MODELING AMMONIA-AMMONIUM CHEMISTRIES IN THE OUTER PLANET REGIONS.

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Introduction: The recent Galileo mission to the Jovian system and the current Cassini-Huygens mission to Saturn and its satellites has stimulated considerable new thinking about the geochemical evolution of Enceladus, Titan, and other icy bodies [1-4]. Among the outer planet questions is the relevance of ammonia and ammonium salts in these cold regions, particularly for freezing point depression of subsurface aqueous solutions, which has possible astrobiological consequences [5-10]. The FREZCHEM model is designed for cold temperatures and high pressures, but did not, until now, contain ammonia and ammonium salts. The specific objectives of this study were to add ammonia-ammonium chemistries to FREZCHEM and explore the role of these chemistries on outer planet satellites.

Approach: FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to I > 20 m) using the Pitzer approach [11] for temperatures from <-70 to 25°C and the pressure range from < 1 to 1000 bars [12]. The prior version of FREZCHEM was parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-Al-H-Cl-ClO_4-Br-SO_4-NO_3-OH-HCO_3-CO_3-CO_2-O_2-CH_4-Si-H_2O system and contained 101 solid phases. In this study we added the following ammonia components: NH_3(g), NH_3(aq), and NH_3•H_2O, and the following ammonium salts: NH_4Cl(cr), NH_4ClO_4(cr), NH_4HCO_3(cr), NH_4NO_3(cr), and $(NH_4)_2SO_4$ (cr). In this preliminary updated version, we do not yet include ammonia dihydrate.

Results: Figure 1 depicts the model fit to experimental data for NH_4Cl; the eutectic temperature in this case is 257.79K (-15.36°C). Figure 2 depicts the model fit to experimental data for $(NH_4)_2SO_4$; the eutectic temperature in this case is 254.15K (-19.0°C). NH_4NO_3 has a similar eutectic (256.35K, -16.8°C) to the latter two cases (254.15-257.8K); but NH_4ClO_4 (270.41K, -2.74°C) and NH_4HCO_3 (269.25K, -3.9·C) have much higher eutectic temperatures.

Figure 3 depicts the model fit to experimental data for ammonia, which has a eutectic temperature of 173.15K (-100.0°C). At ammonia concentrations beyond 35 m (Fig. 3), the ammonia solid phases become complex and extend to a NH_3 weight of 100% [7]. But such high values are beyond the scope of FREZCHEM; similar limitations in FREZCHEM also exist for strong acids such as HCl, HNO_3, and H_2SO_4 [12].

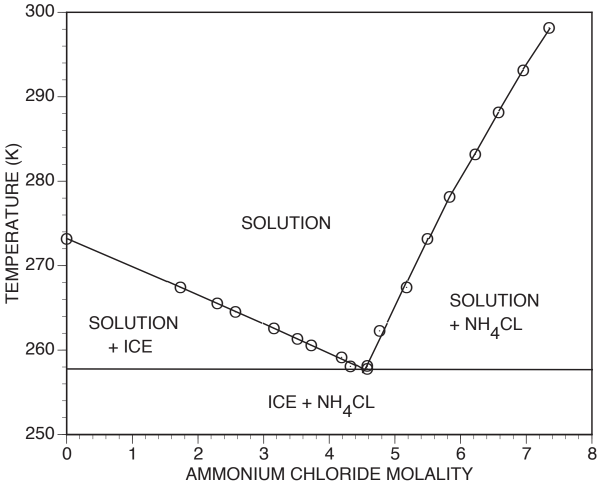

Figure 1. Equilibrium of NH_4Cl from 258 to 298 K. Symbols are experimental data; solid lines are model estimates.

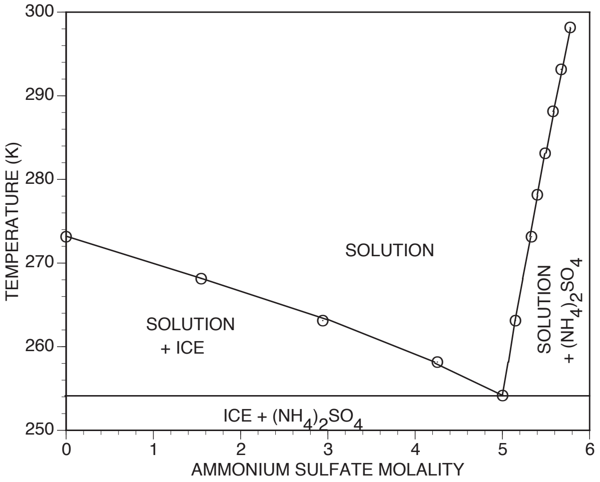

Figure 2. Equilibrium of $(NH_4)_2SO_4$ from 254 to 298 K. Symbols are experimental data; solid lines are model estimates.

