

The H₂SO₄-HNO₃-NH₃ System at High Humidities and in Fogs

2. Comparison of Field Data With Thermodynamic Calculations

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Concentrations of HNO₃(g) and NH₃(g) determined in the field were compared to predictions from aerosol equilibrium models. The products of HNO₃(g) and NH₃(g) concentrations measured under cool and humid nonfoggy conditions agreed in magnitude with predictions from a comprehensive thermodynamic model for the atmospheric H₂SO₄-HNO₃-NH₃-H₂O system. Observed concentrations of NH₃(g) in fogs were generally consistent with those predicted at equilibrium with fog water, but important discrepancies were noted in some cases. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the sampling of nonfoggy pockets of air present within the fog. Detectable concentrations of HNO₃(g) (up to 23 neq m⁻³) were often found in fogs with pH < 5 and were attributed to the sampling of nonfoggy air or to the slow rate of HNO₃(g) diffusion to fog droplets. Concentrations of HNO₃(g) in fogs with pH > 5 were below the detection limit of 4-8 neq m⁻³.

INTRODUCTION

The chemical speciation of the H₂SO₄-HNO₃-NH₃-H₂O system between atmospheric phases has been the subject of much recent interest. Sulfuric acid nucleates with water vapor under usual atmospheric conditions [Kiang et al., 1973], but HNO₃ remains in the gas phase at relative humidities up to about 98% [Nair et al., 1983]. Ammonia is scavenged by acidic sulfate aerosols until eventual neutralization is achieved; however, it has a substantial vapor pressure over ammonium nitrate aerosol. A key question to our understanding of aerosol nitrate formation is the determination of NH₃ and HNO₃ vapor pressures over aerosol formed from H₂SO₄-HNO₃-NH₃ atmospheric mixtures.

A number of thermodynamic models have attempted to answer that question. Tang [1980] and Stelson and Seinfeld [1982a] studied the effect of relative humidity and pH on the vapor pressures of HNO₃ and NH₃ over their aqueous solutions. Stelson and Seinfeld [1982b] determined the dependence on temperature and relative humidity of the ammonium nitrate aerosol dissociation constant $K = P_{\text{HNO}_3} \times P_{\text{NH}_3}$ and later reported [Stelson and Seinfeld, 1982c] that addition of H₂SO₄ to the mixture does not lower K greatly unless the H₂SO₄/HNO₃ ratio is very large. Saxena et al. [1983] and Bassett and Seinfeld [1983, 1984] proposed comprehensive multiphase thermodynamic models for the H₂SO₄-HNO₃-NH₃-H₂O system.

All of the above models are basically consistent one with the other and represent various degrees of sophistication in the treatment of the H₂SO₄-HNO₃-NH₃ system. The Bassett and Seinfeld models offer at present the greatest level of chemical detail. In these models the equilibrium composition is calculated by minimizing the Gibbs free energy of a system composed of the gas phase species H₂SO₄(g), HNO₃(g), and NH₃(g); the aqueous phase species H⁺, HSO₄⁻, SO₄²⁻, NO₃⁻, and NH₄⁺; and the solid phases NH₄HSO₄(s), (NH₄)₃H(SO₄)₂(s), (NH₄)₂SO₄(s), NH₄NO₃(s), (NH₄)₂SO₄ · 3NH₄NO₃(s), and (NH₄)₂SO₄ · 2NH₄NO₃(s). The Bassett and

Seinfeld [1984] model considers in addition the increase in vapor pressure due to the Kelvin effect and thus predicts the size distribution of NO₃⁻ aerosol from the size distribution of SO₄²⁻ aerosol. The Bassett and Seinfeld [1983] model ignores the Kelvin effect, but this is reported to cause only a negligible underestimate of K . In the special case of the HNO₃-NH₃-H₂O system the Bassett and Seinfeld [1983] model reduces to the Stelson and Seinfeld [1982b] model, which uses the same thermodynamic data and ionic strength correction procedures.

The hygroscopic aerosol is an aqueous solution at high humidities, and Table 1 gives the reactions determining the speciation of HNO₃ and NH₃ under those conditions. K decreases rapidly with increasing humidity above the deliquescence point [Stelson and Seinfeld, 1982b]. Above 100% relative humidity, fog droplets form by activation of condensation nuclei, resulting in a considerable increase of the atmospheric liquid water content and a corresponding enhancement of HNO₃ and NH₃ heterogeneous condensation. Fog droplets are not at stable equilibrium with the surrounding water vapor, and thermodynamic models predicting K as a function of relative humidity cannot be applied; however, HNO₃(g) and NH₃(g) concentrations at equilibrium with the fog water can be directly calculated from measured fog water concentrations. Fog droplets are sufficiently dilute solutions that the Debye-Hückel expression for activity coefficients [Stumm and Morgan, 1981] is appropriate.

