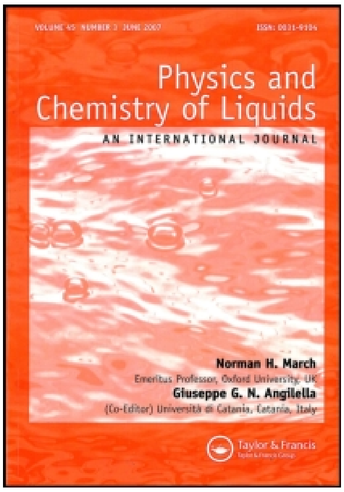

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The Conductivity of $AgNO_3$ in Liquid and Dense Gaseous NH_3 as a Function of Temperature‡

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The main work on dense gaseous electrolytes had been done with water as the solvent. The practical application of such electrolytes is limited due to the high critical temperature and pressure of water (374 °C, 217.7 atm). Ammonia, on the other hand, while not as strongly ionizing a solvent as water, has more convenient critical constants (133 °C, 112 atm) and is, in addition, less reactive toward metals than is water. Consequently, it is of interest as a dense gaseous solvent and the properties of dense gaseous ammonia electrolytes are in need of investigation. Silver nitrate was chosen for the present experiment because of its good solubility in NH_3 and because of the high reversibility of silver electrodes in silver nitrate. The following reports a measurement of the conductivity of a solution of silver nitrate in ammonia over a range of temperatures including the liquid and dense gaseous region.

The principal problem in supercritical experiments is containment of the dense gaseous solution. With ammonia, the critical temperature and pressure are sufficiently low that the solution may be contained in a glass cell under external pressurization. This procedure takes advantage of the ease of fabrication, chemical inertness, and good electrical insulating properties of glass. The size and configuration of the cell, however, are limited by the internal dimensions and configuration of the high pressure system required. In the present case, the special restrictions were such that the problem of interelectrode capacitance made the use of a DC method attractive.

It was decided to use the four-probe method,[1] in which two electrodes are used to produce a current through the cell while two others are used

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to measure the voltage drop across a known portion of the conducting electrolyte. The current electrodes may be allowed to polarize while the voltage probes should be reversible. The cell used for the measurements had a geometrically determinable cell constant and has been described in some detail elsewhere.[2] The electrodes were of 0.4 mm diameter high purity silver wire about 3 cm long coiled inside the cell. Silver nitrate was weighed and introduced into the cell through the filling capillary and the cell sealed to a vacuum system and evacuated. Ammonia was condensed over sodium and allowed to stand as a sodium-ammonia solution for a few hours before being condensed into the cell.

When a liquid, such as ammonia, is held in equilibrium with its vapor in a closed volume and heated to its critical point, the density of the liquid decreases while that of the vapor increases until they become equal at the critical point of the solution, or until either all the liquid evaporates or the liquid expands to fill the cell before the critical point is reached. For the present experiment, the cell had a volume of 30.2 cc and was loaded with 15.2 cc of NH_3 at -78 °C. In this case, the liquid fills the cell below the critical temperature. The predicted pressure and liquid volume as a function of temperature[3] are shown in Fig. 1. During the experiment, the cell was kept under an external nitrogen pressure 30 atm in excess of the predicted internal pressure.

Conductivity measurements were made at intervals of 10 °C from room temperature to 150 °C and back to room temperature. Each measurement involved determining the current-voltage relationship across the geometrically defined portion of the conductivity tube. This was done in each case for currents from 0 to 10 μa in steps of 2μa. At each current, measurements were made with the current flow in one direction and then reversed. This procedure allows any static emf between the voltage probes to be averaged out. The static emf was found to be small (0 to 20 mV) and was independent of current, changing only as the temperature was changed. It is believed that this emf was caused by differences in electrolyte concentrations between the voltage electrode compartments. In some cases, measurements were also made at 80 μa and 800 μa. It was always found that the current-voltage relationship remained linear throughout the whole range of currents used, indicating that the cell was always well behaved.

The measured equivalent conductivity is shown as a function of temperature on Fig. 2. The ascending temperature points between 98° and 127 °C were abnormally low and are not shown. This is believed to be due

