Equilibria of the Marine Multiphase Ammonia System

P. K. QUINN[1], W. E. ASHER[2], AND R. J. CHARLSON[3]

[1] *NOAA/Pacific Marine Environmental Laboratory, Seattle, WA, U.S.A. (Also with the Joint Institute for the Study of the Atmosphere and Ocean (JISAO), University of Washington, Seattle, WA, U.S.A.)*
[2] *Battelle Marine Sciences Laboratory, Sequim, WA, U.S.A.*
[3] *Department of Atmospheric Sciences, University of Washington, Seattle, WA, U.S.A.*

Abstract. A lack of empirical data has made it difficult to ascertain whether ammonia is in equilibrium between the oceanic, atmospheric gas and atmospheric particle phases in the remote marine environment. Reported here are simultaneous measurements of the saturation concentration of ammonia relative to ammonia concentrations in ocean surface waters; total seawater ammonia; atmospheric gas phase ammonia; and atmospheric particulate-phase ammonium, non-seasalt sulfate, methanesulfonate, and nitrate. Sampling was performed in May of 1987 in the northeast Pacific Ocean environment and in April and May of 1988 in the central Pacific Ocean environment.

These measurements were used to determine the degree to which ammonia approached equilibrium between the oceanic and atmospheric gas and aerosol particle phases. The experimental atmospheric gas phase ammonia concentrations were compared with calculated equilibrium concentrations assuming a Henry's law type of partitioning between the gas and condensed phases. Characteristic times of the processes controlling the fate of ammonia in the marine environment also were compared.

The measured atmospheric gas phase and oceanic concentrations of ammonia indicate that ammonia is not in a Henry's law equilibrium across the air/sea interface. This disequilibrium is a result of the long air/sea exchange equilibration time relative to the lifetime of ammonia in the atmosphere. Comparison of the calculated equilibrium gas phase ammonia concentrations with the measured gas phase ammonia concentrations shows that attainment of equilibrium between the atmospheric gas and particle phases is a strong function of the chemical composition of the aerosol particles. The data suggest that fully neutralized aerosol particles are not in Henry's law equilibrium with the gas phase while equilibrium is observed for particles with an average ammonium to non-seasalt sulfate molar ratio less than 1.8.

1. Introduction

In the study of atmospheric multiphase chemical systems, it is often useful to consider the equilibrium case because it represents the thermodynamic endpoint of a system. Furthermore, equilibrium models are mathematically more tractable than non-equilibrium kinetic-diffusive-advective models. Chemical equilibrium models have been used to describe several multiphase atmosphere and atmosphere/ocean systems, including the H_2O-HNO_3-NH_3-H_2SO_4 gas/particle system (Bassett and Seinfeld, 1983; Saxena *et al.*, 1983) and the transport of ammonia across the air/sea interface (Georgii and Gravenhorst, 1977; Ayers and Gras, 1980; Quinn *et al.*, 1987).

Accurate assessment of equilibrium in an atmospheric multiphase system requires consideration of the characteristic times of the relevant physical as well as chemical processes.

For a heterogeneous atmosphere/ocean system, the major processes determining whether equilibrium will be approached are (i) mass transport to and across the air/sea interface, (ii) gas phase diffusion to a particle, (iii) transport across the gas/particle interface with possible chemical reaction at the surface, (iv) aqueous-phase diffusion with possible chemical reaction within the particle, (v) vertical transport by advection of an air parcel into a cloud, and (vi) the removal of atmospheric species by rain. These processes are shown in Figure 1 for the marine ammonia system.
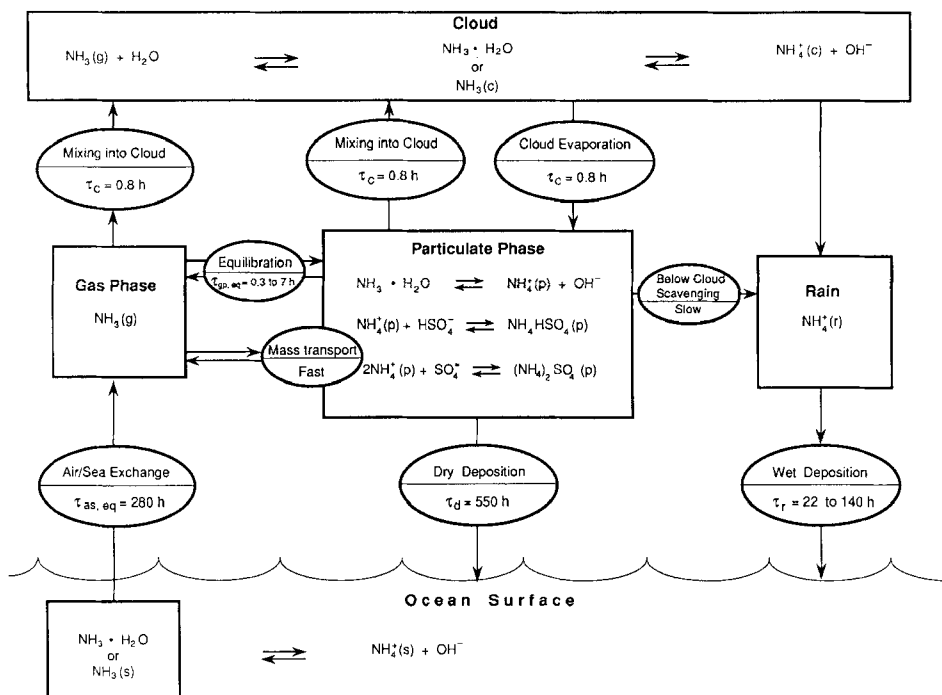

Fig. 1. Physical and chemical processes of the marine ammonia cycle. Each phase is represented as a box and each process as an oval. Ammonia exists in the ocean as un-ionized NH_3 (s) and ionized NH_4^+(s). NH_3 (s) undergoes transport across the air/sea interface. Once in the atmosphere, NH_3 (g) can be directly dissolved into cloudwater or can react with submicrometer acidic sulfate particles to form NH_4^+ (p). These submicrometer particles can act as CCN and become incorporated into clouds whereby NH_4^+ (p) becomes NH_4^+ (c). The main removal pathway of ammonia from the marine atmosphere is through wet deposition. Calculation of characteristic times is described in the text.

Ammonia exists in surface seawater in both the un-ionized and ionized forms, NH_3 (s) and NH_4^+ (s), respectively. NH_3 (s) may be transported into the atmosphere across the air/sea interface. Once in the atmosphere, gas phase ammonia, NH_3 (g), reacts with submicrometer acidic sulfate aerosol particles to form partially or fully neutralized ammoniated sulfate salts transforming NH_3 (g) to particulate ammonium, NH_4^+ (p). These sulfate particles can act as cloud condensation nuclei (CCN) (Pruppacher and Klett, 1980), which results in the transformation of NH_4^+ (p) to cloudwater ammonium, NH_4^+ (c). NH_3 (g) also can be dissolved directly into cloudwater or rainwater where, if the cloud or rain does not evaporate, ammonium will be removed from the atmosphere as rainwater ammonium, NH_4^+ (r). Wet deposition is the main removal pathway of total ammonia, NH_3 (g) + NH_4^+ (p), from the atmosphere because it occurs on a much faster time scale than removal by oxidation (Crutzen, 1983) and dry deposition (Figure 1).

