

# Decomposition of supercritical ammonia and modeling of supercritical ammonia–nitrogen–hydrogen solutions with applicability toward ammonothermal conditions



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## ARTICLE INFO

### Article history:

Received 16 June 2015

Received in revised form 25 July 2015

Accepted 26 July 2015

Available online 17 August 2015

### Keywords:

Supercritical ammonia

Ammonia decomposition

Ammonothermal

Ammonia–nitrogen–hydrogen solutions

Beattie–Bridgeman

Equation of state (EOS)

## ABSTRACT

Ammonothermal growth of nitrides occurs at temperatures in excess of 800 K and pressures greater than 150 MPa. For this region, no experimentally verified equation of state (EOS) exists for ammonia, nor is there any accurate description available for the equilibrium constant of the ammonia decomposition reaction for pressures in excess of 100 MPa. To fill this void, experimental  $P$ - $T$  data was collected for pure ammonia at  $T > 700$  K and compared to extrapolated data from the reference EOS for ammonia. For the extrapolated region, the reference EOS provided excellent agreement to within error of the collected experimental data. A simplified EOS based on the Beattie–Bridgeman (BB) EOS was derived and fit to calculated and, for ammonia, extrapolated reference EOS data for ammonia, hydrogen, and nitrogen ( $T < 1000$  K,  $P < 300$  MPa). By applying mixing rules with separated contributions for polar and non-polar interactions, an EOS was derived for  $\text{NH}_3$ - $\text{N}_2$ - $\text{H}_2$  mixtures. With these expressions, an accurate description for the equilibrium constant for the ammonia decomposition reaction as a function of pressure and temperature was derived and verified against experimental data determined for total system pressures of 92, 151 and 210 MPa at  $T \sim 810$  K. Coupling of the EOSs with the equilibrium constant permitted accurate modeling of a sealed autoclave filled with pure ammonia, after incorporating corrections for the expansion of the internal free volume due to thermal expansion and elastic strain response of the autoclave walls due to internal pressure buildup. Calculated total system pressure and equilibrium ammonia density at various temperatures and initial ammonia fill densities are in very good to excellent agreement with experimental data. This paper thus provides a simple EOS for ammonia, hydrogen, nitrogen and  $\text{NH}_3$ - $\text{N}_2$ - $\text{H}_2$  mixtures accurate to within approximately 1–2% in pressure for temperatures greater than 700 K. The equilibrium constant for the ammonia decomposition reaction includes non-ideal mixing contributions from the second virial coefficient with a resulting accuracy in the equilibrium mole fraction of ammonia of approximately 2% for  $T < 850$  K.

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## 1. Introduction

Gallium nitride (GaN) is a wide band gap semiconductor material with wide spread applications in electronics and optoelectronics. Advances in light emitting diodes (LEDs) and laser diodes (LDs) have led to longer wavelength devices operating at higher optical powers in the visible spectrum [1–3]. The wide band gap material is increasingly used for power electronic devices due to its higher operating temperature regime compared to existing Si technology and due to the superior properties resulting from the two-dimensional electron gas (2DEG) that forms at the

AlGaN/GaN interface. Most industrial technology is based on the use of heteroepitaxial substrates, sapphire or SiC, with resulting GaN epitaxial films oriented along the polar  $\langle 0001 \rangle$  axis. Wide spread availability of large area bulk GaN substrates with arbitrary orientations would enable novel devices and offer additional methods to improve performance and alloying capabilities with other Group III elements [4].

Growth of bulk GaN is challenging as it cannot be easily grown from a molten solution given the high nitrogen over pressure needed to prevent decomposition. Promising growth techniques that overcome this challenge include hydride vapor phase epitaxy (HVPE) [5], Na-flux based methods [6], and the ammonothermal method [7–11].

The ammonothermal method is similar to the hydrothermal method and uses a supercritical ammonia and mineralizer (alkali metal or halogen) solution at elevated temperatures ( $>700$  K) and

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pressures (>100 MPa) to dissolve GaN. Typical hot-walled autoclaves (<300 MPa, <925 K) require 20–25 mol/l of ammonia to achieve desired dissolved GaN concentrations and appreciable growth rates. To improve our understanding of the growth environment, an accurate description of the equilibrium concentrations of ammonia, hydrogen, and nitrogen during growth is needed, especially since experimental evidence suggests that the solubility of GaN is inherently linked to the concentration of ammonia (NH<sub>3</sub>) and resulting derived compounds such as amides (NH<sub>2</sub><sup>-</sup>) [12] or ammonium (NH<sub>4</sub><sup>+</sup>) [13] present during growth.

While some information regarding chemical and physical properties of ammonothermal systems can be extracted from growth runs [14–16], in situ investigations of the fluid properties [17,18] and modeling of the heat and fluid flow within the system [19–21], currently the understanding is incomplete for the dependence of the equilibrium constant for ammonia decomposition on temperature and pressure at typical ammonothermal growth conditions. Furthermore, an experimentally verified equation of state (EOS) is not available for ammonia at temperatures greater than 700 K. The high temperature EOS is necessary to derive many thermodynamic properties.

