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## **Observation based analysis for the determination of equilibrium time constant between ammonia, acid gases, and fine particles**

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**Abstract:** Experimental measurements of ammonia, acid gases, and the inorganic components of atmospheric aerosols were made at a commercial hog farm in eastern North Carolina from May 1998 to June 1999 by an annular denuder system (ADS). The ADS consisted of a cyclone separator, one diffusion denuder coated with sodium carbonate, another diffusion denuder with citric acid, and a filter pack containing Teflon and nylon filters in series. The equilibrium time constant for transfer between ammonia, acid gases, and aerosol phase of ammonium nitrate and ammonium chloride was determined based on kinetic rate constants ( $k_N$  as the rate constant of ammonium nitrate aerosol:  $2.04 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{sec}$ ;  $k_{Cl}$  as the rate constant of ammonium chloride aerosol:  $3.44 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{sec}$ ) and the observed inorganic components of atmospheric aerosols. The equilibrium time constant was determined based on kinetic rate constants and the observed inorganic components of atmospheric aerosols. The equilibrium time constant has a wide range of values, with an average value of 15.26 ( $\pm 10.94$ ) minutes for ambient equilibrium time between ammonia, nitric acid gas and ammonium nitrate aerosol; and 8.22 ( $\pm 6.81$ ) minutes for ammonia, hydrochloric acid, and ammonium chloride. Significant correlations were determined between comparisons of equilibrium time constant estimates with meteorological parameters, such as ambient temperature and relative humidity. The predicted chemical compositions in the particle by EQUISOLV II Model are in good agreement with the observed chemical composition at the experimental site.

**Keywords:** equilibrium time constant; ammonia-ammonium nitrate; ammonia-ammonium chloride; gas-to-particle conversion.

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## 1 Introduction

A particle in the atmosphere may grow in size by mass transfer of gas to its surface followed by conversion of the gas at the surface by condensation, deposition, chemical reaction, dissolution, or dissociation processes (Jacobson, 1997). The chemical composition of an atmospheric particle may be inorganic and/or organic aerosol such as ammonium, sodium, sulphate, nitrate, chloride, water, soil dust, elementary carbon, and organic carbon. Inorganic aerosol salts, comprise 25–50% of dry total fine aerosol mass (Heintzenberg, 1989; Gray et al., 1986). Moreover, the composition of individual particles can be fairly uniform or very different (internally or externally mixed aerosols), depending on their origin and atmospheric aging processes (coagulation, condensation, evaporation, chemical reaction). The particles consist of an aqueous phase at high relative humidity, one or more solid phases at low relative humidity, and both aqueous and solid phases at intermediate relative humidity. Especially, chemical reactions between ammonia with nitric acid and hydrochloric acid to form ammonium nitrate and ammonium chloride are reversible processes in the atmosphere due to higher volatility. The assumption of thermodynamic equilibrium has been employed to partition the volatile compounds between the gas and aerosol phases (Stelson et al., 1979; Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983; Saxena et al., 1986; Pacyna and Benson, 1996). The interaction between the gas and particle surface are not easily resolved and vary amongst particles because many of the processes are tightly coupled. If the ambient gas phase concentration exceeds those over particle surface, the gases diffuse into and condense on the particles.

Over the past decades, considerable effort has been directed towards the understanding of the physical and chemical properties of inorganic aerosols, while several inorganic aerosol thermodynamic models have been developed. All of these models assumed that internally mixed particles, i.e., all particles simulated in a given particle size range have the same chemical composition, and that thermodynamic equilibrium exists between the gas and particulate phases for the volatile compounds. Thus, particles of different size, consisting of primarily ammonium, sulphate, nitrate, and chloride should have the same composition ratios, if they are in equilibrium between the gas and aerosol phases. This assumption has been applied to the thermodynamic equilibrium models. Zhang et al. (2000) also reviewed the similarities and differences in simulation results predicted by five thermodynamic equilibrium models, such as MARS-A (Saxena et al., 1986), SEQUILIB (Pilinis and Seinfeld, 1987), SCAPE2 (Kim et al., 1993a, 1993b, 1995; Meng et al., 1995), AIM2 (Clegg et al., 1998, 1992), and EQUISOLV II (Jacobson, 1999). They recommended that the EQUISOLV II could be applied to simulate particulate matter for any conditions. Moreover, they suggested application of the EQUISOLV II for three-dimensional particulate matter modelling studies.

