



Aqueous phase (catalytic) wet air oxidation of ammonia: Thermodynamic considerations



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ABSTRACT

The equilibrium concentrations in ammonia and ammonium ion in the liquid and gas phases could be calculated in the temperature range 25–250 °C, under typical operating conditions for the catalytic wet air oxidation of ammonia. A satisfactory agreement was obtained with the data collected upon blank experiments as well as in the presence of unreactive catalyst supports. Thermodynamic calculations appeared to be crucial to access a better comprehension of the reaction mixture composition under catalytic wet air oxidation reaction conditions, especially the ammonia partition and speciation among the different phases. New insights were gained in terms of ammonia reactivity.

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1. Introduction

Ammonia is being produced in large amounts for many different applications (e.g. fertilizers, nitric acid, cooling fluid, plastics, synthetic fibers and resins, explosives). The estimated world production of ammonia reached 146 million tons in 2015 [1]. It is mainly produced from molecular nitrogen and hydrogen via the Haber Bosch process. As a result, ammonia might be transferred to the atmospheric and aquatic environments, which represents a major risk both in terms of public health and environment (eutrophication, acidic rains). Ammonia release might also derive from the decomposition, oxidation or reduction of higher nitrogen-containing molecules. While a number of approaches has been developed to treat gaseous ammonia, via adsorption and/or oxidation, only a limited number of research works has been devoted to the treatment of ammonia in the liquid phase directly. Moreover, the most developed process in this later case is the stripping: the ammonia molecule is then transferred to the gas phase before being treated [2]. In addition, adsorption (clinoptilolite) [3,4], biological treatments (nitration–denitration [5], Anammox [6]) and advanced oxidation processes (ozonation [7,8], photocatalysis [9,10]) showed some major limitations either in terms of efficiency, cost and/or selectivity toward molecular nitrogen vs. nitrites and/or nitrates.

To overcome such limitations, some attention has more recently been paid to the catalytic wet air oxidation process. Important improvements have been obtained with the implementation of supported noble metal catalysts [11–15], especially in terms of efficiency and selectivity.

However, the catalytic wet air oxidation reaction being carried out in a three-phase reactor, a better understanding and description of the gas–liquid and liquid–liquid thermodynamic equilibria is necessary. Indeed, such knowledge is required in order to be able to accurately describe the ammonia catalytic wet air oxidation reaction mechanism and further extract the true kinetics for the different processes involved. Insights could also be gained on how to improve the reactivity of ammonia upon catalytic wet air oxidation.

As the result, the objective of this preliminary study was to determine the partition of ammonia between the gas and liquid phases and, in the liquid phase, the speciation between ammonia and ammonium ion, as a function of temperature in the range 25–250 °C. The results of our calculations were then valuably compared with experimental data acquired in the catalytic wet air oxidation of ammonia upon blank experiments and/or in the presence of inert catalyst supports.

2. Materials and methods

Thermodynamic calculations were performed in order to monitor (i) the evolution of the equilibrium concentrations in ammonia

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Table 1
Analytical conditions for the ion chromatography measurements.

Column	Cations	Anions
	Metrosep C4 150/4.0	Metrosep A Supp 5 150/4.0
Stationary phase	Silica gel grafted with carboxylic functional groups	Polyvinyl alcohol with quaternary ammonium groups
Elutant composition	HNO ₃ (1.7 mmol L ⁻¹) + dipicholinic acid (0.7 mmol L ⁻¹)	Na ₂ CO ₃ (3.2 mmol L ⁻¹) + NaHCO ₃ (1 mmol L ⁻¹)
Elutant flow rate (mL min ⁻¹)	0.9	0.7
Working pressure (MPa)	6	9

([NH₃]_l, [NH₃]_g) and ammonium ion ([NH₄⁺]_l) in the liquid and gas phases, respectively; and (ii) the changes in pH as a function of temperature. The initial conditions of the system were set as in the experimental tests ([NH₃]₀ = 60 mmol L⁻¹; T = 25 °C; V_l = 150 mL; V_g = 123 mL). To perform the calculations, the nitrogen mass balance (Eq. (1)) and the electro neutrality equation (Eq. (2)) were considered, as well as the variation with temperature of the acid-base constant (K_b, Eq. (3)), the self-ionization constant of water (K_w, Eq. (4)) and the Henry's constant (K_H or K_H^{cc}, Eqs. (5) and (6), respectively).

$$[NH_3]_0 V_l = [NH_3]_g V_g + [NH_3]_l V_l + [NH_4^+]_l V_l \quad (1)$$

$$[NH_4^+]_l + [H_3O^+]_l = [OH^-]_l \quad (2)$$

$$K_b = \frac{[NH_4^+]_l [OH^-]_l}{[NH_3]_l} \quad (3)$$

$$K_w = [H_3O^+]_l [OH^-]_l \quad (4)$$

$$K_H = \frac{[NH_3]_l}{P_{NH_3}} \quad (5)$$

$$K_H^{cc} = \frac{[NH_3]_l}{[NH_3]_g} = K_H \times RT \quad (6)$$

with R = 0.0821 L atm mol⁻¹ K⁻¹ and T in Kelvin.

