Equation of state of ammonia

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**Abstract.** Ammonia and water are critical components of extraterrestrial bodies, determining the density and physical properties of the Outer Planets, their moons, and of extrasolar planets. Ammonia is unusual in having a high heat capacity relative to other molecular species. Equations of state (EOS) are presented for ammonia and for mixtures of ammonia and water. Their properties are discussed in terms of chemical compositions that evolve as pressure and temperature are varied. The NH₄OH hydrate of ammonia is known to exist as a separate molecular species at pressures above about 5 GPa, and an effort was made to include reaction between NH₃ and H₂O in the mixture EOS. The EOS are suitable for calculating structures of icy planets and exoplanets, and of impacts. mass-radius relations which bound the possible interpretations of composition and structure for extraterrestrial bodies of unknown composition, such as exoplanets.

1. **Introduction**

An accurate EOS for ammonia is important to clarify astrophysical measurements and to the understanding of properties of planets and their moons; gas giants Saturn and Jupiter, moons Enceladus, Titan, Ganymede, and Calypso, and ice giants Neptune and Uranus. Because ammonia has a distinctive absorption around 23.79 GHz, its presence is readily detectable using radar, in either ground-based observations or higher resolution observations made by the Cassini-Huygens probe.

The cores of Saturn and Jupiter likely contain ammonia, and ammonia composes observable cloud decks in both planets. Measurements from the Cassini-Huygens probe confirm that Saturn’s top cloud deck is composed of ammonia clouds [1] with a brightness temperature between 140 and 190 K. Below Jupiter’s tropopause are ammonia clouds, with temperatures between 200 and 800 K and pressures between 0.6 and 0.9 bar, as well as NH₄SH and H₂O clouds at lower altitudes and pressures between 1 and 7 bar.

Measurements of ammonia in Saturn’s Great Storm on 2010 [2] indicate ammonia ices coming to the top of the atmosphere and condensing, indicating the importance of the heat capacity and EOS of ammonia in describing the atmospheric dynamics of Saturn. Moons of Saturn and Jupiter exhibit cryovolcanism, suggesting liquid under the surface. Water maintained in the liquid phase by admixed ammonia is the most likely convective fluid. Detection of nitrogen and ammonia in the atmosphere of Titan [3] suggests that not only Titan, but also Enceladus, Callisto, and Ganymede may contain subsurface ammonia, which, along with water, influences the observable surface geology.

Ice Giants Uranus and Neptune have mantles comprising ammonia, water and methane, at low temperatures. The mantle comprises about 92% of the mass of Uranus and a similar fraction of
Neptune, making the EOS of ammonia a critical tool in understanding the composition and behaviour of these outer planets.

2. Ammonia Properties, Hugoniots, and EOS Surfaces
Ammonia has a trigonal pyramidal symmetry, with a sterically exposed lone pair at the apex of the triangle, making ammonia a strongly hydrogen bonding system, both in its pure form and in mixtures with other compounds, particularly polar molecules such as water. Ammonia is subject to molecular inversion by tunnelling of the hydrogen atoms, leading to a perturbation in the vibrational spectrum, a doubling of each line. The inversion leads to an absorption at and slightly below 23.79 GHz, which makes ammonia readily observable at microwave frequencies [4].

Ammonia has a high specific heat capacity for a molecular substance, which is inconsistent with the simplicity of the isolated molecular structure. Hindered rotation within extensive hydrogen-bonded networks can contribute to a high heat capacity at high densities or low temperatures, and high heat capacities are seen for other highly hydrogen-bonding molecules such as methanol. Additional vibrational modes introduced by inversion contribute to the heat capacity of ammonia.

An EOS was constructed using the Cheetah thermochemical code, version 6.0, employing the exp-6 potential library [5]. Cheetah is restricted to calculations based on isolated molecular species, and does not recognize energetic contributions from hydrogen bonding. The Cheetah EOS was intended for comparison with an ammonia EOS determined using QMD [6]. The complete potentials used in the QMD do allow hydrogen bonding to contribute to the EOS. The Cheetah EOS compared well with the QMD EOS, except at low temperature, and at high temperature where ionization requires terms not included in the Cheetah potentials. The EOS was constructed in the form of a SESAME-type table [7], i.e. rectangular tabulations of pressure and specific internal energy as functions of the mass density and temperature. The EOS was then used to calculate shock Hugoniots, isentropes, and mass-radius relations for self-gravitating bodies.

The Cheetah EOS was compared with measured states on the shock Hugoniot of liquid ammonia, and with a “universal” equation of state for liquids [8] (figures 1 and 2). The Cheetah EOS slightly under-predicted the initial sound speed slightly, and appeared to be slightly soft compared to measurements reported in Marsh [9]. However, the Cheetah Hugoniot lay very close to the measurements reported by Mitchell and Nellis [10] at higher pressures, suggesting that the Cheetah EOS is probably reasonable throughout the measured range. The WCS universal EOS was significantly stiffer than the measured Hugoniot and that from the Cheetah EOS.

![Figure 1. Ammonia Hugoniots in Us and up compared with experimental data.](image-url)
Figure 2. Ammonia Hugoniot in P and ρ compared with experimental data. Experimental isotherm from diamond anvil cell measurements (DAC) [10].

The EOS surface is presented in figure 3. At 1 atm and 203 K, the density predicted by Cheetah was 0.6794 g/cm³, significantly less than the observed value of 0.725 g/cm³.

Figure 3. Ammonia Equation of State surface, (p, e, s, c²)(ρ, T).

