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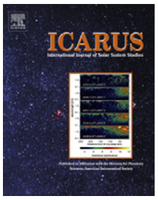

Modeling ammonia–ammonium aqueous chemistries in the Solar System's icy bodies

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ABSTRACT

The properties of ammonia and ammonium compounds in cold, subsurface brines are important for understanding the behavior of outer planet icy moons. The FREZCHEM model of aqueous chemistry was primarily designed for cold temperatures and high pressures, but does not contain ammonia and ammonium compounds. We added ammonia and ammonium compounds to FREZCHEM, and explored the role of these chemistries on Enceladus and Titan, mindful of their astrobiological implications. For the new FREZCHEM version, Pitzer parameters, volumetric parameters, and equilibrium constants for the $Na–K–NH_4–Mg–Ca–Fe(II)–Fe(III)–Al–H–Cl–ClO_4–Br–SO_4–NO_3–OH–HCO_3–CO_3–CO_2–O_2–CH_4–NH_3–Si–H_2O$ system were developed for ammonia and ammonium compounds that cover the temperature range of 173–298 K and the pressure range of 1–1000 bars. Ammonia solubility was extended to 173 K, where $NH_3{\cdot}2H_2O$ and $NH_3{\cdot}H_2O$ precipitate, which is the lowest temperature in existing FREZCHEM versions. A subsurface "ocean" on Enceladus was simulated at 253 K with gas pressures, 1–10 bars, and with Na^+, Cl^-, HCO_3^-, $CO_2(g)$, $CH_4(g)$, and $NH_3(aq)$ that led to precipitation of ice, $NaHCO_3$, and gas hydrates ($CO_2{\cdot}6H_2O$ and $CH_4{\cdot}6H_2O$). The pH on Enceladus (Fig. 10) ranged from 5.74 to 6.76, and water activity, a_w, ranged from 0.80 to 0.82, which are relatively favorable for life. A subsurface "ocean" on Titan was simulated with NH_4^+, Cl^-, SO_4^{2-}, $CH_4(g)$, and $NH_3(aq)$ over the temperature range of 173–273 K that led to precipitation of $(NH_4)_2SO_4$, ice, $CH_4{\cdot}6H_2O$, and NH_4Cl. The CH_4 clathrate should float above the brine and is buoyant with respect to H_2O ice, so has the potential to be a source of CH_4 to replenish what has been photochemically destroyed in Titan's atmosphere over time. The pH in the Titan simulation (Fig. 11) ranged from 11.24 to 18.03 (latter may not be accurate), and a_w ranged from 0.28 to 0.72, which are relatively unfavorable for life as we know it. The Titan simulations, with total pressures of 10, 250, and 1000 bars, led to similar depositions, except for ice that failed to form under 1000 bars of pressure. In the past, there have been arguments for why Titan, given an early environment similar to Earth, could be a highly favorable body in our Solar System for life. But if Titan oceans are strongly alkaline with high pH whereas Enceladus' oceans have moderate pH, as simulated, the latter would seem a better environment for life as we know it. But bear in mind, caution must be exercised in quantifying the ammonia/ammonium cases because of the complexities and limitations of these chemistries in the FREZCHEM model.

1. Introduction

The completed *Galileo* mission to the Jupiter system and the continuing *Cassini–Huygens* mission to Saturn and its satellites, and the anticipation of the *New Horizons* flyby of the Pluto system and the *Dawn* mission that will orbit Ceres have stimulated considerable new thinking about the geochemical evolution of Europa, Enceladus, Titan, Pluto, outer main belt asteroids, and other icy bodies (Kargel et al., 2000; Baker et al., 2005; Cruikshank et al., 2005; Brown et al., 2006; Hussmann et al., 2006; Kieffer et al., 2006; Spencer et al., 2006; Waite et al., 2006, 2009, 2011; Yokano et al., 2006; Fortes, 2007, 2012; Fortes et al., 2007; Manga and Wang, 2007; Matson et al., 2007; Nimmo et al., 2007; Parkinson et al., 2007; Spencer and Grinspoon, 2007; Zolotov, 2007; Grindrod et al., 2008; Kieffer and Jakosky, 2008; Lorenz, 2008; Lorenz et al., 2008; McKinnon et al., 2008; Sotin and Tobie, 2008; Cooper et al., 2009; Postberg et al., 2009, 2011; Zolotov and Kargel, 2009; Sohl et al., 2010; Zolotov et al., 2011). Among the questions concerning the icy moons of the outer planets is the relevance of ammonia and ammonium compounds. These questions date back for decades