The focus of this paper is the marine ammonia multiphase system; specifically, whether the air/sea interface and the atmospheric gas and particle phases are in equilibrium with respect to ammonia. Measured concentrations will be compared with calculated equilibrium concentrations to determine which phases are in equilibrium with respect to ammonia. The time constants of the relevant chemical and physical processes will be used to explain observed deviations from equilibrium.

2. Measurements

In the following discussion, parentheses, ( ), denote gas phase and brackets, [ ], aqueous phase concentrations. The subscripts introduced above are g = gas, p = particle, r = rain, s = surface seawater, sg = at the air/sea interface, and tot = total. Simultaneous measurements were made of $(NH_3)_g$; $[NH_4^+]_p$; particulate non-seasalt sulfate, nss $[SO_4^=]_p$; particulate methanesulfonate or MSA, $[CH_3SO_3^-]_p$; particulate nitrate, $[NO_3^-]_p$; $[NH_4^+]_r$; total seawater ammonia, $[NH_3]_{s,tot} = [NH_3]_s + [NH_4^+]_s$; and the concentration of ammonia in equilibrium with the ocean surface, $(NH_3)_{sg}$. Sampling was performed in May of 1987 over the northeast Pacific Ocean off the coast of Washington State from 5 to 200 km offshore and in April and May of 1988 over the central Pacific Ocean from 53°N to 14°S along 170°W.

A tandem sampling system was used for the collection of gas and particle phase species (Quinn and Bates, 1989). This system consisted of a cyclone separator to avoid sampling of large seasalt particles. The cyclone had a 50% collection efficiency for NaCl particles having a diameter of 0.9 μm. The cyclone was followed by a 47 mm Millipore Teflon filter (1.0 μm pore size) for the collection of particulate species and four 47 mm Whatman 41 filters coated with 0.01 M oxalic acid for the collection of NH_3 (g).

$[NH_4^+]_r$ and $[NH_3]_{s,tot}$ were measured from bulk samples (Quinn et al., 1988). $(NH_3)_{sg}$ was measured with a filter pack in conjunction with an equilibrator (Keeling et al., 1965; Quinn et al., 1988; 1990; Butler et al., 1989). Values of $(NH_3)_{sg}$ measured directly using the equilibrator were compared with those calculated from $[NH_3]_{s,tot}$, pH, and the Henry's law constant for ammonia, K_{hN}, and were found to agree within the experimental error of $\pm40\%$ for the two techniques (Quinn et al., 1988; 1990). The advantage of using the equilibrator is that it does not require the use of K_{hN} or other equilibrium constants which have not been determined for seawater.

The phenolhypochlorite colorimetric technique (Solarzano, 1969) was used to analyze all of the samples for all ammonia species. It has been shown that ammonia in all four phases may be

determined by this technique (Quinn *et al.*, 1988; 1990). Therefore, it is unlikely that observed differences between the concentrations of ammonia in the four phases resulted from systematic errors induced by differences in analytical procedures.

3. The Ammonia Air/Sea System

3.1. COMPARISON OF MEASURED AND CALCULATED EQUILIBRIUM CONCENTRATIONS

To determine whether equilibrium of NH_3 across the air/sea interface existed for the conditions present during the 1987 and 1988 experiments, a distribution coefficient D defined as

$$D = [NH_3]_{s,calc}/(NH_3)_{g, meas} \tag{1}$$

was calculated from $[NH_3]_{s,calc}$ derived from measured $[NH_3]_{s,tot}$ and pH and measured $(NH_3)_g$. If NH_3 were in a Henry's law equilibrium across the air/sea interface, D should be equal to the Henry's law constant for NH_3, K_{hN}, which is defined as

$$K_{hN} = [NH_3]_s/(NH_3)_g. \tag{2}$$

Because the K_{hN} used for comparison was measured in a low ionic strength solution (Stumm and Morgan, 1981), it was activity-corrected assuming that the activity coefficient of a singly charged species in seawater is about 0.65 (Holland, 1978). K_{hN} was temperature corrected using

$$K_{hN,T} = K_{298}exp[-\Delta H^{\circ}_{f,T}/RT(298-T/298)]. \tag{3}$$

As shown in Figure 2, D was found to be 1 to 2 and 2 to 4 orders of magnitude larger than K_{hN} for the 1987 and 1988 experiments, respectively. This indicates that the ocean surface was universally and variably supersaturated with respect to NH_3 (g) and that Henry's law equilibrium did not exist. Low atmospheric $(NH_3)_g$ measured over the central Pacific Ocean in 1988 resulted in the highest values of D and the greatest departure from Henry's law equilibrium.

The net flux of ammonia from the ocean to the atmosphere, F, can be calculated from

$$F = k_g[(NH_3)_{sg} - (NH_3)_g] \tag{4}$$

where F is in μmol m^{-2} d^{-1} and k_g is the gas phase transport velocity of NH_3. The k_g used was that of H_2O, 3000 cm hr^{-1}, because both H_2O and NH_3 are gas phase rate controlled species and have similar molecular weights (Liss and Slater, 1974). Because $(NH_3)_{sg}$ was greater than $(NH_3)_g$ for all cases studied (Figure 3), the use of (4) results in a calculated net flux of ammonia from the ocean to the atmosphere ranging between 2.6 and 16 μmol m^{-2} d^{-1}.

