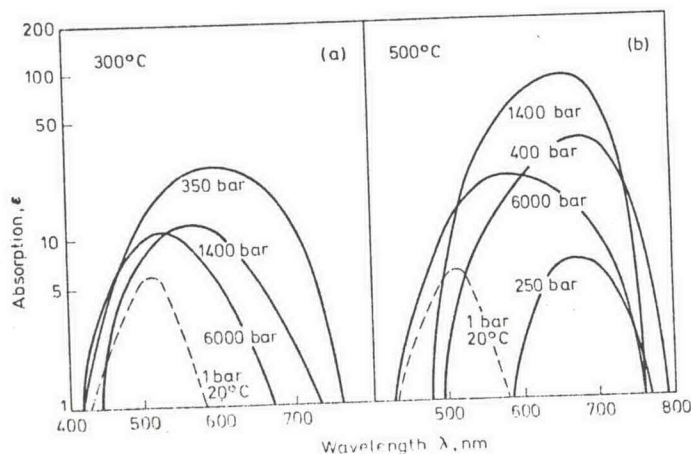


Figure 9. Absorption spectrum of CoCl_2 in water (Molality: 0.01) at (a) 300°C and (b) 500°C between 250 and 6000 bar.

stronger absorption having a maximum around 600 nm is formed. Increasing the pressure to 6 kb reduces the absorption and shifts the maximum to about 520 nm [Figure 9(a)]. This shift in absorption is explained by assuming an equilibrium between bivalent positively charged hexaquocobalt complexes, absorbing at shorter wavelengths and neutral dichlorodiaquocobalt complexes. The first have an octahedral and the second a tetrahedral structure. Increase of temperature favours the lower coordinated complex with four ligands, increase of pressure favours the higher coordinated complex with six ligands. This is even more obvious at 500°C [Figure 9(b)]. At 1400 bar the tetrahedral complexes with their strong absorption predominate. A pressure of 6 kb cannot shift the equilibrium towards the octahedral structure to the same extent as at 300°C. It is suggested that the reduction of absorption caused by a pressure decrease to 250 bar indicates a growing proportion of only slightly hydrated cobalt chloride molecules which are known to exist in the gas phase at high temperatures even without the presence of water.

Similar observations can be made with nickel(II) chloride if a high concentration of chloride ion is added. Figure 10 gives absorption curves at 300°C in 4-molal sodium chloride solution as examples. The curve for 25°C corresponds to the light green normal solution with two absorbing electron transitions. Temperature increase to 300°C produces blue solutions with a

strong broad band at 680 nm. It is caused by a combination of bands from octahedral and tetrahedral complexes. The tetrahedral complexes appear to predominate. Additional spectra indicate that this kind of complex becomes the only stable form in 10-molal lithium chloride solutions at this temperature

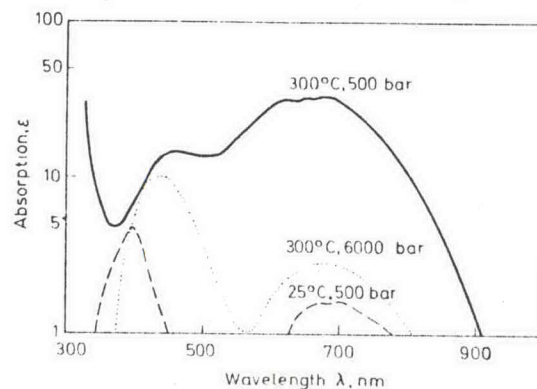


Figure 10. Absorption spectrum of NiCl_2 (Molality: 0.025) in aqueous NaCl solution (Molality: 4.0).

and at pressures between 150 and 300 bar. A detailed analysis of the magnitude of the extinction coefficients suggests that trichloromonoaquo and dichlorodiaquo tetrahedral complexes are the most abundant types. Pressures of several kilobars thus increase the range of stability of higher coordinated aquocomplexes to temperatures which may even be above the critical temperature of pure water. This is probably true also for other heavy metals of geochemical importance.

IV. CRITICAL PROPERTIES OF AQUEOUS MIXTURES

One-component systems have a critical point at the end of the vapour pressure curve. Two-component systems have a critical curve in the three-dimensional pressure/temperature/composition diagram. This curve may be uninterrupted or interrupted and distorted²¹. Figure 11 gives schematically a few examples as pressure/temperature diagrams. Below, to the left, two vapour pressure curves of a low boiling and a very high boiling substance are shown with their triple points TP and critical points C. The projections of gas-liquid-solid three-phase planes connect the triple points with a quadruple point Q. The critical points are connected by a critical curve C, projected on the P/T -plane. Steeply rising melting pressure curves begin at the triple points. At the lower right an isothermal cross section at T_a is shown. The maximum on the liquid-gas phase boundary curve is one point on the critical curve. Diagrams of this kind have been observed for the sodium chloride-water system²². In other systems the Q - TP_2 -three phase boundary surface