In fogs the equilibrium partitioning of HNO₃ and NH₃ between the gas phase and the fog water can be determined from the liquid water content, the fog water pH, and (R1)-(R3). Liquid water contents in fog range from 0.01-1 g m⁻³, and fog water pH values have been found to range from about 2 to 8 [Munger et al., 1983; Jacob et al., this issue]. Over 99% of total HNO₃ at equilibrium with fog water is scavenged as NO₃⁻ in this range of conditions (reaction (R1)). No measurable HNO₃(g) should therefore be found at equilibrium in fog, even acidic fog. On the other hand, the equilibrium speciation of NH₃ is strongly dependent on droplet pH, liquid water content, and temperature. The fraction F of total NH₃ scavenged by fog is given by:

$$F = \frac{LRTK_2[1 + (K_3[H^+])]}{1 + LRTK_2[1 + (K_3[H^+])]} \quad (1)$$

where the equilibrium constants K_2 and K_3 are the K_{298} values of Table 1 corrected for temperature with the Van't

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TABLE 1. Dissociation and Vapor Pressure Equilibria of HNO₃ and NH₃

Reaction Number	Reaction	K_{298} , kcal mol ⁻¹	ΔH_{298} , kcal mol ⁻¹	Reference
(R1)	HNO ₃ (g) = NO ₃ ⁻ + H ⁺	$3.2 \times 10^6 M^2 \text{ atm}^{-1}$	-17.3	Schwartz and White [1981]
(R2)	NH ₃ (g) = NH ₃ (aq)	$7.4 \times 10^1 M \text{ atm}^{-1}$	-6.8	Hales and Drewes [1979]
(R3)	NH ₃ (aq) + H ⁺ = NH ₄ ⁺	$1.7 \times 10^9 M^{-1}$	-12.5	Smith and Martell [1976]

Hoff equation, L is the liquid water content (cubic meters of water per cubic meter of air), R is the gas constant ($8.20568 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature. Note that in the derivation of (1) the Debye-Hückel activity coefficients cancel each other. F is plotted in Figure 1 as a function of pH under various conditions.

The thermodynamic approaches outlined above provide simple ways for treating aerosol formation and composition in atmospheric chemistry models; therefore it is important to determine the accuracy with which they can describe real atmospheric conditions. The model of Stelson and Seinfeld [1982b] has been tested with field data in three studies [Stelson and Seinfeld, 1982b; Harrison and Pio, 1983; Hildemann et al., 1984], which all reported that the products of measured HNO₃(g) and NH₃(g) concentrations agreed in magnitude with predicted values of K . Tanner [1983] found that the model of Tang [1980] adequately predicted concentrations of HNO₃(g) and NH₃(g) over dry aerosol, but he found large discrepancies at high humidities between his field data and the model of Tang [1980] for vapor pressures over aqueous aerosol. Bassett and Seinfeld [1983] reexamined the data of Tanner [1983] in light of their own model and again noted large discrepancies at high humidities between model and observations. No further tests of the Bassett and Seinfeld [1983] model have been reported to date.

Measurements of HNO₃(g) and NH₃(g) in fogs or clouds are few. Daum et al. [1984] found concentrations of both gases to be below the detection limit of 0.4 ppb (17 neq m^{-3}) in acidic stratus clouds (pH 3.2–4.2). No measurements are available in nonacidic fogs, where NH₃ should have a substantial vapor pressure. Ayers et al. [1984] have compared measured ground level NH₃(g) concentrations to those predicted from [H⁺] and [NH₄⁺] rainwater concentrations and reported large discrepancies between the two.

Over the course of an extensive sampling program in the wintertime atmosphere of the San Joaquin Valley of California [Jacob et al., this issue], we determined HNO₃(g) and NH₃(g) concentrations simultaneously with aerosol and fog water composition. In this paper we compare the concentrations of HNO₃(g) and NH₃(g) determined under non-foggy conditions to those predicted by the Bassett and Seinfeld [1983] model for the H₂SO₄-HNO₃-NH₃-H₂O system. Our data is well suited for such a comparison because the ions SO₄²⁻, NO₃⁻, and NH₄⁺ contributed over 90% of the ionic content of the aerosol. In fogs we compare measured concentrations of HNO₃(g) and NH₃(g) to those expected at equilibrium with the fog water concentrations; fog water pH values ranged from 2.9 to 7.6, thus spanning a broad range of predicted NH₃(g)-scavenging efficiencies (Figure 1).