During both field experiments, only one measurement of $[NH_4^+]_r$ was possible. The average rainwater flux of ammonium during this one storm was compared with the overall experimental average air/sea flux of ammonia. During the 1987 experiment rain event, $[NH_4^+]_r$ was found to be 1.0 ± 0.1 μmol l^{-1}. Based on a total rainfall amount of 2.0 cm and the time since it last rained, two days, the average wet depositional flux was calculated to be 10 μmol m^{-2} d^{-1}. This rainwater flux agrees well with the range measured by Galloway over the Pacific Ocean of 2 to 14 μmol m^{-2} d^{-1} (Galloway, 1985).
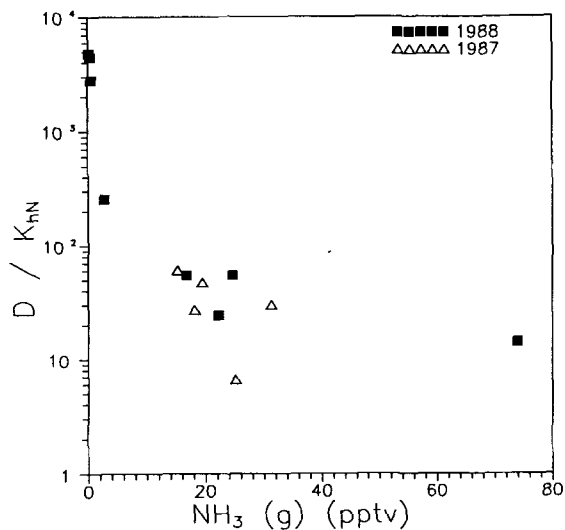
Fig. 2. The ratio of D to K_{hN} where $D = [NH_3]_{s,calc}/(NH_3)_{g,meas}$ and $K_{hN} = [NH_3]_s/(NH_3)_g$ versus measured $(NH_3)_g$ for the 1987 and 1988 experiments. Open triangles are the 1987 data points and solid squares are the 1988 data points.
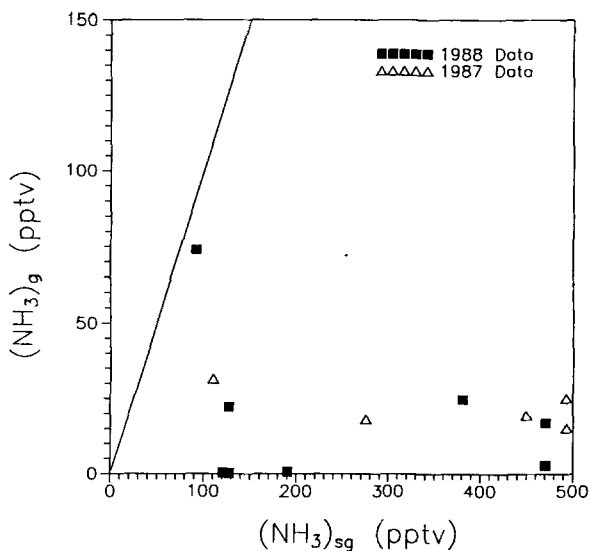

Fig. 3. $(NH_3)_g$ versus measured $(NH_3)_{sg}$ for samples collected during both the 1987 and 1988 experiments. Data key is identical to Figure 2.

The wet-depositional flux of NH_4^+ (r) measured in this study and that measured by Galloway (1985) fall within the calculated range of 2 to 16 μmol m^{-2} d^{-1} for the flux of NH_3 (g) from the ocean. The agreement of the gas flux of ammonia from the ocean to the atmosphere with the rainwater flux of ammonium to the ocean suggests that ammonia may be in a quasi-steady state in the marine atmosphere with emission from the ocean being balanced by removal by rain. As shown by the lack of Henry's law equilibrium at the sea surface, however, this does not imply that ammonia is in equilibrium between all relevant phases that make up the marine ammonia cycle. For ammonia to be in equilibrium between ocean surface waters and the atmosphere, the time of equilibration must be short relative to the time of processes controlling the fate of NH_3 (s) and atmospheric NH_3 (g).

4. The Ammonia Atmospheric Gas/Particle System

4.1. DESCRIPTION OF THE EQUILIBRIUM MODEL

Because the aqueous particle phase NH_3 concentration, $[NH_3]_p$, could not be measured directly, it was necessary to calculate it using an equilibrium model. This calculated $[NH_3]_p$ then was used to predict an equilibrium $(NH_3)_g$ assuming Henry's law. The predicted equilibrium $(NH_3)_g$ then was compared to the measured atmospheric concentration. Aerosol particles were assumed to consist of both an aqueous and solid phase and to contain the major condensed phase ionic species found in the remote marine troposphere: H^+; OH^-; NH_4^+; NO_3^-; HSO_4^-; SO_4^-; and $CH_3SO_3^-$. It was assumed that particle diameters were constant, i.e., condensation and/or evaporation did not occur. Reactions included in the model were the aqueous-phase equilibria,

$$H_2O \text{ (aq)} \rightleftharpoons OH^- \text{ (aq)} + H^+ \text{ (aq)} \tag{5}$$

$$NH_3 \text{ (g)} \rightleftharpoons NH_3 \text{ (aq)} \tag{6}$$

$$NH_3 \text{ (aq)} + H^+ \text{ (aq)} \rightleftharpoons NH_4^+ \text{ (aq)} \tag{7}$$

$$HSO_4^- \text{ (aq)} \rightleftharpoons SO_4^- \text{ (aq)} + H^+ \text{ (aq)} \tag{8}$$

$$CH_3SO_3H \text{ (aq)} \rightleftharpoons CH_3SO_3^- \text{ (aq)} + H^+ \text{ (aq)} \tag{9}$$

$$HNO_3 \text{ (aq)} \rightleftharpoons NO_3^- \text{ (aq)} + H^+ \text{ (aq)} \tag{10}$$

and dissolution equilibria between the solid and aqueous phase,

$$2NH_4^+ \text{ (aq)} + SO_4^- \text{ (aq)} \rightleftharpoons (NH_4)_2SO_4 \text{ (s).} \tag{11}$$

The thermodynamic values of the equilibrium constants for reactions (5) through (11) are listed in Table 1. H_2SO_4 was assumed to be completely deprotonated in the pH range of interest and was not included in the model. It was assumed that NH_4HSO_4 (s) and NH_4NO_3 (s) were not present in the solid phase because their deliquescence points of 40% and 60%, respectively, are below the lowest relative humidities measured during both field measurement periods.

Using (5)–(11) and the aqueous phase charge balance equation (Stumm and Morgan, 1981), an equilibrium pH of the solution was calculated based on concentrations of total S(VI), HSO_4^- + $SO_4^=$, total ammonia, NH_3 + NH_4^+, NO_3^-, and $CH_3SO_3^-$. The concentration of NH_3 (g) in equilibrium with the condensed phase was calculated from $[NH_3]_p$ and K_{bN}. The Kelvin effect is negligible at the particle diameters considered and was not included in the model.

4.2. ACTIVITY CORRECTIONS

The activities of all species in the condensed phase particles were strongly non-ideal because the ionic strength ranged from 4 to 40 over a range of relative humidities from 65 to 88%. Therefore, aqueous phase concentrations were activity corrected using the method of Bromley (1973). This procedure allowed for the prediction of activity coefficients of strong electrolytes in multi-electrolyte solutions based on binary solution activity coefficients (Pilinis and Seinfeld, 1987).

Using the notation of Bromley (1973) and Pilinis and Seinfeld (1987), where cations and anions are indexed using odd and even integers, respectively, the activity coefficient of electrolyte 12, γ_{12}, consisting of cation 1 and anion 2 in a strong electrolyte solution of n separate components is

$$\log(\gamma_{12}) = -A_\gamma Z_1 Z_2 I^{1/2}/(1+I^{1/2}) + [Z_1 Z_2/(Z_1+Z_2)][F_1/Z_1+F_2/Z_2] \tag{12}$$

TABLE 1. Values of equilibrium constants used in (5) through (11).