The kinetic chemical rate constants of ammonia with gaseous sulphuric acid, gaseous nitric acid, and gaseous hydrochloric acid in the atmosphere have been estimated (Baek and Aneja, 2004). The objective of the present study is to estimate the equilibrium time constant for transfer between gas to aerosol phase of ammonium nitrate and ammonium chloride, and to compare the observed data with those predicted by a thermodynamic equilibrium model, EQUISOLV II that is recommended for any condition by Zhang et al. (2000). The correlations between the equilibrium time constant and meteorological factors, such as relative humidity and ambient temperature are analysed.

## 2 Measurement and input

The study area consisted of two measurement sites (North Farm (NF) and South Farm (SF)) at a commercial swine production facility in eastern North Carolina, one of the major sources of atmospheric ammonia (Aneja et al., 2000). The NF site was located approximately 50 m northeast of a hog waste storage and treatment lagoon, and the SF site was located approximately 400 m south-southwest of the hog waste lagoon. Samples were collected using an annular denuder system (ADS) from May to July 1998 at the NF site and from May 1998 to April 1999 at the SF site. For comparison between NF and SF sites, ADS data from May to July 1998 were only used for this study. The ADS system consisted of a cyclone separator to remove coarse particles ( $PM_{\text{coarse}} \geq 2.5 \mu\text{m}$ ), two diffusion denuders in series coated with sodium carbonate and citric acid, respectively, and a filter pack containing a Teflon and a nylon filter all in series. The sodium carbonate coated denuder yielded average acid gas concentrations of hydrogen chloride (HCl), nitrous acid (HONO), nitric acid (HNO<sub>3</sub>), and sulphur dioxide (SO<sub>2</sub>). The citric acid coated denuder yielded average concentrations of ammonia (NH<sub>3</sub>). The combined Teflon and nylon filters yielded fine aerosol concentrations of ammonium (NH<sub>4</sub><sup>+</sup>), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulphate (SO<sub>4</sub><sup>2-</sup>) ions. The latter nylon filter collects ammonia released from the Teflon filter due to the volatility of ammonium nitrate and ammonium chloride. ADS measurements were derived from 12 hour integrated samples, representing daytime and nighttime averages. After sampling, the sampler was sealed immediately and extreme care was taken in handling the samples both during transport and inside the laboratory to protect samples from neutralisation of acidic particles. Meteorological parameters were measured at a 10 m tower near the SF site. Wind direction, wind speed, and air temperatures were measured at both 2 m and 10 m elevation. Relative humidity was measured at 2 m. Solar radiation and precipitation were measured at ground level.

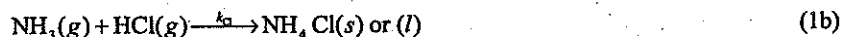
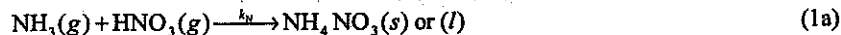
In this present study, a swine lagoon and barns were considered as sources of ammonia gas with respect to the prevailing winds, and measurements were conducted from both upwind and downwind of these sources. During the measurement period, not only was the southwest wind direction dominant but also higher concentrations of ammonia occurred at the NF site, which was effected from the nearby waste lagoon. On the other hand, during the northeast wind direction, higher ammonia concentrations occurred at the SF site (Baek and Aneja, 2004). To consider additional ammonia emission from lagoons and barns for this study, ammonia flux was estimated by a coupled mass transfer and chemical equilibrium reaction model (Aneja et al., 2001). The average estimated ammonia emission from the waste lagoon was  $5.38 \times 10^2 \mu\text{g NH}_3/\text{m}^2/\text{min}$  during the measurement periods. Harris and Thomson (Harris and Thompson, 1999) estimated barn ammonia emission of around 3.09 kg NH<sub>3</sub>/animal/yr. Ammonia emissions from swine lagoons and barns were converted to atmospheric ammonia concentration using the Gaussian dispersion model. In this study, the area source was modelled as a combination of the point sources. The contributions of each point grid cell divided into 40 cells, measuring approximately 25 × 20 m and two animal housing exhaust fans were considered. Emission distribution from each point source was selected by comparing the crosswind distance to the estimated plume half-width ( $2.15\sigma_y$ ) at the downwind distance from the centre of the lagoon to the receptor site (SF). When the crosswind distance was less than the plume half-width, the point source was considered to contribute to the observed concentration at the receptor. The additional