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and remain incompletely answered by observation (Lewis, 1972; Croft et al., 1988; Kargel et al., 1991; Kargel, 1992, 1998; Hogenboom et al., 1997; Brown and Calvin, 2000; Young, 2000; Leliwa-Kopystynski et al., 2002; Mousis et al., 2002). Whereas ammonia is widely considered, theoretically, to be broadly distributed and abundant in the outer Solar System, nondetections are the rule; definitive or probable observations of extraterrestrial ammonia and/or ammonium ion in our Solar System are rarer; these substances occur in the atmospheres of the gas giant planets, the plumes of Enceladus (Waite et al., 2009, 2011; Pizzarello et al., 2011; Zolotov et al., 2011), on large Kuiper Belt Objects such as Quaoar (Jewitt and Luu, 2004) and Orcus, and on Pluto's largest moon, Charon (Cook et al., 2007). Intense theoretical interest remains in possible ammonia–water volcanism on Titan and other icy satellites. Interest in possible sequestration of ammonia in ammonium solids and reactive destruction of ammonia (Kargel, 1992) has renewed timeliness to help explain why ammonia is rarely observed despite decades of searching for it. Recent investigations on the nature of internal fluids on icy moons has been stimulated by the *Cassini–Huygens* Mission (Baker et al., 2005; Tobie et al., 2005; Hussmann et al., 2006; Waite et al., 2006; Fortes et al., 2007; Spencer and Grinspoon, 2007; Smythe et al., 2009; Waite et al., 2009, 2011; Zolotov et al., 2011) and is pertinent to the upcoming Pluto/Charon/Kuiper Belt mission of *New Horizons*. On Earth, aqueous ammonia and ammonium salts are important in biology; the chemistries dealt with in this work may also have astrobiological consequences, which we briefly explore.

Ammonia and ammonium have not been found in the Solar System with the high abundances predicted theoretically, but after decades of fruitless searching, in the past decade especially, both ammonia and ammonium have been turning up in meteorite analyses and reflectance spectroscopic studies. Many comets emit 0.1–0.3% NH_3 and 3–10% CO_2 relative to H_2O. Carbonaceous chondrites generally contain ammonium at levels a few ppm to several tens of ppm. Direct detection of ammonia released by chemical treatment of the CM2 Murchison carbonaceous chondrite meteorite was thought to be due largely to release from ammonium salts as well as amines, amino acids and other compounds (Pizzarello et al., 1994); total NH_4^+ is ~20 ppm by mass. These compounds in carbonaceous chondrites all probably trace their origins to ammonia-based chemistry, including Strecker-type organic synthesis of ammonium cyanide from ammonia and hydrogen cyanide (Callahan et al., 2011), both comet-type volatiles. CR chondrites also are known to contain a similar suite of ammonia-related compounds, and additionally free ammonia was extracted (Pizzarello et al., 2011), though we suspect this may have been a break-down equilibrium product of decomposition of ammonium salts, some of which have a high ammonia vapor pressure. However, as mentioned, these all probably trace an origin back to ammonia chemistry.

Ammonia and derivatives such as amino acids are usually considered in the context of extant life, but biogenesis and prebiotic chemistry also emphasizes the key roles of these materials (e.g., Santana et al., 2010). Ammonium ion can be produced abiotically from other nitrogen compounds using a meteoritic nickel-rich metal catalyst (Smirnov et al., 2008). Ammonium thiocyanate, other ammonium compounds, and amino acids can be produced by electric discharges in CO_2–NH_3-bearing gas mixtures representing a popular model of Earth's primordial atmosphere.