	K_{298}	Reference
K_w	1×10^{-14}	Smith and Martell, 1976
K_{a,NH_4^+}	5.71×10^{-10}	Smith and Martell, 1976
K_{a,H_2SO_4}	1.02×10^{-2}	Smith and Martell, 1976
K_{a,CH_3SO_3H}	15.8	Streitweiser and Heathcock, 1976
K_{a,HNO_3}	15.4	Schwartz, 1984
K_{bN}	57.6	Stumm and Morgan, 1981
$K_{sp,(NH_4)_2SO_4}$	788	Saxena *et al.* (1983)

where Z_1 and Z_2 are the absolute values of the charges of the ions, I is the ionic strength, given by

$$I = 1/2\Sigma_i m_i Z_i^2, \tag{13}$$

A_γ is a constant equal to (Pilinis and Seinfeld, 1987)

$$A_\gamma = 0.511 \text{ kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}}, \tag{14}$$

F_1 is the ion-pair interaction term for cation 1 with all anions in solution,

$$F_1 = Y_{21}\log(\gamma^\circ_{12}) + Y_{41}\log(\gamma^\circ_{14}) + Y_{61}\log(\gamma^\circ_{16}) + \dots$$

$$+ [A_\gamma I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})][Z_1 Z_2 Y_{21} + Z_1 Z_4 Y_{41} + Z_1 Z_6 Y_{61} + \dots] \tag{15}$$

where γ°_{ij} is the binary-activity coefficient of the ion pair ij in a pure solution and Y_{i1} is given by

$$Y_{i1} = [1/2(Z_i + Z_1)]^2 m_i/I \tag{16}$$

where m_i is the concentration of anion i. F_2 is the ion-pair interaction term for anion 2 with all cations in solution

$$F_2 = X_{12}\log(\gamma^\circ_{12}) + X_{32}\log(\gamma^\circ_{32}) + X_{52}\log(\gamma^\circ_{52}) + \dots$$

$$+ [A_\gamma I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})][Z_1 Z_2 X_{12} + Z_3 Z_2 X_{32} + Z_5 Z_2 X_{52} + \dots] \tag{17}$$

where X_{i2} is given by

$$X_{i2} = [1/2(Z_i + Z_2)]^2 m_i/I \tag{18}$$

and m_i is the concentration of cation i. The pure-solution binary activity coefficient of electrolyte ij, γ°_{ij}, is calculated using the method of Pitzer and Mayorga (1973) which has the explicit form for electrolyte 12

$$\ln(\gamma^\circ_{12}) = Z_1 Z_2 f^\gamma + m_{12}[2v_1 v_2/(v_1+v_2)]B^\gamma_{12} + m_{12}^2[2(v_1 v_2)^{3/2}/(v_1+v_2)]C^\gamma_{12} \tag{19}$$

where v_1 and v_2 are the numbers of cations and anions in the electrolyte formula, m_{12} is the molality for the specified ionic strength, and f^γ is given by

$$f^\gamma = -0.392[I^{\frac{1}{2}}/(1+1.2I^{\frac{1}{2}} + 2/1.2\ln(1+1.2I^{1/2}))] \tag{20}$$

and

$$B^\gamma_{12} = 2B^\circ_{12} + (2B'_{12}/4I)[1 - \exp(-2I^{\frac{1}{2}})(1+2I^{\frac{1}{2}} - 2I)] \tag{21}$$

TABLE 2. Constants used in the calculation of binary activity coefficients (Pilinis and Seinfeld, 1987).

Species	B°_{12}	B'_{12}	C'_{12}
$(NH_4)_2SO_4$	0.04763	0.44459	–0.001966
NH_4HSO_4	0.04494	0.23594	–0.004380
(H^+,HSO_4^-)	0.25713	0.35308	–0.004245
$(2H^+,SO_4^-)$	–0.09330	0.32381	0.031740
HNO_3	0.11190	0.32060	0.001500
NH_4NO_3	–0.01540	0.11200	–0.000045
CH_3SO_3H	0.1298	0.62900	0.005200

where the values used for the constants B°_{12}, B'_{12}, and C'_{12} for all relevant species are those listed in Table 2.

The NH_4^+/H^+ activity coefficient ratio in a multi-electrolyte solution can be estimated from the binary activity coefficients of a salt and strong acid of the form NH_4X and HX respectively (Stelson *et al.*, 1984). In these calculations, the activity coefficient ratio of NH_4^+ to H^+ was estimated from the binary solution activity coefficients of NH_4^+,HSO_4^- and H^+,HSO_4^- as

$$\gamma_{NH_4^+}/\gamma_{H^+} = \gamma^{\circ}_{NH_4^+,HSO_4^-}/\gamma^{\circ}_{H^+,HSO_4^-} = (\gamma^{\circ}_{NH_4^+}/\gamma^{\circ}_{H^+})^{\frac{1}{2}} . \tag{22}$$

This activity-correction term was used for the equilibrium constant for the reaction listed in (7).

The activity of NH_3 was assumed to be equal to the activity of H_2O and was calculated from I using the method of Cohen *et al.* (1987) for concentrated binary electrolyte solutions. Assuming that the aqueous phase is composed of $(NH_4)_2SO_4$, the activity of H_2O, a_w, can be written as

$$a_w = 1.0151 - 4.478 \times 10^{-2}I + 1.041 \times 10^{-3}I^2 - 8.258 \times 10^{-6}I^3. \tag{23}$$

A more rigorous estimate of a_w would include terms for a multi-electrolyte solution. However, the necessary constants for this procedure currently are not available.

4.3. RESULTS OF THE EQUILIBRIUM MODEL

The aqueous concentrations of $SO_4^=$, $CH_3SO_3^-$, and NO_3^- used in the model corresponded to particulate concentrations found in the remote marine atmosphere for particle diameters of 0.1 to 0.25 μm at 65 to 88% RH. The aqueous concentration of NH_4^+ was increased from a molar ratio of NH_4^+ (p) to nss $SO_4^=$ (p), R_{AS}, of 0.1 to 2.0. The equilibrium pH of the aqueous phase was calculated for each set of input conditions. As shown in Figure 4, for a solution containing 12 M total $SO_4^=$ and no NO_3^- or $CH_3SO_3^-$, the equilibrium pH increased from about -1 to 0.8 as R_{AS} increased from 0.1 to 1.9. Based on $K_{sp, (NH_4)_2SO_4}$, $(NH_4)_2SO_4$ was observed to precipitate at an R_{AS} of approximately 0.25 resulting in an acidic solution saturated with $(NH_4)_2SO_4$ in accord with Tang (1976). As $SO_4^=$ became fully neutralized (R_{AS} = 2.0), the pH increased to 3.0. The addition of NO_3^- and/or $CH_3SO_3^-$ lowered the pH throughout the range of R_{AS} studied with the greatest effect occurring at R_{AS} equal to 2.0. For example, a 12 M $SO_4^=$ and 24 M NH_4^+ solution had a calculated pH of 3.0 while a 12 M $SO_4^=$, 24 M NH_4^+, 4 M $CH_3SO_3^-$, and 2 M NO_3^- solution had a calculated pH of -0.6.
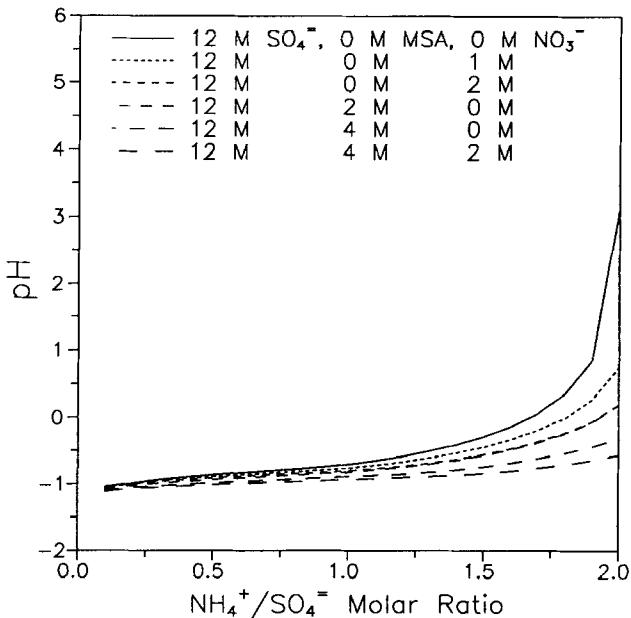
Fig. 4. Calculated equilibrium solution pH as a function of NH_4^+ to $SO_4^=$ molar ratio for $SO_4^=$, $CH_3SO_3^-$, and NO_3^- concentrations of 12, 0, and 0 M; 12, 0, and 1 M; 12, 0, and 2 M; 12, 2, and 0 M; 12, 4, and 0 M, and 12, 4, and 2 M.