ammonia concentration for each contributed lagoon point source was indicated as  $[\text{NH}_3]_{\text{Lagoon}}$ . The ammonia concentration at the NF site was indicated as the background concentration expressed as  $[\text{NH}_3]_{\text{NF}}$ . Thus, having multiple point sources in the model, the input concentration data,  $[\text{NH}_3]_{\text{NF+Lagoon}}$ , is defined by ammonia concentration at the NF site,  $[\text{NH}_3]_{\text{NF}}$ , plus the sum of concentration,  $[\text{NH}_3]_{\text{Lagoon}}$ , at the receptor from each contributed point sources ( $[\text{NH}_3]_{\text{Lagoon}} = \sum_i [\text{NH}_3]_{i,\text{Lagoon}}$ ) where  $i$  is the number of cells which contribute ammonia concentration to the receptor ammonia concentration. Therefore, the ammonia input data for estimating the reaction rate constants between the gas-to-particle conversion process was defined as the sum of ammonia concentration from the background NF site and the emission associated with the waste lagoon.

### 3 Time constant for equilibrium state

The chemical composition of the sample is assumed to consist primarily of ammonium, sodium, sulphate, nitrate, and chloride, which is in equilibrium with the gaseous species. The measured gas phase concentrations can then be compared to those predicted from the chemical composition of the aerosols (Doyle et al., 1979; Tanner, 1982; Hildeman et al., 1984). Estimating the time constant for an equilibrium state between gas and aerosol phases, we assumed that ammonia, acid gases, and fine particles are already in an equilibrium state at the NF site before reaching additional ammonia emission from a swine lagoon. After passing a swine lagoon at the experimental site, due to an additional emission of ammonia, the state between the gas and aerosol phases are in non-equilibrium. The thermodynamic aerosol model based on equilibrium constants has been used for predicting the concentrations of gas and aerosol phases at the upwind NF site as an input data for this modelling.

Gaseous ammonia in the troposphere is converted, among other processes, into ammonium aerosols by neutralisation processes of ammonia with sulphuric acid, nitric acid, and hydrochloric acid in the atmosphere. In this study, we have focused on ammonium nitrate and ammonium chloride equilibrium chemical reactions (equation (1a), (1b)), since sulphuric acid is non-volatile at ambient conditions, and not considered. For estimating the equilibrium time constant, chemical reactions in this study were considered as irreversible chemical reactions. The following gas (g), liquid (l) and solid (s) phase reactions summarise ammonium aerosol production (Finlayson-Pitts and Pitts, 1986):



Using the following boundary conditions, and  $k_N$  as the rate constant of ammonium nitrate aerosol ( $2.04 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{sec}$ ),  $k_{\text{Cl}}$  as the rate constant of ammonium chloride aerosol ( $3.44 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{sec}$ ) from Baek and Aneja (2004),  $t=0$ :  $[\text{NH}_3]_0 = [\text{NH}_3]_{\text{NF+Lagoon}}$ ;  $t = \tau$ :  $[\text{NH}_3]_\tau = [\text{NH}_3]_{\text{Equilibrium}}$  ( $\tau$  is the equilibrium time constant from source to receptors), the following solutions are obtained:

$$\int_{[\text{NH}_3]_{\text{NF+Lagoon}}}^{[\text{NH}_3]_{\text{Equilibrium}}} \frac{1}{[\text{NH}_3]\{[\text{NH}_3] - A\}} d[\text{NH}_3] = -\int_0^t k dt \quad (2)$$

where  $[\text{NH}_3]_{\text{NF+Lagoon}}$  is the concentration of ammonia associated with the background value (i.e.,  $[\text{NH}_3]_{\text{NF}}$ ) plus ammonia emitted from the waste lagoon (i.e.,  $[\text{NH}_3]_{\text{Lagoon}}$ ).  $[\text{NH}_3]_{\text{Equilibrium}}$  is the predicted equilibrium concentration of ammonia from EQUISOLV II using concentrations of ammonia, acid gases, and components of inorganic aerosol from NF site as input information, and  $A = [\text{NH}_3]_{\text{NF+Lagoon}} + [\text{HNO}_3]_{\text{NF}}$ . Thus, the equilibrium time constant,  $\tau_{\text{NH}_4\text{NO}_3}$ , between  $\text{NH}_3$  and  $\text{HNO}_3$  aerosol is defined as:

$$\tau_{\text{NH}_4\text{NO}_3} = \frac{1}{A k_N} \ln \left[ \frac{[\text{NH}_3]_{\text{Equilibrium}} ([\text{NH}_3]_{\text{NF+Lagoon}} - A)}{[\text{NH}_3]_{\text{NF+Lagoon}} ([\text{NH}_3]_{\text{Equilibrium}} - A)} \right] \quad (3)$$

Similarly, the equilibrium time constant,  $\tau_{\text{NH}_4\text{Cl}}$ , between ammonia and nitric acid aerosol is also derived ( $B = [\text{NH}_3]_{\text{NF+Lagoon}} + [\text{HCl}]_{\text{NF}}$ ):

$$\tau_{\text{NH}_4\text{Cl}} = \frac{1}{B k_N} \ln \left[ \frac{[\text{NH}_3]_{\text{Equilibrium}} ([\text{NH}_3]_{\text{NF+Lagoon}} - B)}{[\text{NH}_3]_{\text{NF+Lagoon}} ([\text{NH}_3]_{\text{Equilibrium}} - B)} \right] \quad (4)$$

#### 4 Results

The equilibrium time constant between acid gases with  $\text{NH}_3$  are estimated at an ammonia-rich commercial hog farm based on the kinetic rate constants from Baek and Aneja (2004). The observed measurements were segregated by wind direction from the swine lagoon to a receptor site. In this study, we assume that chemical reactions between ammonia and acid gases are considered as irreversible. Table 1 shows the equilibrium time constant and distance scales between  $\text{NH}_3$ , and  $\text{HNO}_3$  and  $\text{HCl}$  reactions. The values of time constants between  $\text{NH}_3$  and  $\text{HNO}_3$  are generally in the range of 3.34 to 44.72 min, and distance scales are in the range of 0.25 to 5.37 km. Average equilibrium time and distance scales between  $\text{NH}_3$  and  $\text{HNO}_3$  (15.26 min, and 1.74 km) are greater than those average scales between  $\text{NH}_3$  and  $\text{HCl}$  (8.22 min, and 0.92 km), due to a higher average rate constant value of  $\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$  ( $2.04 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{sec}$ ) than that of  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \leftrightarrow \text{NH}_4\text{Cl}(\text{s})$  ( $3.44 \times 10^{-4} \text{ m}^3/\mu\text{mole}/\text{s}$ ) (Baek and Aneja, 2004). Wexler and Seinfeld (1992) also indicated that the equilibrium time constant values between ammonia and nitric acid gas and aerosol phases might range from a few seconds to over a day under certain conditions. Thus, these study values are in good agreement with published results.

Time constants during daytime are generally less than nighttime, because higher relative humidity conditions subsequently increase the condensation processes. Volatility of ammonium nitrate and chloride decreases under higher relative humidity and low ambient temperature.