Moreover, for the calculations, the binary solution of ammonia in water was considered to be infinitely diluted. Indeed, the concentration in water was 55.5 mol L⁻¹, while the concentration in ammonia was 60 mmol L⁻¹. As a result, the Raoult law and the simplified Duperray's empirical law (Eq. (7)) could be accurately applied to calculate the water vapor pressure (P_{H₂O}) in equilibrium with the liquid at a given temperature (T).

$$P_{H_2O} = \left(\frac{T}{100}\right)^4 \quad (7)$$

with T in Celsius in the range 100–250 °C.

Similarly, the solute (ammonia) was assumed to follow Henry's law (Eqs. (5) or (6)).

Finally, for comparison/validation purposes, preliminary tests were performed in a 273 mL batch reactor made of Hastelloy C22 equipped with a magnetically driven stirrer. In a typical run, 150 mL of a 60 mmol L⁻¹ ammonia solution (Sigma Aldrich, 28–30 vol.% NH₃) was initially loaded into the autoclave. After purging the reactor with argon several times, to eliminate any trace of oxygen, a 4 bar residual pressure of argon was maintained in the reactor to avoid any boiling phenomenon upon heating the solution up to the desired reaction temperature. The reactor was subsequently heated up to 200 °C under continuous stirring (1200 rpm). The time when air was introduced in the autoclave, to reach 50 bar total pressure (34 bar of synthetic air, i.e. 6.8 bar of oxygen), was considered as zero time for the reaction. All along the reaction, liquid samples were periodically withdrawn from the reactor and analyzed to measure the total nitrogen content in the solution (TN), the pH of the solution at atmospheric pressure and ambient temperature and the ammonia, nitrites and nitrates concentrations in the liquid phase.

Table 2
Ammonia acid-base constant (K_b).

T(°C)	T(K)	pK _b ^a	K _b ^a	pK _b ^b	K _b ^b
25	298	4.751	1.774 × 10 ⁻⁵	4.753	1.765 × 10 ⁻⁵
30	303	4.740	1.820 × 10 ⁻⁵	4.742	1.810 × 10 ⁻⁵
35	308	4.733	1.849 × 10 ⁻⁵	4.734	1.843 × 10 ⁻⁵
40	313	4.730	1.862 × 10 ⁻⁵	4.729	1.865 × 10 ⁻⁵
45	318	4.726	1.879 × 10 ⁻⁵	4.727	1.874 × 10 ⁻⁵
50	323	4.723	1.892 × 10 ⁻⁵	4.727	1.873 × 10 ⁻⁵
75	348			4.763	1.726 × 10 ⁻⁵
100	373			4.845	1.429 × 10 ⁻⁵
125	398			4.963	1.089 × 10 ⁻⁵
150	423			5.110	7.771 × 10 ⁻⁶
175	448			5.280	5.253 × 10 ⁻⁶
200	473			5.470	3.385 × 10 ⁻⁶
225	498			5.681	2.085 × 10 ⁻⁶
250	523			5.912	1.223 × 10 ⁻⁶

^a R.G. Bates, G.D. Pinching, Journal of American Chemical Society, 72 (3) (1950) 1393–1396.

^b J.R. Fisher, H.L. Barnes, The Journal of Physical Chemistry, 76 (1) (1972) 90–99 [Data were recalculated using Helgeson's full equation and the five parameters fitted by the authors].

The liquid samples were analyzed by ion chromatography (Metrohm 881 IC Pro) with an automated sampler (863Compact Autosampler, 36 positions) and two distinct conductivity detectors for the anions and the cations, respectively. The characteristics for the two different separation columns and the corresponding mobile phases used for the analysis of both the anions (NO₂⁻, NO₃⁻) and the cations (NH₄⁺) are presented in Table 1. Calibration curves in the range below 10 mg L⁻¹ were established using NH₄Cl (Normapur 99.5%), NaNO₃ (Sigma-Aldrich > 99%) and NaNO₂ (Sigma-Aldrich > 97%). In addition, the total nitrogen content (TN) in the liquid samples was measured using a TOC-VCSH analyzer coupled with a TN unit (TNM-1) from Shimadzu. In our study, TN corresponds to the total nitrogen content in ammonium, nitrites and nitrates. The nitrogen balance could be assessed from the comparison between the TN values and the ion chromatography results.

3. Results and discussion

3.1. Thermodynamic calculations

To start with, a throughout survey of the literature was performed in order to collect all the data already available concerning the ammonia acid-base constant (K_b) [16,17], the self ionization constant of water (K_w) [17–20] and the Henry's constant for ammonia (K_H, K_H^{cc}) [21,22]. Several sources could be identified in the literature for such data. These data are summarized in Tables 2–4, respectively. While the values collected for K_b and K_w were quite numerous and totally coherent, much scarce data could be directly found for K_H and/or K_H^{cc}.

In addition to the very limited data provided by Jones et al. at 149, 175, 203 and 245 °C [21], the raw data provided by Sander et al. (K_H⁰ and $\frac{-d \ln K_H}{d(\frac{1}{T})}$) had to be reprocessed [22]. Since the values for K_H⁰ varied between 10 and 78 mol L⁻¹ atm⁻¹ and the values for $\frac{-d \ln K_H}{d(\frac{1}{T})} = \frac{\Delta_{sol} H}{R}$ varied between 1500 and 4400 K,

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