The $(NH_3)_g$ in equilibrium with the solution is strongly dependent on solution pH such that as pH decreases, the dissolved ammonia concentration and $(NH_3)_g$ decreases. As shown in Figure 5, for a solution consisting of 12 M $SO_4^=$ but no NO_3^- or $CH_3SO_3^-$, the calculated equilibrium $(NH_3)_g$ was about 2 pptv for R_{AS} = 1.0. As R_{AS} increased from 1.0 to 2.0, $(NH_3)_g$ increased to nearly 10^4 pptv.

Because the addition of acid lowers the pH, the calculated $(NH_3)_g$ is significantly lower for particles containing both NO_3^- and $CH_3SO_3^-$ even as R_{AS} approaches 2.0. A 12 M $SO_4^=$, 12 M NH_4^+, 4 M $CH_3SO_3^-$, and 2 M NO_3^- solution (R_{AS} = 1.0) had a calculated equilibrium $(NH_3)_g$ of 0.6 pptv while the corresponding solution with R_{AS} = 2.0 had a calculated $(NH_3)_g$ of 3 pptv. Therefore, the addition of NO_3^- and $CH_3SO_3^-$ corresponding to a NO_3^- to $SO_4^=$ molar ratio of 0.17 and a $CH_3SO_3^-$ to $SO_4^=$ molar ratio of 0.33 resulted in a decrease in the equilibrium $(NH_3)_g$ by a factor of 10^4. This is significant because these NO_3^- to $SO_4^=$ and $CH_3SO_3^-$ to $SO_4^=$ ratios are consistent with field data.

In the remote marine troposphere, the submicrometer R_{AS} often has been observed to be less than one (Covert, 1988; Quinn $et\ al.$, 1990), the NO_3^- (p) to nss $SO_4^=$ (p) molar ratio can be as high as 0.15 (this work), and the $CH_3SO_3^-$ (p) to nss $SO_4^=$ (p) molar ratio can reach 0.33 (Savoie and Prospero, 1989; Calhoun $et\ al.$, 1989). If equilibrium exists under these conditions, concentrations of NH_3 (g) should be about 1 pptv at R_{AS} equal to 1. As the sulfate becomes fully neutralized by NH_4^+, the $(NH_3)_g$ should increase to about 3 pptv.
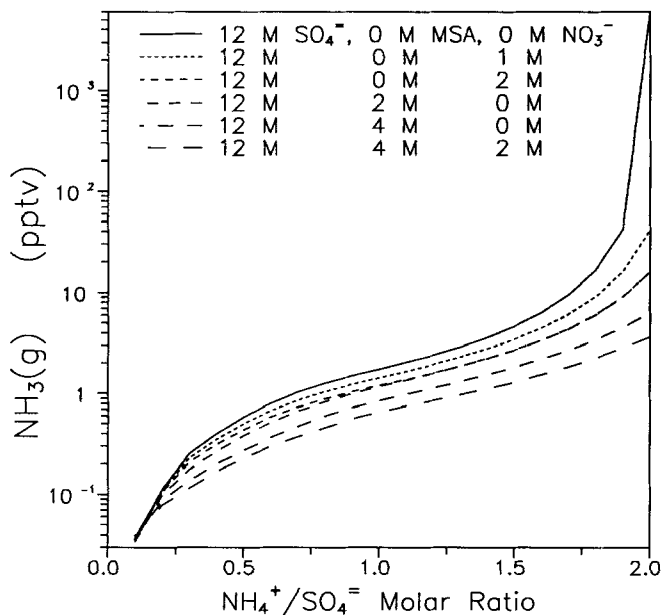

Fig. 5. Calculated equilibrium $(NH_3)_g$ as a function of NH_4^+ to $SO_4^=$ molar ratio for $SO_4^=$, $CH_3SO_3^-$, and NO_3^- concentrations of 12, 0, and 0 M; 12, 0, and 1 M; 12, 0, and 2 M; 12, 2, and 0 M; 12, 4, and 0 M; and 12, 4, and 2 M.

4.4. Comparison of Measured and Calculated Equilibrium Concentrations

Measured vapor pressures of NH_3 (g) are plotted versus the measured R_{AS} in Figure 6 for both the 1987 and 1988 experiments. Measured $(NH_3)_g$ ranged between 0.2 and 77 pptv with no apparent correlation between $(NH_3)_g$ and R_{AS}. Measured NO_3^- (p) to nss SO_4^- (p) molar ratios ranged between 0 and 0.15 and measured $CH_3SO_3^-$ (p) to nss SO_4^- (p) molar ratios ranged between 0.002 and 0.11. Based on measured particle size distributions (Quinn *et al.*, 1990) and sulfate aerosol growth curves (Charlson *et al.*, 1978), the radii of the sampled particles were estimated to range from 0.05 to 0.12 μm.

An equilibrium $(NH_3)_g$ was calculated for each sample collected by using the measured $[NH_4^+]_p$, non-seasalt $[SO_4^-]_p$, $[CH_3SO_3^-]_p$, and $[NO_3^-]_p$ in the aqueous phase chemical model. The difference between the calculated equilibrium ammonia concentration, $(NH_3)_{g,c}$, and the measured ammonia concentration, $(NH_3)_{g,m}$, is plotted as a function of R_{AS} in Figure 7. For R_{AS} less than about 1.8, the agreement between $(NH_3)_{g,c}$ and $(NH_3)_{g,m}$ is within the experimental uncertainty of 30%. Between molar ratios of 1.8 and 2.0 however, the $(NH_3)_{g,c}$ becomes greater than $(NH_3)_{g,m}$ by a factor of 1600.