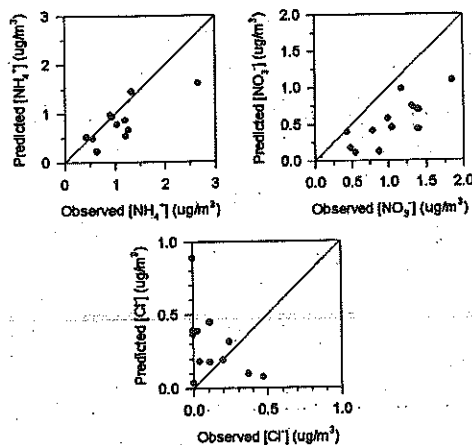
Table 1 Mean values of the equilibrium time constants of ammonia ( $\text{NH}_3$ ) with nitric acid ( $\text{HNO}_3$ ) and hydrochloric acid ( $\text{HCl}$ )

Time	Time scale (min)		Distance scale (km)	
	$\text{NH}_4\text{NO}_3$	$\text{NH}_4\text{Cl}$	$\text{NH}_4\text{NO}_3$	$\text{NH}_4\text{Cl}$
Mean	15.26	8.22	1.74	0.92
(STD*)	( $\pm 10.94$ )	( $\pm 6.81$ )	( $\pm 1.53$ )	( $\pm 0.85$ )
Daytime	10.52	5.84	1.55	0.81
(STD)	( $\pm 5.84$ )	( $\pm 3.21$ )	( $\pm 1.53$ )	( $\pm 0.66$ )
Nighttime	16.82	8.93	1.66	0.89
(STD)	( $\pm 13.44$ )	( $\pm 9.04$ )	( $\pm 1.67$ )	( $\pm 1.08$ )
Min	3.34	1.94	0.25	0.14
Max	44.72	27.15	5.37	3.26

STD = Standard deviation.

If the chemical composition of the sample is then assumed to represent the chemical composition of each particle in equilibrium, the measured gas and particle phase concentrations can be compared to those predicted with equilibrium state concentrations from a thermodynamic equilibrium aerosol model (Doyle et al., 1979; Tanner, 1982; Hildeman et al., 1984). However, if each aerosol particle is not in equilibrium with gas phase concentrations, the measured chemical composition of the sample could not be compared with those predicted by the model. Wexler and Seinfeld (1992) mentioned that a comparison of the measured aerosol particle composition concentrations to those predicted the thermodynamic calculations often leads to a serious disagreement, with the source of disagreement being unidentifiable transport limitations. Thus, based on the distance scale for equilibrium state between the gas and particle phases, the observed aerosol concentration are compared with the predicted aerosol concentrations by the thermodynamic equilibrium model EQUISOLV II (Jacobson, 1999) when the estimated equilibrium distance scales are less than 500 m only from a source to a receptor (Figure 1).

Figure 1 Comparison of observed and predicted ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) aerosol composition by the thermodynamic equilibrium model, EQUISOLV II



Both ammonium and nitrate cases show that the predicted aerosol compositions are in general good agreement, but slightly underestimated. In the case of chloride, the highest errors are due to the lack of sodium chloride (NaCl) data as input for the thermodynamic equilibrium model. During the measurement of aerosol concentrations, sodium chloride was not measured, and could not be used as an input parameter for equilibrium model.

## 5 Conclusions

Based on the kinetic rate constant between the chemical reaction  $\text{NH}_3$  and  $\text{HNO}_3$ , and  $\text{NH}_3$  and  $\text{HCl}$  to form atmospheric aerosols, the equilibrium time constant has been estimated from the measured ammonia, acid gases, and fine particles in an ammonia-rich environment, i.e. at a commercial hog farm in the eastern North Carolina. Even though the volatile inorganic compounds are not in equilibrium between the gas and aerosol phases in the real atmosphere, a thermodynamic equilibrium model, EQUISOLV II, is used in this study for predicting the equilibrium gas and aerosol phase concentrations.

The estimated equilibrium time constant may range from a few minutes to over a few hours under different meteorological conditions. Under certain transport cases, less than 500 m from the source, the comparison of ammonium and nitrate concentrations with observed and predicted aerosol compositions from the thermodynamic equilibrium model are in good agreement.

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