The FREZCHEM model was primarily designed for cold temperatures and high pressures (Marion and Kargel, 2008), but until now did not contain ammonia and ammonium compounds. The specific objectives of this study were to (1) add ammonia–ammonium compounds to FREZCHEM, and (2) explore the role of these chemistries on outer planet satellites, especially with respect to low temperatures, high pressures, and the possibility of astrobiology. We note that there is also potential relevance of ammonia chemistry, not explored here, to (1) aqueous chemistry on Mars and large icy Main Belt asteroids, and to the origins of (2) the nitrogen-rich atmospheres of Earth and Titan, and of the solid nitrogen cryospheres and tenuous atmospheres of Triton, Pluto and some large Kuiper Belt Objects, such as Eris. And finally, the purpose of this paper is not to construct structural or thermal models of outer Solar System bodies, but to quantify the phase equilibria that should occur under relevant conditions and for a range of plausible constituents.

2. Methods and materials

2.1. FREZCHEM model

FREZCHEM is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions (to ionic strengths = 20 molal) using the Pitzer approach (Pitzer, 1991, 1995) for the temperature range from 173 to 298 K (CHEMCHAU version has temperature range from 273 to 373 K) and the pressure range from 1 to 1000 bars (Marion and Farren, 1999; Marion, 2001, 2002; Marion et al., 2003, 2005, 2006, 2008, 2009a, 2009b, 2010a, 2010b, 2011; Marion and Kargel, 2008). Pressure beyond 1 bar was first added in Marion et al. (2005). The new version of the model, which includes ammonia and ammonium compounds, is parameterized for the Na–K–NH_4–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–NH_3–Si–H_2O system and includes 108 solid phases including ice, 16 chloride minerals, 36 sulfate minerals, 16 carbonate minerals, five solid-phase acids, four nitrate minerals, seven perchlorates, six acid-salts, five iron oxide/hydroxides, four aluminum hydroxides, two silica minerals, two ammonia minerals, two gas hydrates, and two bromide sinks (see above references for these model parameters, especially Marion and Kargel, 2008).

2.2. Pitzer approach

In the Pitzer approach, the activity coefficients (γ) as a function of temperature at 1.01 bar pressure for cations (M), anions (X), and neutral aqueous species (N), such as CO_2(aq) or CH_4(aq), are given by

$$\begin{aligned}\ln(\gamma_M) = {} & z_M^2 F + \sum m_a(2B_{Ma} + ZC_{Ma}) + \sum m_c\Big(2\Phi_{MC} + \sum m_a \Psi_{Mca}\Big) \\ & + \sum\sum m_a m_{a'} \Psi_{maa'} + z_M \sum\sum m_c m_a C_{ca} + 2\sum m_n \lambda_{nM} \\ & + \sum\sum m_n m_a \zeta_{nMa} \end{aligned} \tag{1}$$

$$\begin{aligned}\ln(\gamma_X) = {} & z_X^2 F + \sum m_c(2B_{cX} + ZC_{cX}) + \sum m_a\Big(2\Phi_{Xa} \\ & + \sum m_c \Psi_{cXa}\Big) + \sum\sum m_c m_{c'} \Psi_{maa'X} \\ & + |z_X| \sum\sum m_c m_a C_{ca} + 2\sum m_n \lambda_{nX} \\ & + \sum\sum m_n m_c \zeta_{ncX} \end{aligned} \tag{2}$$

$$\ln(\gamma_N) = 2\sum m_a \lambda_{Na} + \sum\sum m_c m_a \zeta_{Nca} + 2\sum m_n \lambda_{Nn} \tag{3}$$

where B, C, Φ, Ψ, λ and ζ are Pitzer-equation interaction parameters, m_i is the molal concentration, and F and Z are equation functions. In these equations, the Pitzer interaction parameters and the F function are temperature dependent. The subscripts c, a, and n refer to cations, anions, and neutral species, respectively. The coefficients c' and a' refer to cations and anions, respectively, that differ from c and a. The activity of water (a_w) at 1.01 bar pressure is given by

$$a_w = \exp\left(\frac{-\phi \sum m_i}{55.50844}\right) \tag{4}$$