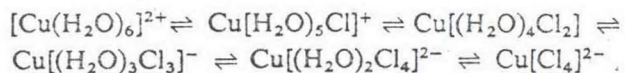Comparison of the 25°C curves of Fig. 11 with the results and discussions in the literature shows that curves A, B, and C for dilute solutions indicate a predominance of hexaquo complexes. In the yellow solutions F which contain 10 m LiCl the tetrahedral complex $(CuCl_4)^{2+}$ clearly prevails even at 25°C. Temperature increase to 350°C at 2 kbar (Fig. 12) causes enhancement of intensity and red shift, particularly for the solutions with lower chloride content. This is attributable to stronger distortion of the octahedra and increased copper-ligand distances as well as to the exchange of water ligands by chloride. The appearance of the spectra suggests a successive exchange of H_2O by Cl^- with rising temperature and Cl^- concentration, although no band can be detected, which is characteristic for one particular type of aquo-chloro complex. A more detailed discussion is given elsewhere.[24] Formally, the sequence of transitions from hexaaquo complexes to tetrachloro complexes with increasing temperature and chloride content can be described by

$$[Cu(H_2O)_6]^{2+} \rightleftharpoons Cu[H_2O)_5Cl]^+ \rightleftharpoons Cu[(H_2O)_4Cl_2] \rightleftharpoons$$
$$Cu[(H_2O)_3Cl_3]^- \rightleftharpoons Cu[(H_2O)_2Cl_4]^{2-} \rightleftharpoons Cu[Cl_4]^{2-}.$$

6. AMMONIUM CHLORIDE

Although some of the solutions discussed so far, with electrolyte molalities of 10 or more, have very high ion concentrations, they are still quite different from fused salts where there may be only ions in the fluid. One might ask whether it is possible to study pure ionic fluids at temperatures where the intermolecular distance and possibly the degree of ionization can be changed continuously over wide ranges by variation of pressure. This would be of considerable basic thermodynamic interest because of the possibility of investigating compressible fluids with coulombic interactions. Such dense gaseous ionic fluids may also have some geochemical and technical interest.

It is difficult, though, to find suitable examples. Fused alkali halides have critical temperatures at 2500°C or higher, which at present excludes static high-pressure experiments. At lower temperatures, only small expansions are possible. Salts with lower critical temperatures, $BiCl_3$ for example, are only ionized to a small extent at critical conditions.[25, 26] Stable polar fluids such as water and ammonia need very high pressures and temperatures to become higher ionized (see Sec. 7).

From recent experiments, it appears that certain ammonium halides may be examples for fluids which are highly ionized at not-so-high critical temperatures. This is suggested by results obtained with ammonium chloride.[27] NH_4Cl has a solid–liquid–gas triple point at 520°C and 48 bar. Using several types of internally heated corrosion-resistant cells, made mainly of sapphire and gold–platinum, it can be shown that NH_4Cl has a single vapor-pressure curve which extends from the triple point to a critical point at
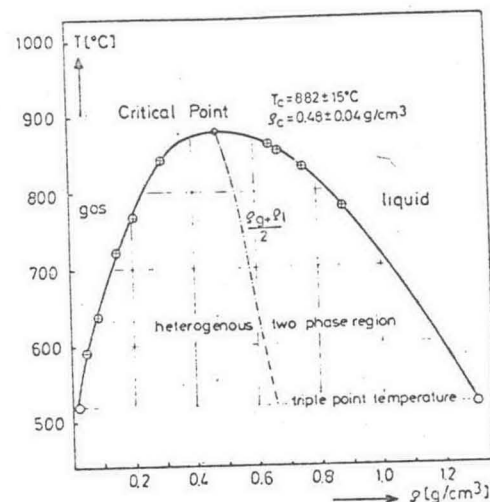
Fig. 13. Gas–liquid coexistence curve of NH_4Cl in a temperature–density diagram.

$882 + 15°C$ and 1635 ± 20 bars. The coexistent gaseous and liquid densities can be measured and are shown in Fig. 13.

