Ionization Constants of Aqueous Ammonia from 25 to 250°C and to 2000 Bar

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Received June 15, 1982; revised September 29, 1982

The ionization constant of ammonia has been determined by conductivity measurements and found to vary from $1.77 \times 10^{-5}$ at 25°C to $1.3 \times 10^6$ mol·kg$^{-1}$ at 250°C. The pressure effect to 2000 bar has been measured and the ratio $K_{2000}/K_1$ is 6.8 at 25°C and 11 at 250°C. The standard molar volume change for the ionization at 1 bar, $\Delta V^o_1$, changes from -28.8 at 25°C to -67 cm$^3$·mol$^{-1}$ at 250°C.

KEY WORDS: Ionization constant; ammonium hydroxide; ammonia; conductivity; volume of ionization; thermodynamics; high temperature; high pressure.

1. INTRODUCTION

Few acid or base ionization constants have been measured to moderate temperatures as a function of pressure. As part of a program for determining the behavior of solutions in natural geothermal systems, this paper reports the temperature effect to 250°C and the pressure effect to 2000 bar on the ionization of ammonia

$$\text{NH}_3\text{(aq)} + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$$

(1)

where NH$_3$(aq) refers to the total of unionized forms of dissolved ammonia.

The investigations of reaction (1) to 50°C by Bates and Pinching,$^{(1,2)}$ who used an EMF method, provide the most reliable figures for the ionization constant at low temperatures. Everett and Landsman,$^{(3)}$ who used a concentration cell with liquid junction, obtain-
ed results in close agreement with these values. Reaction (1) has also been studied by conductivity measurements of dilute solutions by Noyes at saturation water vapor pressure (s.w.v.p.) to 306°C, by Wright et al. at 2000 psi to 290°C, and by Quist and Marshall with moderate precision to 700°C and 4000 bar. Another approach has been the calorimetric investigation to 145°C by Olofsson, while more recently, Hitch and Mesmer studied the ionization reaction from 50°C to 295°C using a potentiometric technique. While the pressure effect on Reaction (1) has been studied to 3000 bar at 25°C by Buchanan and Hamann and for small increments of \( P \approx 70 \text{ bar} \) to 295°C by Hitch and Mesmer, this report presents the first precise study of the effect of pressure to 2000 bar at temperatures to 250°C.

2. EXPERIMENTAL

The construction of the conductivity cell and of the pressure vessel and details of the procedure for recording a series of measurements have already been described. Temperatures were monitored with mercury-in-glass thermometers. These were calibrated with a standard platinum resistance thermometer. Temperatures are considered accurate to better than \( \pm 0.02°C \) at 25°C and to better than \( \pm 0.1°C \) at all other points.

Conductivities for 0.001\( m \) solutions of \( \text{NaCl, NH}_4\text{Cl, NaOH and 0.066m NH}_4\text{OH} \) were measured with a Wayne-Kerr B641 conductivity bridge. The \( \text{NaCl and NH}_4\text{Cl} \) were of analytical reagent quality (B.D.H.-AnalaR) and triply distilled water was used for all solutions. The \( \text{NH}_4\text{OH} \) (Merck Suprapur) and carbonate-free \( \text{NaOH} \) solutions were stored in P.T.F.E. containers and standardized against \( \text{HCl} \) by weight titration. Dissolved \( \text{CO}_2 \) (and \( \text{O}_2 \)) in the triply distilled water was removed by bubbling with \( \text{N}_2 \) (several hours is necessary as monitored by conductivity) prior to solution preparation. Separate \( \text{NH}_4\text{Cl} \) solutions, to which has been added sufficient \( \text{NH}_4\text{OH} \) to supress hydrolysis of the ammonium ion, were prepared for measurement at each temperature. The concentration of ammonium hydroxide required to give a neutral solution at the measurement temperature was calculated from the temperature dependence of the hydrolysis constant for the ammonium ion obtained from the ionization constants of ammonia and of water tabulated by Fisher and Barnes. The effect of pressure on the hydrolysis constant was ignored.

In contrast to the behavior at lower temperatures, the conductivities of \( \text{NaOH} \) solutions at 200 and 250°C were not stable but