This paper develops a practical EOS for ammonia, hydrogen, nitrogen, and ammonia–hydrogen–nitrogen mixtures applicable to typical ammonothermal conditions and derives an accurate thermodynamic expression for the equilibrium constant of the ammonia decomposition reaction. This will be done by extrapolating the existing reference EOS for ammonia beyond 700 K and comparing it to experimental data. The reference EOSs for ammonia, nitrogen and hydrogen will then be fit to a simpler, more practical EOS based on the Beattie–Bridgeman (BB) EOS. Using the existing thermodynamic framework for the BB EOS, an EOS for the H<sub>2</sub>–N<sub>2</sub>–NH<sub>3</sub> fluid mixture will be derived and compared to experiment. With these four EOSs, a thermodynamic expression for the equilibrium constant for the ammonia decomposition reaction, and hence equilibrium concentration of ammonia, will be derived and compared to experimental data. Lastly, by coupling the EOS for NH<sub>3</sub>–H<sub>2</sub>–N<sub>2</sub> mixtures and the equilibrium constant, the changes in total system pressure and corresponding dependence of the equilibrium mole fractions of NH<sub>3</sub>, H<sub>2</sub>, and N<sub>2</sub>, are determined for a sealed autoclave and compared to experimental data.

## 2. Theoretical background

### 2.1. Equation of states

#### 2.1.1. Pure gases

An EOS provides a relationship between state variables of a system and can be used to determine various thermodynamic properties of a system. Various EOSs have been developed over the years, with the most accurate ones being empirical multiparameter equation of states (MEOS), which typically become the reference for the properties of that substance. MEOS typically represent the reduced Helmholtz free energy  $\alpha$  of the substance as a sum of ideal and residual terms, both of which are explicit in reduced temperature  $\tau = T_c/T$  and density  $\delta = \rho/\rho_c$ , where  $c$  denotes its critical value,  $T$  absolute temperature and  $\rho$  its density. A summary of the critical properties for ammonia, hydrogen and nitrogen is provided in Table 1.

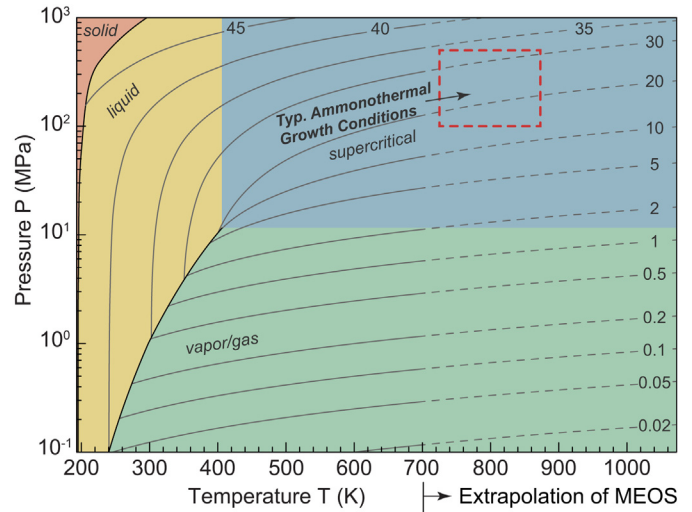
$$\alpha(\tau, \delta) := \frac{a(T, \rho)}{RT} = \alpha^0(\tau, \delta) + \alpha^r(\tau, \delta) \quad (1)$$

Ideal and real contribution is parametrized and fits to experimental data for the specific fluid. Derived thermodynamic properties

**Table 1**

Critical temperature ( $T_c$ ), pressure ( $P_c$ ) and density ( $\rho_c$ ) for ammonia (NH<sub>3</sub>), hydrogen (H<sub>2</sub>) and nitrogen (N<sub>2</sub>), respectively.

Fluid	$T_c$ (K)	$P_c$ (MPa)	$\rho_c$ (mol/l)	Ref.
NH <sub>3</sub>	405.37	11.345	13.75	[22]
H <sub>2</sub>	33.145	1.2964	15.508	[24]
N <sub>2</sub>	126.192	3.3958	11.1839	[23]



**Fig. 1.**  $P$ - $T$  phase diagram of pure ammonia (NH<sub>3</sub>) with contour lines of density  $\rho$  (mol/l) and superimposed phases present at equilibrium. Calculated and extrapolated beyond 700 K using the reference multiparameter equation of state (MEOS) as provided by the National Institute of Standards and Technology (NIST) [25–29].

can be calculated from the Helmholtz free energy, including pressure:

$$P(\tau, \delta) = \rho RT \left[ 1 + \delta \left( \frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} \right] \quad (2)$$

The current reference properties for N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> as provided by the National Institute of Standards and Technology (NIST) are derived from the MEOS for N<sub>2</sub> (applicable for temperatures between 63.151 and 1000 K and pressures up to 2200 MPa) [23], H<sub>2</sub> (applicable up to 1000 K and 2000 MPa) [24] and NH<sub>3</sub> (applicable up to 700 K and 1000 MPa) [25]. Using the reference MEOS for NH<sub>3</sub>, a  $P$ - $\rho$ - $T$  phase diagram was calculated and extrapolated beyond the experimentally verified 700 K temperature. Fig. 1 shows this  $P$ - $T$  phase diagram for ammonia with overlaid contours of NH<sub>3</sub> density and applicable stable phase for the given  $P$ - $\rho$ - $T$  condition.

While highly accurate, MEOSs typically have a large number of terms (>20) with varying exponential forms making it tedious and cumbersome to use in thermodynamic derivations and applying toward mixture of fluids, suggesting the use of a simpler, uniform EOS. For the purpose of this paper, it is of interest to determine the feasibility of using a modified Beattie–Bridgeman (BB) EOS given its ability to accurately determine the equilibrium constant of ammonia at elevated pressures (<100 MPa) and temperatures (<775 K) [30]:

$$P = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2} \quad (3)$$

where  $R$  is the universal gas constant,  $P$  is pressure,  $T$  is absolute temperature, and  $v$  the molar volume calculated by dividing the volume  $V$  by  $n$  moles of gas:  $V/n$ .

The constant  $A$  in this equation originates from the observation that the potential energy between molecules is directly related to the density. Differentiating the potential energy with respect to

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