At this triple point, the specific conductance of liquid NH_4Cl is 2.07 $ohm^{-1}-cm^{-1}$, only 5% lower than that of liquid KCl at the melting point. Liquid NH_4Cl near the triple point is therefore to be considered as an ionic melt. The electrolytic conductance can be measured in the liquid at saturation condition to 850°C—about 32° below the critical temperature.[28] Since the liquid at 850°C has expanded already to about twice its molar volume at the triple point, a decrease of ionization and conductance can be expected. Actually, however, the conductance increases, and the ratio of specific conductance over molar volume, the molar conductance Λ at 850°C, is three times higher than Λ_T at the triple point (see Fig. 14). Reasonable
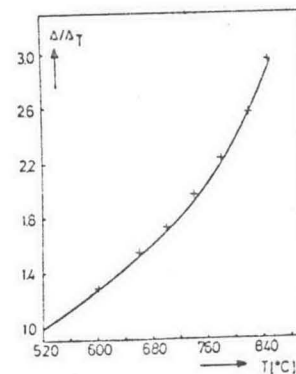

Fig. 14. Relative molar conductivity Λ/Λ_T of liquid NH_4Cl at saturation conditions. Λ_T is the molar conductivity of liquid NH_4Cl at the triple point.

estimates of ion mobilities and utilization of data for fused alkali halides suggest the approximate relation[2] for the temperature and density dependence of Λ for a fully ionized fluid. The quantity E_a is the activation energy for

$$\Lambda(T_1 \rho) = \text{const.} \times e^{-E_a/R_r} \rho^{-5\,6} \tag{2}$$

ionic conductance at constant density. If $E_a = 3$ kcal-mole^{-1}, as for comparable alkali halides, one obtains the curve of Fig. 14. The agreement with the experimental points is good, which would mean that at 850°C liquid NH_4Cl is still an ionic fluid. It is believed that even in the critical region at 882°C the fluid is still predominantly ionized. This may be the first known nonmetallic fluid exhibiting such a behavior. Preliminary investigations with NH_4HF_2 indicate the possibility of similar phenomena.

7. CONCLUSION

It cannot be excluded that pure fluids of small, polar, and stable molecules may become very concentrated electrolyte solutions if self-ionization can be increased by many orders of magnitude. Self-ionization is favored by increasing temperatures and high pressures. From recent static conductance measurements with pure ammonia,[29] which were extended to 500°C and 40 kbar, it follows that the ion product at these conditions should be between 10^{-4} and 10^{-3} mole^2-liter^{-2}. This is still far from a concentrated ionic solution. Similar conductance measurements with water, however, have been made with shock waves and with a static method to 1000°C and more than 100 kbar.[30, 31] An ion product in the vicinity of 10^{-2} mole^2-liter^{-2} for water has been derived from these experiments.

Figure 15, taken from Hamann and Linton,[31] gives a compilation of **ion-product data for pure water as a function of water density obtained from**
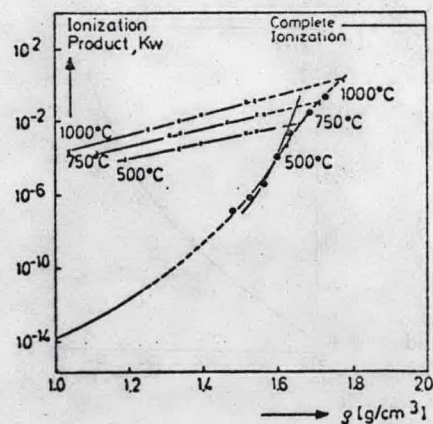

Fig. 15. Ionization product of compressed water as a function of density (after Hamann and Linton[31]). —o—o—o— From shock-wave experiments; ×—×—×—× from static experiments.

the shock-wave and static measurements. The agreement is good, considering the difficulty of the experiments. The authors have made the well-justified proposition that complete ionization of water at high supercritical temperatures would be achieved if it could be compressed to a density of 1.8 to 2.0 g-cm^{-3}, that is, twice the normal density. This range is indicated in the upper right part of Fig. 15. It is interesting to note that under these conditions the molar volume of $(H_2O)_2$ would be similar to the molar volume of fused NaOH at normal pressure.

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DISCUSSION

Dr. F. H. Stillinger (*Bell Laboratories, New Jersey*). I am afraid that seeing this $\beta = \frac{1}{2}$ is very disturbing—I am referring to the coexistence curve for