Gaseous HNO₃ and NH₃ were determined by dual-filter methods [Russell and Cass, 1984]. Aerosol was collected on an open-faced Teflon filter surmounted by a cover to prevent collection of large particles by sedimentation. Fog water was collected with a rotating arm collector [Jacob et al., 1984].

The reader is referred to Jacob et al. [this issue] for a description of sampling sites, analytical methods, and a detailed analysis of measurement errors and biases associated with our sampling techniques.

We will generally present HNO₃(g) and NH₃(g) concentrations in units of equivalents per cubic meter, for consistency with the units of NO₃⁻ and NH₄⁺ aerosol concentrations. "Equivalent" in that sense refers to the proton donor or acceptor capacity of the gas when scavenged by the aerosol. Both HNO₃(g) and NH₃(g) contribute one equivalent per mole; 1 ppb = 43 neq m⁻³ at 5°C.

NONFOGGY CONDITIONS

The main site of the San Joaquin Valley sampling program was located in Bakersfield, California. The Bakersfield data are given in Table 2. For comparison with the Bassett and Seinfeld [1983] model the aerosol compositions were reduced to model mixtures of SO₄²⁻, NO₃⁻, NH₄⁺, and H⁺. This was done by assuming concentrations of H⁺ and OH⁻ to satisfy electroneutrality with the measured concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺. The presence of other ions in the real aerosol will perturb the thermodynamics, but this perturbation should be small because the ions SO₄²⁻, NO₃⁻, and NH₄⁺ contributed over 90% of the total aerosol ionic content [Jacob et al., this issue]. Aerosol concentrations of HCO₃⁻ and RCOO⁻ were not determined, but the balances of NH₄⁺ to (NO₃⁻ + SO₄²⁻) in Table 2 show no evidence of excess NH₄⁺ attributable to HCO₃⁻ or RCOO⁻ ammonium salts. Alkaline ammonium salts appear to be volatile under non-foggy conditions [Jacob et al., this issue]. Therefore the (SO₄²⁻, NO₃⁻, NH₄⁺, H⁺) mixture is an adequate model for the ionic content of the Bakersfield aerosol.

We applied the Bassett and Seinfeld [1983] model to describe two different partitioning modes for SO₄²⁻ and NO₃⁻: (1) SO₄²⁻ and NO₃⁻ present exclusively in different aerosol phases ("external mixture"), and (2) SO₄²⁻ and NO₃⁻ al-

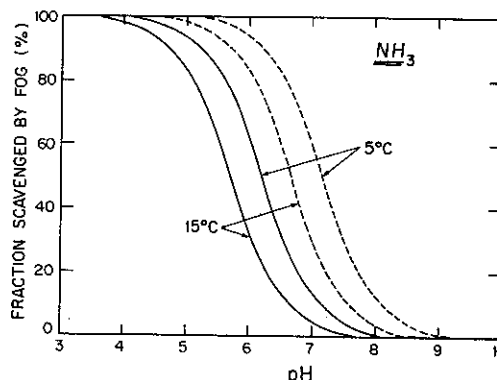


Fig. 1. Fraction of NH₃ scavenged by fog water at equilibrium. All fog droplets are assumed to be at the same pH. Liquid water contents of 0.05 g m⁻³ (solid line) and 0.5 g m⁻³ (dashed line) are considered.

TABLE 2. Bakersfield 1983–1984 Data for Aerosol and Gaseous H₂SO₄-HNO₃-NH₃ Species