Although the overprediction of $(NH_3)_g$ by the model may indicate a lack of equilibrium in the gas/particle ammonia system, it may be that the equilibrium model is not able to describe the empirical data for the higher molar ratios. Overprediction of $(NH_3)_g$ would occur if acidic species

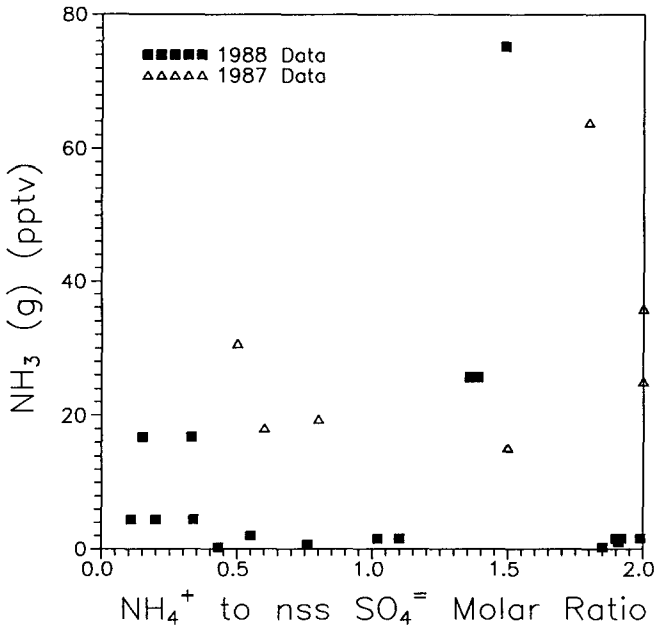Fig. 6. Measured $(NH_3)_g$ versus measured NH_4^+ to nss SO_4^- molar ratios for the 1987 and 1988 experiments. Solid triangles are the 1987 data and solid squares are the 1988 data.
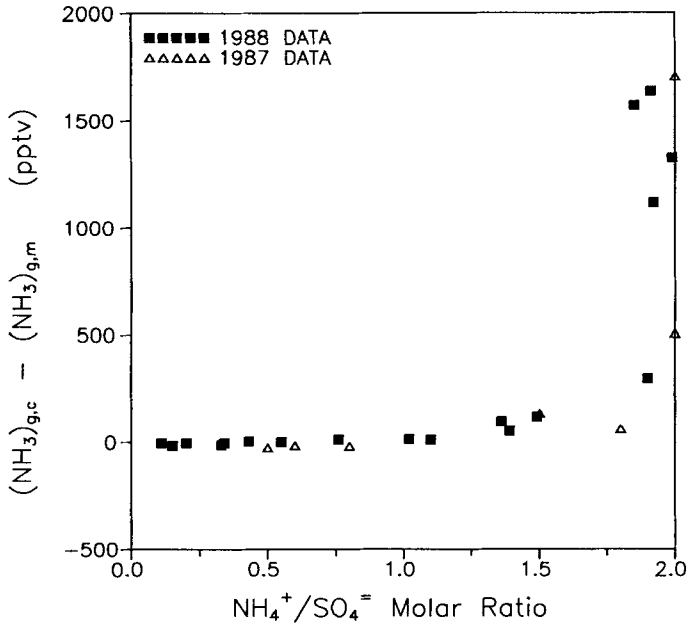
Fig. 7. The difference between calculated equilibrium $(NH_3)_g$ and measured $(NH_3)_g$ versus the NH_4^+ to $SO_4^=$ molar ratio. Data key is identical to Figure 6.

present in the collected particulate samples were not included in the charge-balance equation. Model calculations (Pilinis and Seinfeld, 1987) have predicted an increase in the NO_3^- concentration in the particle phase when NaCl is added to the $NH_4^+/NO_3^-/SO_4^=/H_2O$ system at 90% RH. Alternatively, overprediction of $(NH_3)_g$ would occur if solids such as $(NH_4)_3H(SO_4)_2$ were present in the particle phase. As discussed below, comparison of the characteristic equilibration times of the processes involved suggests that the gas/particle system should be in equilibrium even at high R_{AS}.

The model results indicate that equilibrium was closely approached between the atmospheric gas and particle phases under the conditions encountered in this study for R_{AS} less than about 1.8. At values of R_{AS} greater than about 1.8, the calculated $(NH_3)_g$ was greater than the measured value indicating that the particles were supersaturated with NH_3. However, in studying an atmosphere/ocean multiphase system, it is necessary to examine these results in the context of the characteristic equilibration times of the physical processes involved in reaching equilibrium.

5. Comparison of Relevant Characteristic Times

Estimates of the characteristic times for the multiphase marine ammonia system are listed in Table 3 and are shown in Figure 1. These characteristic times are highly variable parameters having uncertainties that are difficult to assess but which may be as large as a factor of two.

TABLE 3. Characteristic times of the chemical and physical processes of the multiphase marine ammonia system. Values are based on parameters listed in the text.

Process		Hours
Henry's law equilibration across the air/sea interface	$\tau_{as,eq}$	280
Gas phase diffusion plus interfacial mass transport	τ_{mt}	5×10^{-13}
Reversible protonation of NH_3	τ_{chem}	5×10^{-17} at pH -2 5×10^{-10} at pH 5
95% equilibration of NH_3 between the atmospheric gas and particle phases	$\tau_{gp,eq}$	0.3 ($R_{AS} = 2.0$) 6.7 ($R_{AS} = 0.1$)
Vertical mixing of an air mass into a cloud	τ_c	0.8
Removal of NH_3 (g) and NH_4^+ (r) by rain	τ_r	22 to 140
Removal of NH_4^+ (p) by dry deposition	τ_d	550

For equilibrium to exist between the atmospheric gas and particle phases, the lifetime of the particle must be long relative to the transport time of NH_3 (g) to the particle, the transport time across the interface, the time of the reversible protonation of NH_3, and the gas/particle equilibration time. The gas/particle mass transport characteristic time, τ_{mt}, may be estimated as the sum of the gas phase diffusion characteristic time, $\tau_{d.g.}$, and interfacial mass transport characteristic time, τ_i, (Schwartz, 1986). This has the explicit form

$$\tau_{mt} = \tau_{d.g.} + \tau_i = r^2/3D_g + 4r/3\upsilon\alpha \tag{24}$$

where D_g is the gas phase diffusion coefficient equal to 0.234 cm^2 sec^{-1} for NH$_3$, r is the particle radius in cm, υ is the mean molecular speed in cm sec^{-1}, and α is the accommodation coefficient. For r = 0.12 μm and α = 0.12 (Huntzicker, 1980), τ_{mt} = 2 × 10^{-9} sec (5 × 10^{-13} h).

The characteristic time of the reversible reaction of NH$_3$ + H$^+$ $\rightleftharpoons$ NH$_4^+$, τ_{chem}, is given by

$$\tau_{chem} = (k_D + k_R[H^+])^{-1} \tag{25}$$

where k_R, the rate of recombination, is 4.3 × 10^{10} M^{-1} sec^{-1} and k_D, the rate of dissociation, is 24.6 sec^{-1} (Eigen *et al.*, 1964). τ_{chem} ranges from 2 × 10^{-13} to 2 × 10^{-6} sec (5 × 10^{-17} to 5 × 10^{-10} h) as the solution pH increases from −2 to 5.