The specific heat capacity predicted by Cheetah is shown in figure 4. The decrease in heat capacity at about 1000 K is associated with the dissociation of the ammonia molecule to hydrogen and nitrogen, consistent with results of other calculations [12]. When compressed to a density around 1 g/cm³ or greater, dissociation is suppressed. The increases in heat capacity just below 10,000 K are associated with the dissociation of molecular hydrogen and, at higher temperature, the dissociation of molecular nitrogen. The plateau visible between 2000 and 6000 K is consistent with results of QMD calculations, which also report atomic and ionic species above 6000K [13]. QMD calculations suggest dissociation in the compressed phase at about 2.2 g/cm³ and 220 GPa, [13] consistent with our observation of a cusp emerging at 2.2 G g/cm³ and 250 GPa.
The Grüneisen parameter is not constant, as shown in figure 5. In particular, it varies with temperature as well as density, thus the thermal EOS of ammonia cannot be represented accurately with Grüneisen EOS. Dissociation of ammonia to hydrogen and nitrogen leads to a slight increase above 1000 K, as do dissociations of molecular hydrogen and nitrogen to atoms above 10,000 K. A distinct increase in the Grüneisen parameter at densities above 1 g/cm³, particularly at high temperature, arises from the presence of molecular ammonia at these relatively high compressions.

![Figure 4. Ammonia specific heat capacity.](image)

![Figure 5. Ammonia Grüneisien parameter.](image)

3. Mixtures of ammonia and water
The EOS of mixtures of ammonia and water were investigated to explore the sensitivity to chemistry and free energies in this more complicated system. Cheetah was used to construct a tabular EOS for a 1:1 molar mixture of ammonia and water. The major features of the EOS were found to be very similar to those of pure ammonia. The location of oscillations in the heat capacity and Grüneisen parameter was dominated by the behaviour of ammonia. The main effects of water were the increased amount of atomic hydrogen at high temperatures, changes in the Hugoniot from the contribution of water at densities above 1 g/cm³, and the exact values of parameters at each point on the EOS. The addition of water resulted in a surprisingly small perturbation to the EOS [14].
Experimental observation indicates that mixtures of water and ammonia can take a number of distinct structures at low temperatures, including hydrogen bonding networks. In the presence of organics, mixtures can form complex ordered networks or clathrate hydrates [15]. Clathrate hydrates in particular are likely to play a role in cryovolcanism and geology of moons and ice giants [3]. Neither Cheetah nor QMD calculations will address these complex structures within reasonable computational time. However, the EOS presented here provide a useful survey of properties of ammonia and ammonia water mixtures over a large portion of the relevant range of thermodynamic parameters.

4. Conclusions
The ammonia EOS was predicted fairly accurately by the chemical equilibrium code Cheetah, despite the omission of some contributions to the free energy, such as hydrogen bonding. Cheetah calculations provide a thermodynamically-complete EOS that is adequate for many applications in planetary structures and impacts. Cheetah calculations can interpolate between more sophisticated calculations such as QMD, and can be used where QMD calculations are impractical, such as at low densities.

Over the range of states considered, the heat capacity and Grüneisen parameter were far from constant or simply-varying. Analytical EOS models should thus be used with caution, as they would not be accurate over wide ranges of thermodynamic states.

According to the Cheetah calculations, the admixture of water into pure ammonia has a surprisingly small effect on the general behaviour of the EOS, although the calculation omitted detailed geometrical configurations involving water and ammonia. The simplicity and similarity to ammonia of the mixed ammonia-water EOS indicates that planetary structures calculated using simple mixture models [14] should be relevant and useful, even when the exact proportions or chemistry are not precisely known.

References
[1] Fletcher L N, Baines K H, Momary T W, Showman A P, Irwin P G J, Orton G S, Roos-Serote and Merlet C 2011 Icarus 214 510–33
[2] Sromovsky L A, Baines K H and Fry P M 2013 Icarus 226 402–18
[3] Lopes R M C, Kirk R L, Mitchell K L, LeGall A, Barnes J W, Hayes A, Kargel J, Wye L, Radebaugh J, Stefan E R, Janssen M A, Neish C D, Wall S D, Wood C A, Lunine J I and Malask M 2013 J. Geophys. Res.: Planet 118 1–20
[4] Devaraj K, Steffes P G and Karpowicz B M 2011 Icarus 212 224–35
[5] Bastea S, Fried L E, Glaesemann K R, Howard W M, Kuo I W, Souers P C and Vitello P A 2010 Cheetah 6.0 User’s Manual Lawrence Livermore National Laboratory Tech. Rep. LLNL-SM-416166
[6] Hamel S 2013 private communication
[7] Lyon S P and Johnson J D 1992 SESAME database: The Los Alamos National Laboratory Equation of State Database Los Alamos National Laboratory Tech. Rep. LA-UR-92-3407
[8] Woolfolk RW, Cowperthwaite M and Shaw R 1973 Thermochim. Acta 5 409–14
[9] Marsh S P 1980 LASL Shock Hugoniot Data (Berkeley: University of California Press) p 548
[10] Mitchell A C and Nellis W J 1982 J. Chem. Phys. 76 6273
[11] Datchi F, Ninet S, Gauthier M, Saitta A M, Canny B, and Decremps F 2006 Phys. Rev. B 73 174111
[12] Ojwang J G O, McWilliams R S, Ke X and Gonchrov A F 1999 J. Chem. Phys. 137 064507
[13] Li D, Zhang P and Yan J 2013 J. Chem. Phys. 139 134505
[14] Correa A, Swift D C, Mulford R N and Hamel S 2013 Planetary structure and impact calculations using new mixture equation of state Submitted to these proceedings
[15] Shina K, Kumar R, Konstantin A, Udachina K A, Alavia S and Ripmeester J A 2012 P. Natl. Acad. Sci. USA 109 14785–90