Date	Time	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	NH ₃ (g)	HNO ₃ (g)	Temperature, °C	Relative Humidity, %
Dec. 31	0000–0345	573	351	351	19	17	7.8 ± 0.9	96
	1200–1610	669	467	297	158	4	10.8 ± 0.6	93
Jan. 1	0215–0815	242	170	89	212	<4	10.4 ± 0.6	96
	1200–1615	275	161	161	68	35	13.3 ± 0.7	76
Jan. 2	0000–0415	273	168	109	67	14	7.2 ± 1.1	89
	1200–1620	344	201	124	107	25	11.8 ± 0.7	74
Jan. 3	0000–0415	545	370	226	483	<4	9.1 ± 0.8	87
	1200–1615	769	445	445	113	11	9.2 ± 0.6	81
Jan. 4	1200–1700	1057	427	660	55	24	9.9 ± 1.3	80
Jan. 5	0100–0510	1141	442	731	63	6	6.9 ± 0.8	95
	1200–1615	923	362	596	60	19	8.8 ± 0.6	85
Jan. 6	0000–0415	1149	388	855	47	7	7.4 ± 0.6	95
Jan. 8	0000–0405	272	142	118	52	6	6.8 ± 0.6	95
Jan. 9	1420–1825	260	85	219	139	8	7.3 ± 0.6	86
Jan. 10	0000–0415	621	117	570	60	46	6.2 ± 0.6	89
	1200–1615	533	152	417	48	14	6.9 ± 0.8	85
Jan. 11	1200–1615	144	105	78	65	46	9.0 ± 0.7	71
Jan. 12	0000–0415	345	204	149	157	<4	3.0 ± 0.9	91
	1200–1615	331	244	169	334	26	11.2 ± 1.0	66
Jan. 13	0000–0400	486	283	407	208	<4	4.6 ± 0.7	96
	0700–1115	729	349	475	122	6	5.9 ± 0.8	91
	1200–1615	855	437	507	240	14	9.9 ± 1.1	73
	1800–2210	692	402	306	161	10	6.4 ± 0.8	85
Jan. 14	0050–0410	567	423	229	180	5	4.9 ± 1.2	89
	0735–1130	641	423	214	470	6	6.4 ± 1.0	85
	1200–1615	318	263	129	118	43	10.7 ± 1.5	61

Complete aerosol analyses are reported by *Jacob* [1985a].

Values are in nanoequivalents per cubic meter unless otherwise indicated; time is local time (PST); and relative humidity is calculated from temperature and dew point.

lowed in the same aerosol phases ("internal mixture"). The actual partitioning will lie somewhere between these two extremes, depending on the aerosol formation processes, the kinetics of coagulation, and the Kelvin effect on HNO₃ vapor pressure [Bassett and Seinfeld, 1984]. Since NH₄⁺ was always in excess of SO₄²⁻, the external mixture case was treated by assuming that all SO₄²⁻ was present as (NH₄)₂SO₄ and solving the equilibrium problem for the remaining HNO₃ and NH₃ with no SO₄²⁻ present. The internal mixture case was treated by directly solving the equilibrium problem for the H₂SO₄-HNO₃-NH₃-H₂O atmospheric system. The presence of SO₄²⁻ and NO₃⁻ in the same aqueous phase increases the solubility of HNO₃ and NH₃, compared to an external mixture [Stelson and Seinfeld, 1982c].

Samples were collected over 4-hour sampling periods, during which temperatures and relative humidities remained stable because of the prevalent low-overcast conditions (Table 2). Temperature and dew point were measured hourly at the National Weather Service (NWS) station 8 km north of the Bakersfield sampling site, and standard deviations for temperature over the 4-hour period were calculated from the hourly temperature record; 0.5°C was added to the standard deviation to account for the sensitivity of the readings. The dew point did not change significantly over the 4-hour sampling periods. A few temperature measurements taken at our sampling site were within 1°C of those taken by NWS. Measurements by the NWS confirm that temperatures and relative humidities at the NWS station are representative of those found at our Bakersfield site (D. Gudgel, Bakersfield NWS, private communication, 1984).

The Bassett and Seinfeld [1983] model was run with the computer code provided by Bassett [1984]. This code required as input the total (gas plus aerosol) concentrations of H₂SO₄,

HNO₃, and NH₃, the temperature, and the relative humidity. To calculate the errors on the predictions from the errors on the measurements, 100 sets of input variables were generated for each data point from a random scheme based on the observed values and standard errors for each of the variables; standard errors on the experimental determinations of concentrations were taken from *Jacob et al.* [this issue]. The expected values and standard errors for the output variables were determined from the outputs for the 100 sets of input variables. Results are shown in Figures 2a and 2b. The aerosol was predicted to be entirely aqueous except in a few cases (indicated on Figures 2a and 2b). The standard errors on the predicted values of *K* were mostly due to errors on the determinations of temperature and relative humidity; they were not affected by errors on H₂SO₄, HNO₃, and NH₃ concentrations in the external mixture assumption and were affected only very weakly in the internal mixture assumption. On the other hand, errors on the concentrations of the individual gases were strongly affected by errors on the determinations of concentrations, especially when a close balance existed between total NH₃ and total acids (HNO₃ + H₂SO₄). In those cases error bars were very large.