The time for 95% of specie i to come to equilibrium between the gas and aqueous phases, $\tau_{gp,eq}$, can be estimated by (Jacob, 1985)

$$\tau_{gp,eq} = 3r^2[W+(H_{eff}RT)^{-1}]^{-1}[1+4\lambda/3r\alpha][\lambda(8RT/m\pi)^{\frac{1}{2}}]^{-1} \tag{26}$$

where r is the particle radius, W is the liquid water content of the particle, H_{eff} is the effective Henry's law constant in M atm^{-1} and takes into account the ionization of species i in solution, R is the gas constant, T is temperature, α is the accommodation coefficient of species i, λ is the mean free path in air, and m is the molecular weight of species i.

Using (26), $\tau_{gp,eq}$ was calculated based on H_{eff} which was derived from calculated equilibrium concentrations of NH$_3$ (aq) and NH$_4^+$ (aq), for each set of model input conditions. The equilibration time is a strong function of pH. As the pH of the solution increases, the ratio of aqueous NH$_3$ to NH$_4^+$ increases. If the gas phase is undersaturated relative to the particle phase, this will result in an increase in the concentration gradient of NH$_3$ between the particle and gas phases and a decrease in the equilibration time. As shown in Figure 8, for r = 0.12 μm, W = 4 × 10^{-9} l H$_2$O m^{-3} air, α = 0.12 (Huntzicker *et al.*, 1980), a SO$_4^=$ concentration of 12 M, and an NH$_4^+$ concentration of 12 M, $\tau_{gp,eq}$ is about 2.4 × 10^4 s (5.5 h). Figure 8 also shows that for the same conditions with R$_{AS}$ = 2, $\tau_{gp,eq}$ is only a few seconds. The addition of CH$_3$SO$_3^-$ and/or NO$_3^-$ to the solution increases the equilibration time, particularly at high R$_{AS}$, because additional CH$_3$SO$_3^-$ and/or NO$_3^-$ decreases both the pH and the aqueous phase NH$_3$ concentration. A particle with r = 0.12 μm and consisting of 4 M CH$_3$SO$_3^-$, 2 M NO$_3^-$, and 12 M SO$_4^=$ at R$_{AS}$ = 2 has a calculated $\tau_{gp,eq}$ of about 2.4 × 10^4 s (5.5 h). The use of larger radii in (26) would result in longer times because $\tau_{gp,eq}$ is proportional to r^2.

The atmospheric gas/particle equilibration time was calculated for each collected sample and found to decrease from 2.4 × 10^4 sec to 1000 sec (6.7 to 0.3 h) as R$_{AS}$ increased from 0.1 to 2.0 (Figure 9). Particle radii varying between 0.05 and 0.12 μm contributed to this wide range of $\tau_{gp,eq}$. Furthermore, $\tau_{gp,eq}$ may have been underestimated if a solid phase of precipitated (NH$_4$)$_2$SO$_4$ existed. In any case, it is clear that $\tau_{gp,eq}$ is much longer than τ_{mt} and τ_{chem} and is the quantity that should be compared with the characteristic times controlling the lifetime of atmospheric NH$_3$ (g) and NH$_4^+$ (p).

The major removal pathways of submicrometer ammoniated aerosol particles and NH$_3$ (g) are vertical mixing into clouds, scavenging by rain, and dry deposition. The characteristic time of vertical mixing of an air mass into a typical marine stratus cloud, τ_c, is about 3 × 10^3 s (0.8 hrs) (Brown, 1980). However, under conditions where clouds are not present or stable air stratifications exist, τ_c could be significantly longer.

The characteristic time of removal of ammonia from the atmosphere via rain, τ_r, may be defined as the burden of total ammonia divided by the rainwater flux. Based on the average total
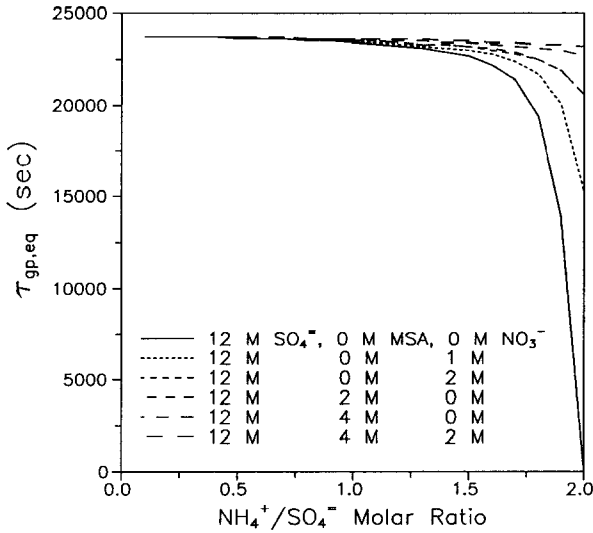
Fig. 8. The time for 95% of the NH_3 present to come to equilibrium between the gas and aqueous phases, $\tau_{gp,eq}$, as a function of NH_4^+ to $SO_4^=$ molar ratio. $\tau_{gp,eq}$ was calculated using (26) and H_{eff} derived from calculated equilibrium concentrations of NH_3 (aq) and NH_4^+ (aq), for $SO_4^=$, $CH_3SO_3^-$, and NO_3^- concentrations of 12, 0, and 0 M; 12, 0, and 1 M; 12, 0, and 2 M; 12, 2, and 0 M; 12, 4, and 0 M; and 12, 4, and 2 M.

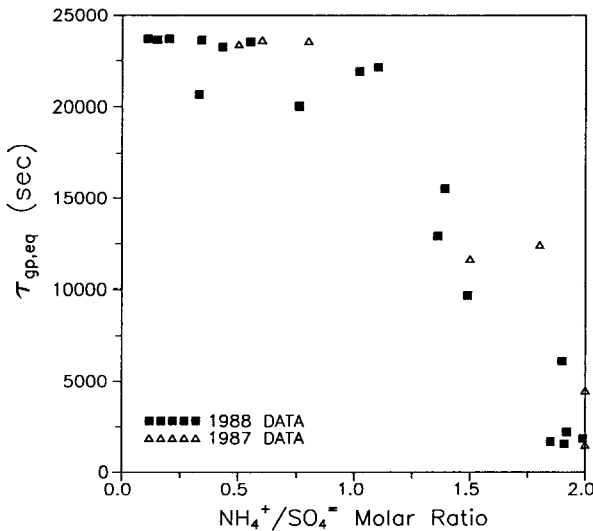Fig. 9. The time for 95% of the NH_3 present to come to equilibrium between the gas and condensed phases, $\tau_{gp,eq}$, as a function of NH_4^+ to nss $SO_4^=$ molar ratio for the 1987 and 1988 experiments. Data key is identical to Figure 6.

atmospheric ammonia concentration, $(NH_3)_g + (NH_4^+)_p$, during this study of 7.4 nmol m^{-3}, an average scale height of 1.5 km derived from radiosonde measurements, and a wet deposition rate ranging between 1.9 and 12 μmol m^{-2} d^{-1} (Galloway, 1985), the τ_r of total ammonia ranges from 8×10^4 sec to 5×10^5 sec (22 to 140 hrs).

