

example spheres with 'square well' interaction potentials combined with small 'hard sphere' particles³².

V. CONDUCTANCE OF ELECTROLYTE SOLUTIONS

From the knowledge of the dielectric constant it can be expected that dense water at high temperatures will remain a good electrolytic solvent. Figure 14 demonstrates the effect of increased pressure on the conductance of three types of electrolytes at relatively low temperatures. Detailed discussions of these phenomena have been given elsewhere^{33,34}. In Figure 14 the

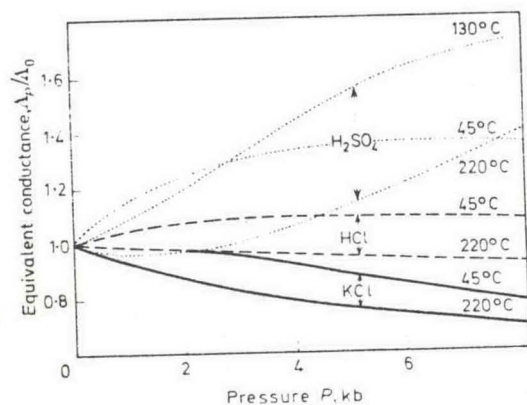


Figure 14. Pressure dependence of the equivalent conductance A of 0.001 M KCl, HCl and H_2SO_4 in water.

relative changes of the equivalent conductances with pressure are shown. For a normal strong electrolyte such as potassium chloride, pressure increase causes a decrease in conductance³⁵; this is in qualitative accordance with Walden's rule, which predicts that the equivalent conductance should be proportional to the inverse of solvent viscosity. The conductance decrease of potassium chloride with pressure is smaller, however, than estimated by this rule, since the effective ionic radii are not independent of pressure. For hydrogen chloride the conductance decreases only very slightly at 220°C and increases at 45°C. This is due to the enhancement of the abnormal mobility of protons in associated water³⁶. A similar effect would be observable for hydroxyl ions. The pressure dependence of the conductance of sulphuric acid, shown in Figure 14, can be understood as the result of the combined pressure dependences of water viscosity, abnormal proton mobility and dissociation of HSO_4^- ions into protons and sulphate ions. The equilibrium constant for this dissociation has a negative temperature dependence and a positive pressure dependence³⁶. At 100°C for example, the constant rises from 0.8×10^{-3} to 48×10^{-3} mole/l. if the pressure is increased to 8 kb. The increase of electrolytic dissociation with pressure is mainly due to the

fact that water molecules within the hydration spheres of the produced ions are more densely arranged than in the free fluid. This effect is particularly evident in supercritical aqueous solutions where the compressibility of the fluid is high. A number of electrolytes, simple acids, alkali hydroxides and halides have been investigated in recent years to about 700°C and 6 kb^{37,38,39}. Maximum equivalent conductances have been observed at water densities between 0.4 and 0.8 g/cm³ which are up to one order of magnitude greater than at room temperature. The conductivity of dilute aqueous potassium chloride solutions could be measured to 1000°C and 12 kb⁴⁰. A piston-cylinder type apparatus with internal heating has been used. The electrolyte solution was compressed by a uniaxial press within a micro conductance cell which could be heated in a few minutes to the desired temperature, thus reducing contamination by corrosion. A platinum-sheathed thermocouple served as one of the conductance electrodes. Results are shown in Figure 15. The equivalent conductance is plotted as a function of temperature for

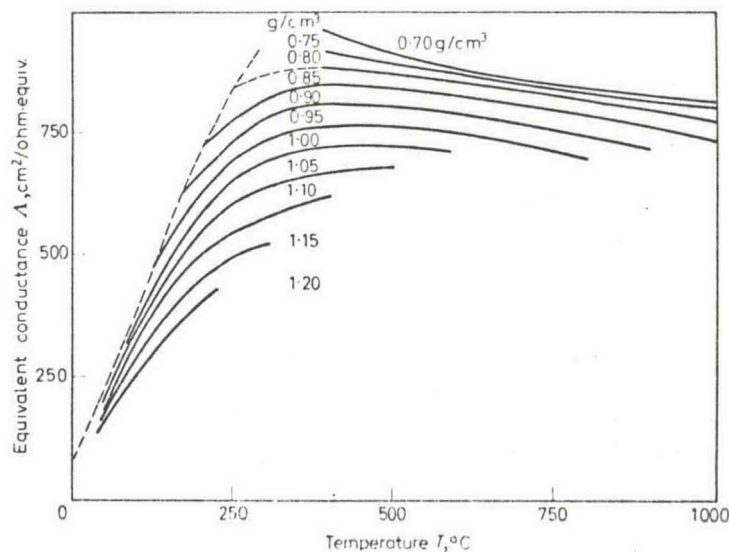


Figure 15. Equivalent conductance A of 0.01 M KCl in water as a function of temperature at high densities. Dashed line denotes boundary of two-phase region.

different densities of the solution. Since the salt concentrations were low, the densities were assumed to be equal to the density of pure water under the same conditions. At the normal density of 1.0 g/cm³, for example, the conductance increases with temperature as expected. Above 400°C, however, the curve levels off and may even have a flat maximum. The other constant density curves show similar behaviour at conductances which are seven to