The products of partial pressures observed in the field agreed in magnitude with the values of *K* predicted by the model. However, the model predictions were consistently too low. Predictions with the external mixture assumption were closer to observations than with the internal mixture assumption. The model appeared to give better predictions for individual gases than for *K*, but this is deceiving. First, the errors on the predicted gas concentrations were large. Second, *K* was often so small that one of the gases was almost entirely depleted, and the remaining gas was then simply present at its concentration in excess of the neutralized aerosol.

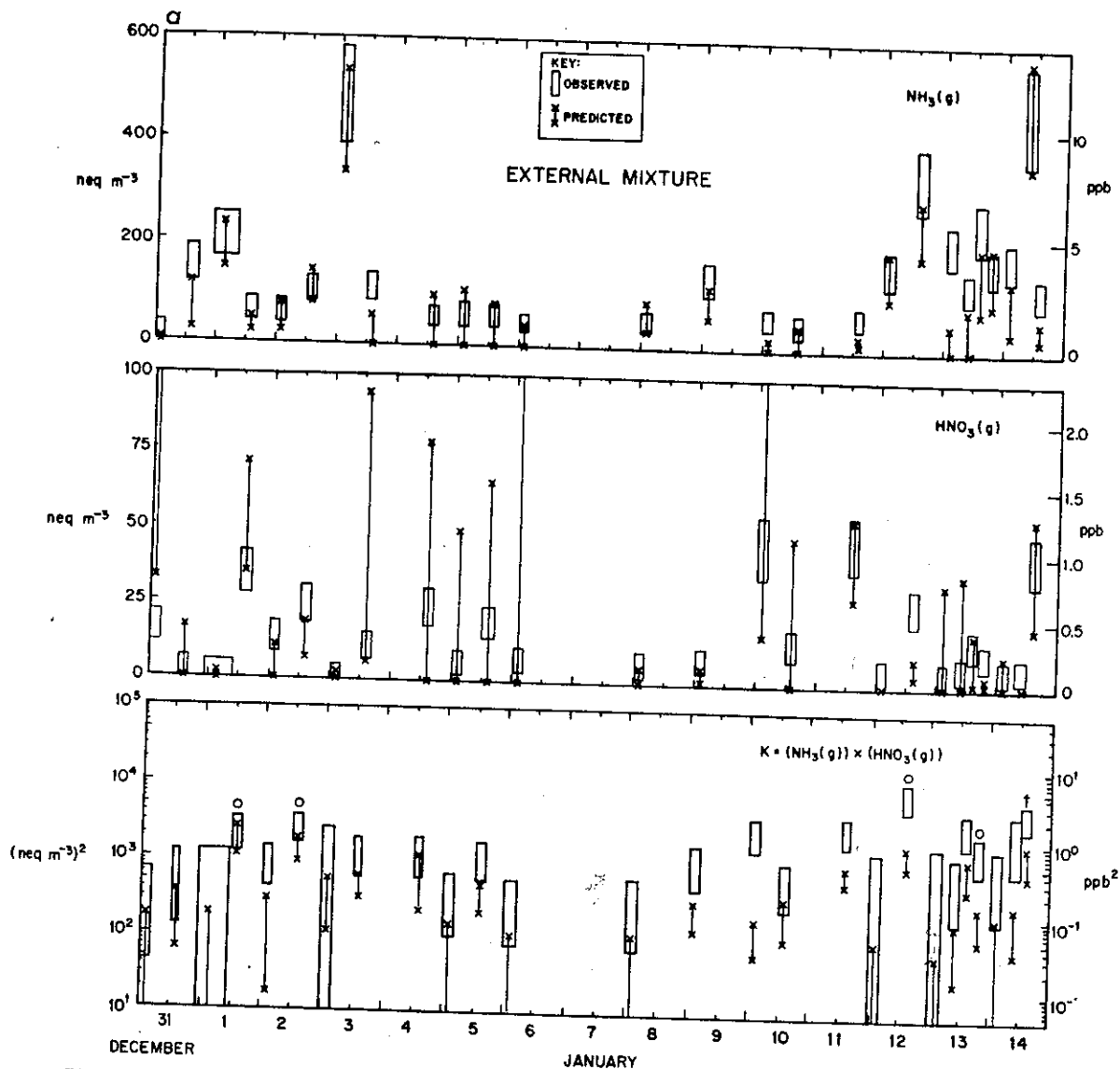


Fig. 2. Comparison of Bakersfield field data to the Bassett and Seinfeld [1983] aerosol equilibrium model: concentration products $(\text{HNO}_3(\text{g})) \times (\text{NH}_3(\text{g}))$, and individual concentrations of $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$. Results are given as error bars extending between the limits (mean $-\sigma$) and (mean $+\sigma$). The aerosol was predicted by the model to be an aqueous solution except when indicated by mixed aqueous-solid (open circle), or solid (dagger). Two limiting cases were considered: (a) SO_4^{2-} and NO_3^- present exclusively in different aerosol phases (external mixture assumption) and (b) SO_4^{2-} and NO_3^- allowed in the same aerosol phases (internal mixture assumption).

Stelson and Seinfeld [1982b] also found that the products of vapor pressures over aqueous aerosol were systematically underpredicted by their model, by factors similar to the ones we observed. Harrison and Pio [1983] did not find such a systematic trend, although their determinations may have been subject to large errors because of the considerable fluctuations in temperatures and relative humidities