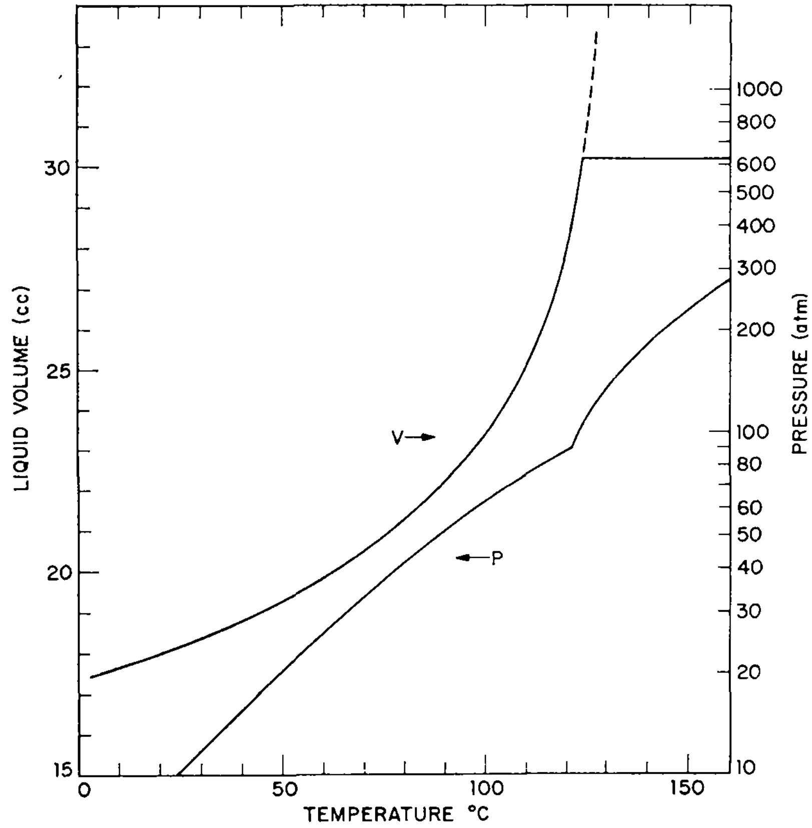

Fig. 1. Calculated Pressure and Liquid Volume of NH_3 Inside Conductivity Cell.

to formation of a bubble in the conductivity tube. Such bubbles form very easily at temperatures slightly below the critical temperature. The equivalent conductivity behaves in a manner similar to that observed (Franklin and Kraus[4]) for other salts in ammonia. The decrease in Λ with increasing temperature reflects the decrease in dissociation due to decreasing dielectric constant as the solution expands. Above the temperature where the cell fills and the density of the solution becomes constant the conductivity is seen to decrease much less rapidly with increasing temperature.

The equilibrium constant for the ionic dissociation of silver nitrate in ammonia can be calculated from the equivalent conductivity on the basis

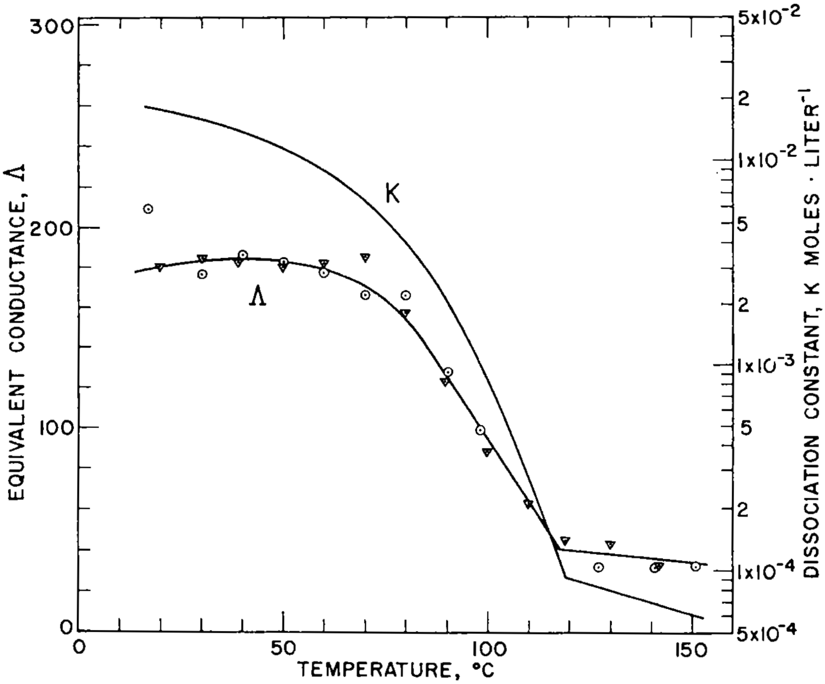

Fig. 2. Temperature Dependence of Equivalent Conductivity and Estimated Dissociation Constant for $AgNO_3$ in NH_3.

of the following assumptions. If the concentration of ions in the solution is sufficiently low that interionic forces can be neglected, then the equivalent conductivity, Λ, is related to the ionization constant, K, and the concentration, C, by the expression

$$K = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} \tag{1}$$

where Λ_0 is the equivalent conductivity at infinite dilution. The concentration C was found from the calculated liquid volumes (see Fig. 1). In the absence of additional conductivity measurements, Λ_0 was found from the known value at $-33\,°C$[5] and the known values for the viscosity of ammonia. Assuming that the solvation states of the ions are essentially independent of temperature, Λ_0 is then given by

$$\Lambda_0(T) = \frac{7.32 \times 10^5}{\eta(T)} \tag{2}$$

where $\eta(T)$ is the viscosity of NH_3 in micropoise. The viscosity was found by interpolation between the measured values of Carmichael and Sage.[6] The K curve shown on Fig. 2 was then calculated from the curve drawn through the measured values of Λ.

