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

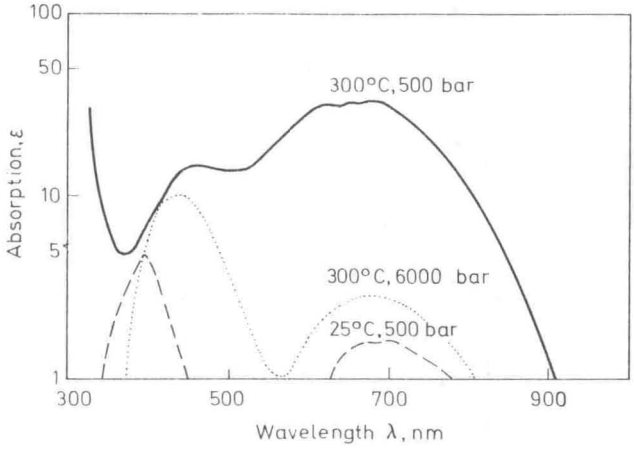

Figure 10. Absorption spectrum of $NiCl_2$ (Molality: 0·025) in aqueous NaCl solution (Molality: 4·0).

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 distorted[21]. *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 system[22]. In other systems the Q–TP_2–three phase boundary surface

extends to high temperatures and intersects the C_1C_2 critical curve at 'critical end points'. The silica–water system is an example for this behaviour[23].

Two fluid components which are not too different, as for example ethane and hexane, have a normal critical curve as in the upper left diagram of

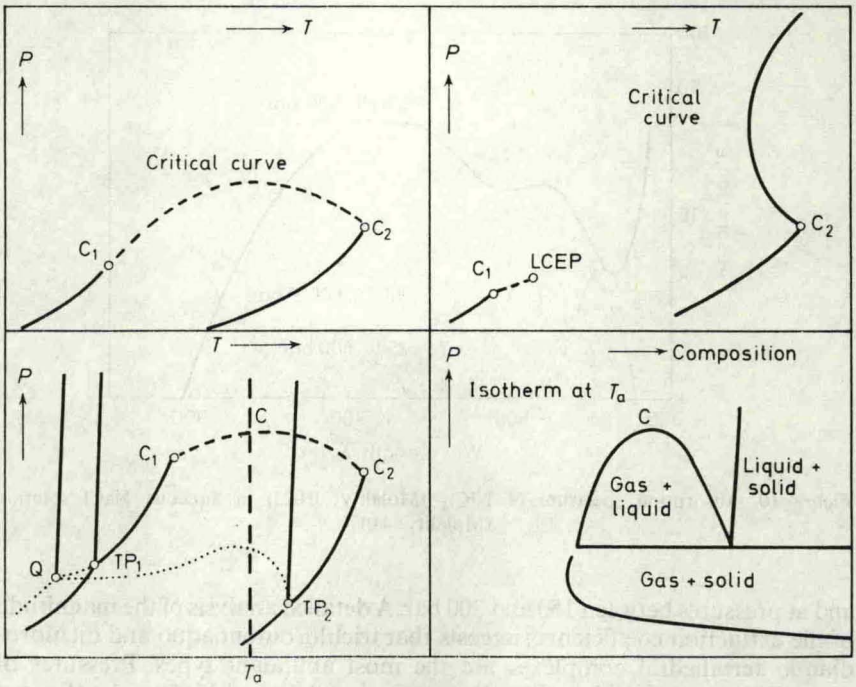

Figure 11. Critical curves of two-component systems.

Figure 11. If there is a greater difference in size, polarity, etc., the critical curve may also be interrupted at a lower critical end point (LCEP) with an upper branch as shown in the upper right diagram of *Figure 11.* This behaviour can be interpreted as an interference between a liquid–liquid miscibility range with the liquid–gas critical curve[24]. If this upper branch of the critical curve has a minimum temperature as in the diagram then the behaviour described by the critical curve at pressures higher than the pressure of this minimum temperature is sometimes called 'gas–gas-immiscibility'. It has been predicted by van der Waals and was demonstrated experimentally first by Krichevskii[25, 26] with nitrogen and ammonia in 1940. Since then, other examples have been found[24, 26] and discussed[27]. Among these are carbon dioxide–water[28], benzene–water[29], ethane–water[30] and argon–water[31]. The upper branches of the critical curves of these systems are shown in *Figure 12.*

They begin at the critical point of water and have a minimum temperature with the exception of the water–argon system. The range of complete miscibility is always on the right side, that is on the high temperature side, of these curves. One can have homogeneous mixtures of liquid-like densities at all