over the course of the sampling periods. Because of the many complicated processes occurring in the atmosphere it is difficult to assess the significance of the model underpredictions. Consideration of droplet curvature would increase the predicted K , but Bassett and Seinfeld [1984] found this increase to be negligible. Laboratory data of vapor pressures over concentrated ammonium nitrate solutions should provide a check on the accuracy of the thermodynamic calculations, but they are unavailable at this time.

The dual-filter method is known to be subject to positive interferences, that is, concentrations of $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$

may be overestimated [Appel et al., 1980]. Volatilization of NH_4NO_3 from the Teflon prefilter leads to artifact $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$, but in our case this problem is minimized because temperatures and relative humidities remained stable over the course of the sampling periods (Table 2). Another source of positive interference is the displacement of NO_3^- or NH_4^+ by nonvolatile material collected on the filter, for example, acid sulfates or alkaline carbonates. However, if such displacement reactions occurred on the filter, this would mean that the atmosphere itself was not at equilibrium; in that case, $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$ atmospheric concentrations could have differed substantially from their equilibrium values.

Indeed, a possible explanation for the discrepancies observed is that the atmosphere was not at chemical equilibrium. The NH_3 observed at Bakersfield originated mostly from local ground level sources [Jacob et al., this issue]; HNO_3 and NH_3 may not have had time to mix sufficiently for equilibrium to be achieved. The incorporation of $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$