Neglecting vibrational and electronic excitation, the dissociation constant may be expressed theoretically in the form[7]

$$K = \frac{C_{Ag^+} \cdot C_{NO_3^-}}{C_{AgNO_3}} = AT^{n/2}\, e^{-\chi/kT}. \tag{3}$$

The value of n is equal to the total number of degrees of translational and rotational freedom for Ag^+ and NO_3^- less the number of degrees of translational and rotational freedom for $AgNO_3$. Assuming that the Ag^+ is solvated, each species has 3 degrees of rotational freedom in addition to 3 degrees of translational freedom so that $n = 6$. The dissociation energy χ, in the presence of the solvent is assumed to be of the form

$$\chi = E_0/D + x$$

where E_0 is the coulombic part of the dissociation energy in the absence of the solvent, D is the dielectric constant of the solvent, and x is the non-coulombic or electron exchange part of the dissociation energy. The non-coulombic energy is smaller than the covalent bond energy, since the latter is partially ionic.

The dielectric constant of NH_3 is known from -77.7 °C to 35 °C[8] and K for dilute solutions of $AgNO_3$ in NH_3 has been measured at -33°C[5]. Using this value ($K = 2.8 \times 10^{-3}$ moles/liter) plus our value at 25 °C, values of A and x were obtained for assumed lower and upper limits of 4 eV and 7 eV for E_0. This lead to values of $x = 0.18$ eV and $x = 0.23$ eV, respectively, indicating that the binding is more than 95% coulombic. The corresponding values for A were 8.25×10^{-3} and 50.5. Using these values in Eq. (3), the dielectric constants corresponding to the K curve on Fig. 2 were calculated and are shown on Fig. 3 along with the measured values of Grubb *et al.*[8]

It is seen that the dielectric constant is not very sensitive to the assumed value of E_0. Furthermore, the points of Grubb *et al.* are in best agreement with the curve for $E_0 = 7$ eV and suggest that an even larger value of E_0 should be assumed. It should also be noted that in the constant density region, D continues to fall with increasing temperature, presumably

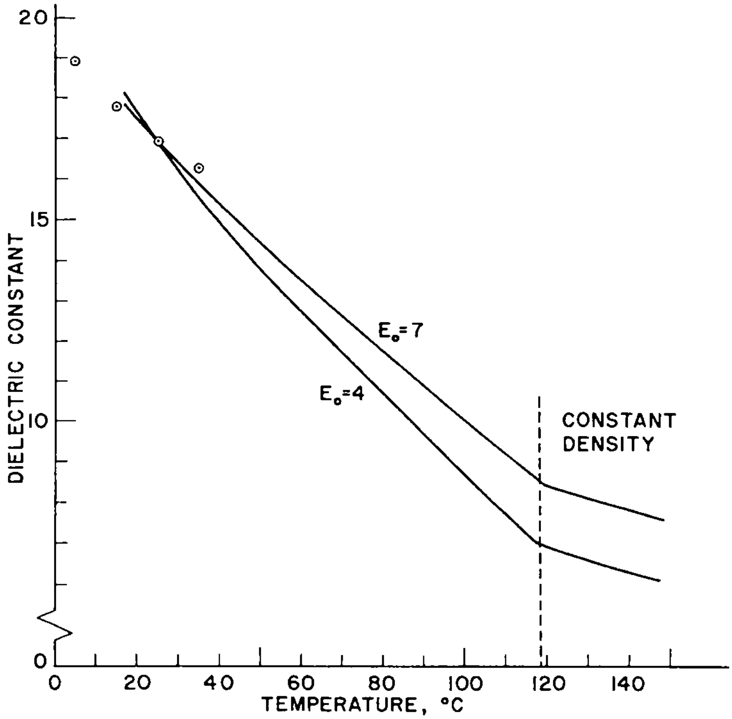

Fig. 3. Estimated Dielectric Constants for Liquid and Dense Gaseous NH_3. Circled points are measurements of Grubb, *et al.*[8]

due to further breaking of hydrogen bonds. Also, there is no apparent discontinuity at the critical temperature of NH_3, indicating that the transition from the liquid to the dense gaseous state is continuous. Finally, the measurements of Keyes *et al.*[9] on ammonia gas at densities of 1 to 4 moles/liter in the 100° to 175 °C temperature range yielded values of D between 1.3 and 1.6. In the present case, the NH_3 concentration in the constant density region is 22 moles/liter so that the values of 6 to 9 obtained for D appear reasonable.

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