A dry deposition characteristic time may be estimated using the same concentrations and a deposition velocity of 0.1 cm sec^{-1} (corresponding to a particle diameter of less than 0.5 μm). Under these conditions, the time of removal of NH_4^+ from the atmosphere through dry deposition, τ_d, is estimated to be 20 days. Since τ_d is much larger than τ_r and τ_c, it will be considered to be negligible.

For R_{AS} less than 1.8, $\tau_{gp,eq}$ was greater than τ_c by a factor of 3 at most. This suggests that the gas/particle system did not have time to attain equilibrium. However, because sampling was conducted during the 1987 and 1988 experiments under fair weather conditions, it is likely that τ_c was much longer than 0.8 hrs. Therefore, this difference in the estimated τ_c and $\tau_{gp,eq}$ may not be significant in terms of attainment of equilibrium. In support of this, the results of the chemical equilibrium model suggest that the gas/particle system was in equilibrium for R_{AS} less than 1.8.

For cases when $\tau_{gp,eq}$ is significantly less than τ_c and τ_r (i. e. for particles with R_{AS} close to 2.0), the lifetime of the NH_4^+ (p) should be sufficient for the atmospheric gas/particle system to come to equilibrium. However as discussed in Section 4.3, comparison of $(NH_3)_g$ calculated using the chemical equilibrium model with the measured value suggests that gas/particle equilibrium did not exist for R_{AS} between 1.8 and 2.0. This contradiction provides evidence that the equilibrium chemical model was not accurate in calculating $[NH_3]_p$ for R_{AS} close to 2.0.

The gas/particle system is complicated further if a non-uniform particle chemical composition exists at any one time in the atmosphere. In this case, a wide range of $\tau_{gp,eq}$ would result such that some particles may be in equilibrium with the gas phase while others will not (Hegg and Larson, 1990).

The lack of a Henry's law equilibrium for ammonia between the ocean surface and the atmosphere suggests that the equilibration time between these two phases is long compared with other concurrent processes. The time required to reach Henry's law equilibrium of NH_3 (g) across the air/sea interface, $\tau_{as,eq}$, can be estimated by: (1) calculating the atmospheric NH_3 (g) burden at equilibrium from K_{hN}, measured $[NH_3]_{s,tot}$, and an assumed boundary layer height and (2) dividing the equilibrium burden so calculated by the air/sea flux of NH_3. For a seawater temperature of 12°C, a pH of 8.2, and the average $[NH_3]_{s,tot}$ during this study of 0.45 μmol l^{-1}, the Henry's law equilibrium $(NH_3)_g$ is 1900 pptv. Assuming that the only sink for NH_3 (s) is transport to the atmosphere, that there are no direct sinks for atmospheric NH_3 (g), that the boundary layer height is 1.5 km, and that F from the ocean to the atmosphere is 10 μmol m^{-2} d^{-1}, the time required to reach a Henry's law concentration of NH_3 (g) is 1×10^6 sec (280 hrs).

During the 1987 and 1988 experiments, the measured $(NH_3)_g$ ranged from 0.2 to 77 pptv for R_{AS} less than 1.8. Corresponding calculated $\tau_{gp,eq}$ ranged between 1000 and 2.4×10^4 sec (0.3 and 6.7 hrs). Because $\tau_{as,eq}$ was much larger than $\tau_{gp,eq}$ and the $(NH_3)_g$ resulting from the atmospheric gas/particle equilibration was not sufficient to maintain the air/sea equilibration, a Henry's law equilibrium was not approached across the air/sea interface. In addition, $\tau_{as,eq}$ was estimated to be longer than both τ_c and τ_r, further preventing the establishment of a Henry's law equilibrium across the air/sea interface.

6. Conclusions

Measured concentrations of atmospheric NH_3 (g) were compared with calculated equilibrium concentrations to determine whether the atmospheric gas and particle phases were in equilibrium. The modeled and measured results agreed within experimental uncertainty for NH_4^+ to nss SO_4^- molar ratios less than 1.8. This indicates that for the conditions of this study, the gas and particle phases were in equilibrium at least for NH_4^+ to nss SO_4^- molar ratios less than 1.8. At greater molar ratios, the model overpredicted $(NH_3)_g$ by up to a factor of 1600. Although this overprediction could indicate that the gas/particle system was not in equilibrium, evaluation of the characteristic times suggests that the apparent disequilibrium resulted from the presence of acidic particulate species in the collected samples and/or solid phases in the particles that were not accounted for in the model. An increase in particle acidity would lead to a decrease in $(NH_3)_g$.

Gas/particle equilibration times calculated for the measured $(NH_3)_g$ ranged between 1000 and 2.4×10^4 sec (0.3 and 6.7 hrs) as the NH_4^+ to nss SO_4^- molar ratio decreased from 2.0 to 0.1. Processes removing ammonia from the atmosphere, vertical mixing into cloud and wet deposition, are estimated to have time constants of 3×10^3 sec (0.8 hrs) and 8×10^4 to 5×10^5 sec (22 to 140 hrs), respectively. A comparison of these times indicates that equilibrium may be approached for NH_4^+ to nss SO_4^- molar ratios near 2.0. For partially neutralized sulfate aerosol, the ability to reach equilibrium will be sensitive to the time of mixing into cloud. Particles of different composition exist together in the atmosphere at any one time. As a result, situations may arise where both equilibrated and non-equilibrated particles exist simultaneously.

Measured concentrations of atmospheric NH_3 (g) and NH_3 (s,tot) compared to Henry's law concentrations indicate that for the experimental conditions studied, a Henry's law equilibrium did not exist for ammonia across the air/sea interface. The calculated Henry's law equilibrium $(NH_3)_g$ was 1900 pptv resulting in a $\tau_{as,eq}$ of about 1×10^6 sec (280 hrs). Because $\tau_{as,eq}$ was longer than $\tau_{gp,eq}$ and the $(NH_3)_g$ resulting from the atmospheric gas/particle equilibration was less than that required to maintain an air/sea Henry's law equilibrium, equilibrium was not established across the air/sea interface. In addition, $\tau_{as,gp}$ was longer than both τ_c and τ_r, further preventing the establishment of a Henry's law equilibrium across the air/sea interface before NH_3 (g) and NH_4^+ (p) were removed from the atmosphere.

It is apparent that both chemical (reaction of NH_3 (g) with acidic sulfate particles) and physical processes (phase changes, vertical mixing into cloud, and wet deposition) affect the ability of the marine ammonia system to attain equilibrium between each of its phases. The most complete understanding of the equilibrium state of the system is obtained by considering the nature and characteristic times of all of the relevant processes.

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