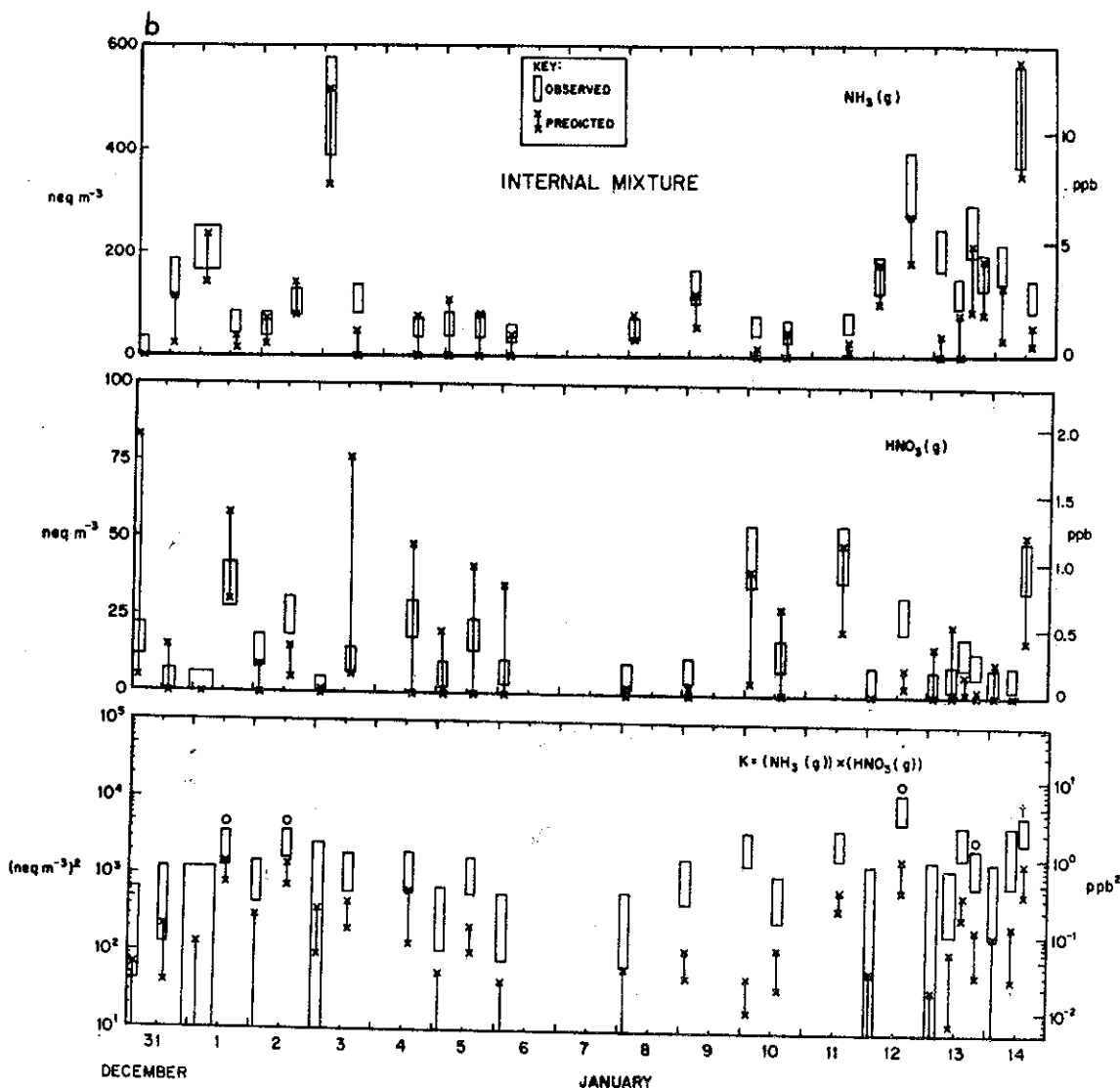


Fig. 2. (continued)

into the aerosol at high humidities proceeds mostly by heterogeneous condensation, which can be a slow process. Based on the calculations of *Fuchs and Sutugin* [1971] over a range of representative conditions, one finds that the diffusion-controlled equilibration time of a gas with low vapor pressure may range from minutes to hours (depending, among other things, on the "sticking coefficient" of the gas molecule on the aerosol).

FOGGY CONDITIONS

Nine concurrent samples of fog water, HNO₃(g), and NH₃(g) were collected during the winter 1983–1984 San Joaquin Valley sampling program at Bakersfield and several other sites, and 19 more samples were collected in a similar program conducted the following winter. All samples were collected during intervals with dense fog throughout. The data are given in Table 3. Concentrations of NH₃(g) at equilibrium with the fog water were calculated from (R2) and (R3):

$$(\text{NH}_3(\text{g})) = \frac{1}{RTK_2K_3} [\text{NH}_4^+]/[\text{H}^+] \quad (2)$$

where [NH₄⁺] and [H⁺] are the fog water concentrations (equivalents per liter of water), and (NH₃(g)) is the NH₃(g)

concentration (equivalents per liter of air). The standard errors on predicted (NH₃(g)) were determined from standard errors of $\pm 1^\circ\text{C}$ on temperature and 15% on the determinations of [NH₄⁺] and [H⁺] [*Jacob et al.*, this issue]. Several fog water samples were generally collected over the course of one NH₃(g)-sampling period; equilibrium NH₃(g) concentrations were calculated from the fog water concentrations in each individual sample and then time averaged. Results are shown in Table 3 and Figure 3.

The NH₃(g) concentrations calculated from (2) were consistent with observed NH₃(g) concentrations in 22 of the 28 comparisons: they agreed to within a factor of 2 for NH₃(g) concentrations above the detection limit (nine cases) and correctly predicted NH₃(g) concentrations below the detection limit (13 cases). In the remaining six comparisons, however, the agreement was poor. Nonattainment of equilibrium is an unlikely explanation for the observed discrepancies; equilibrium of NH₃(g) with fog water at $\rho\text{H} > 5$ is achieved rapidly because of the relatively low solubility of NH₃ [*Chameides*, 1984]. Also, see discussion by *Jacobs* [1985b] and *Chameides* [1985]. However, a major source of error in our calculations is that the fog droplets collected in a fog water sample were not of uniform composition. Fog droplets supporting a