Applications to Outer Planet Satellites: A simulation was arranged to demonstrate how NH_3(aq) will affect the solubility of salts in extremely cold regions (Fig. 4). In this case, we arbitrarily assigned NH_3(aq) = 10 m, NH_4Cl(aq) = 1.0 m, and $(NH_4)_2SO_4$(aq) = 1.0 m. We then lowered the temperature from 273.15 K to 170.05 K, the eutectic in this case where NH_3•H_2O starts to precipitate (Fig. 4).

The first salt to begin precipitating is $(NH_4)_2SO_4$ at 272 K. Next ice starts forming at 241 K. As tempera

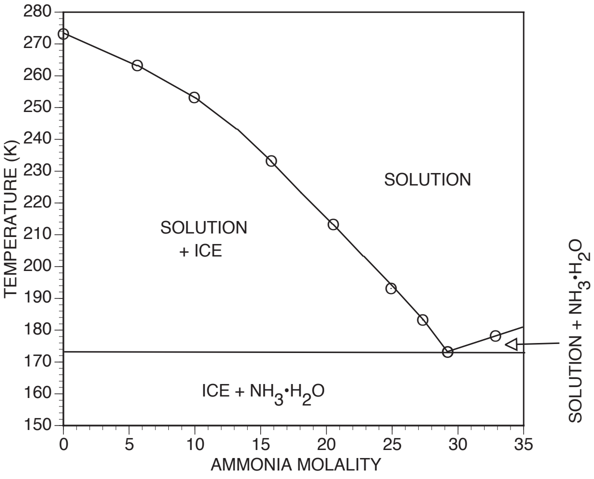

Figure 3. Equilibrium of NH_3(aq) from 173 to 273 K. Symbols are experimental data; solid lines are model estimates.

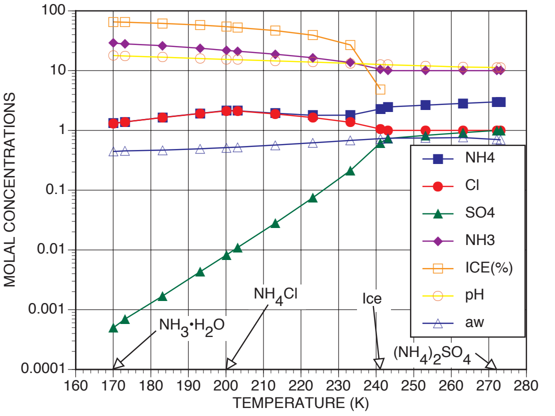

Figure 4. The molal concentrations of NH_4, Cl, SO_4, and NH_3, and the ice percent pH, and activity of water (a_w) during the freezing of NH_4Cl = 1.0 m, $(NH_4)_2SO_4$ = 1.0 m, and NH_3 = 10.0 m. The eutectic is 170.05 K. Arrows point to where solid phases start to precipitate.

ture drops further, the sulfate ion is rapidly removed from the solution as $(NH_4)_2SO_4$. NH_4Cl starts precipitating at 200 K, which is far removed from the pure NH_4Cl case that has a eutectic temperature of 258 K (Fig 1). Despite the fact that NH_4Cl starts precipitating at 200 K, the NH_4 and Cl concentrations remain above the initial value of 1.0 m (Fig. 4) throughout this process until the eutectic temperature is reached at 170.05K.

We also estimated the activity of water (a_w) and pH as indicators for life in these environments. pH was estimated from the equations:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \qquad (K1)$$

$$H_2O \Leftrightarrow H^+ + OH^- \qquad (K2)$$

which were combined to yield:

$$\left(H^+\right) = \frac{\left(NH_4^+\right)(K2)}{\left(NH_3\right)(K1)}$$

with pH = -log(H^+). In this case, pH varied from 11.24 at 273 K to 17.87 at the eutectic, and a_w varied from 0.696 at 273 K to a maximum of 0.759 at 263 K, then dropping to a minimum of 0.443 at the eutectic. Bacteria can only live at pH values < 12 [13], and the minimum a_w for known life is 0.61 [14]. Such a system as given in Fig. 4 would not be conducive for life.

We also ran a simulation at a lower NH_3 = 0.1 m. In this case, the pH varied from 9.09 at 273 K to 17.87 at the eutectic, and a_w varied from 0.934 at 273 K to a minimum of 0.443 at the eutectic. At higher temperatures, this low NH_3 system was better for life, but by the time the system reached 233 K, the pH was > 12, and by the time the system reached 213 K, the a_w was < 0.60. The amount of water just before the eutectic in this case was only 3.46 g (initial water = 1000 g), which would lead to brine pockets at low temperatures. In Fig. 4, there were 346 g of water near the eutectic, which could lead to brine oceans.

These examples demonstrate how the presence of NH_3 can lead to high solution concentrations at very low temperatures in subsurface oceans on outer planet satellites. There is evidence today that NH_3 may be present as ammonia-ice on Charon [15], models predict ammonia-water in the interior of Titan [16], and NH_3(g) is present as part of the Enceladus plume [17]. Such examples of NH_3 in the outer planets could be beyond the limits for known terrestrial life if NH_3-H_2O conditions prevail, although we are unable to exclude more exotic biochemistry [18].

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