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# Ionization Equilibria in Ammonia–Water Solutions to 700° and to 4000 Bars of Pressure



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The electrical conductances of 0.0100 and 0.0501 *m* aqueous ammonia solutions were measured to 800° and 4000 bars. Measurements are also reported for 0.0098 *m* NaOH solutions to 300°, together with estimates of $\Lambda_0$(NaOH) over the same temperature range. From the measurements on the ammonia solutions and estimates of the limiting equivalent conductances of ammonium hydroxide, conventional equilibrium constants for the hydrolysis of ammonia were calculated. From these values and their isothermal variation with the concentration of water, the complete constants, $K^0$, were obtained that are independent of changes in dielectric constant or in density.

## Introduction

A convenient method for studying equilibria involving ions in aqueous electrolyte solutions at supercritical temperatures and pressures is the measurement of their electrical conductances. Equilibrium constants for ionic dissociation reactions have been calculated from measurements of this kind over wide ranges of temperature and density. Recent studies in our laboratory have included those of NaCl,[2a] NaBr,[2b] and HBr.[3] This present paper gives conductance measurements on 0.01 and 0.05 *m* solutions of ammonia to 700°. Measurements were also performed at 800°, but the conductances at this temperature were essentially zero even at 4000 bars. From these measurements and with estimates for the limiting equivalent conductance of $NH_4^+ + OH^-$ at several temperatures and densities, conventional equilibrium constants for the hydrolysis of ammonia were calculated to 700°.

The present paper also includes some measurements on 0.0098 *m* NaOH solutions to 300°. From these measurements, estimates were made of the limiting equivalent conductances of NaOH as a function of density to 300°. By using these limiting conductances along with assumptions based on the previously observed behavior of other strong electrolytes at high temperatures and pressures, estimates were made of the limiting equivalent conductance of NaOH to 800°.

## Experimental Section

The equipment and procedures used for these measurements have been described previously.[2a] All conductance measurements were made with the cell containing no pressure seals in the high-temperature region. A stock solution of approximately 1 *m* ammonia was prepared from reagent grade ammonium hydroxide (J. T. Baker Chemical Co., Phillipsburg, N. J., 30% $NH_3$) and conductivity water. This stock solution was standardized, by using weight buret techniques, against potassium acid phthalate. From the stock solution, 0.0100 and 0.0501 *m* ammonia solutions were prepared and their conductances were measured to 800° and 4000 bars.

A 0.0098 *m* NaOH solution was prepared from a standard 1.0 *N* NaOH solution (Fisher Scientific Co., Fair Lawn, N. J.) and standardized in the same manner as described for the stock solution of ammonium hydroxide. Reliable measurements on the NaOH solution were obtained only at temperatures below 300°. At 400° and above, the solution concentration changed rapidly because of the reaction of NaOH with the $Al_2O_3$ insulation tube in the high-temperature region of the cell. Thorough flushing of the conductance cell was carried out at the temperature and pressure of the experiment, but even then reliable values of conductances could not be obtained above 300°.

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(2) (a) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 684 (1968); (b) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 2100 (1968).

(3) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 1545 (1968).