TABLE 3. Concentrations of HNO₃(g) and NH₃(g) in Fogs

Date	Temperature, °C	HNO ₃ (g)/NH ₃ (g) Sampling Period, PST	Fog Water Sampling Periods	pH ^a	NH ₄ ⁺ , μeq L ⁻¹	NH ₃ (g) ^b Predicted, neq m ⁻³	NH ₃ (g) Observed, neq m ⁻³	HNO ₃ (g) Observed, neq m ⁻³
<i>Bakersfield</i>								
Jan. 13, 1984	4	0000-0400	0130-0200	6.38	3190	370 ± 86	208	4 ^c
			0200-0300	5.92	2800			
			0300-0330	6.72	5920			
			0330-0400	6.74	3300			
Dec. 28, 1984	4	0000-0225	0035-0115	6.80	2680	309 ± 73	363	N/A
			0130-0215	6.20	2780			
Jan. 2, 1985	3.5	2115-0000	2100-2300	6.20	1100	38 ± 15	<25	<6
			2300-0000	5.60	1990			
Jan. 3, 1985	4	0000-0300	0000-0200	5.72	1340	19 ± 7	39	<6
			0200-0305	5.66	1290			
Jan. 3, 1985	2	0300-0700	0305-0500	4.30	781	64 ± 30	262	<4
			0530-0700	6.83	928			
Jan. 3, 1985	1	0700-0930	0700-0830	6.82	1070	161 ± 47	118	<7
			0830-0930	6.51	2900			
Jan. 3-4, 1985	-1	2300-0155	2300-0000	7.08	592	143 ± 42	91	<6
			0000-0100	7.57	379			
			0124-0155	6.76	268			
Jan. 4, 1985	3	2000-2255	2010-2100	6.26	946	22 ± 7	40	<6
			2100-2130	5.16	1340			
			2200-2300	5.46	1440			
Jan. 4-5, 1985	3.5	2310-0205	2300-0000	5.55	1860	11 ± 3	<25	<6
			0000-0100	5.20	1770			
			0100-0200	5.10	1850			
Jan. 5, 1985	2	0400-0805	0400-0500	4.96	1500	7 ± 3	<17	<4
			0500-0600	5.92	1080			
			0600-0700	4.80	1660			
			0700-0800	4.52	720			
Jan. 14, 1985	4.5	0130-0430	0130-0230	6.17	2430	165 ± 45	<25	N/A
			0230-0330	5.56	2390			
			0330-0430	6.72	2170			
Jan. 18, 1985	4	2015-2315	2005-2105	5.85	2400	14 ± 7	<25	9
			2105-2200	4.85	1710			
			2200-2300	4.18	1610			
Jan. 19, 1985	4	0000-0300	0000-0100	3.99	1450	<1	<25	9
			0100-0200	3.86	1450			
Jan. 20, 1985	4	0720-0940	0200-0300	3.67	1590	<1	<29	23
			0715-0800	3.06	3130			
			0800-0845	3.06	3360			
			0845-0930	2.92	3500			
<i>McKittrick</i>								
Jan. 5, 1984	5	0045-0415	0005-0100	4.02	399	<1	<19	<5
			0100-0200	4.00	347			
			0200-0300	4.02	344			
			0300-0435	4.21	357			
Jan. 6, 1984	5	0000-0410	0035-0100	4.23	241	<1	<16	7
			0100-0200	4.03	294			
			0200-0300	4.22	499			
			0300-0400	4.20	333			
Jan. 7, 1984	5	0000-0415	0400-0500	4.14	345	<1	<16	9
			0000-0100	3.96	136			
			0115-0150	4.41	186			
			0200-0300	4.26	162			
Jan. 7, 1984	5	1200-1615	0300-0400	4.40	204	<1	<16	11
			0400-0500	4.44	166			
			1030-1230	4.23	683			
			1230-1440	4.24	870			
Jan. 8, 1984	5	0000-0410	1440-1540	4.28	740	1 ± 1	<16	5
			1540-1655	4.12	522			
			2035-0035	4.18	599			
Jan. 10, 1984	5	0045-0445	0035-0205	4.50	555	<1	<17	10
			0205-0405	5.01	658			
			0010-0120	3.71	845			
			0120-0525	3.85	351			
<i>Buttonwillow</i>								
Jan. 7, 1984	6	0100-0500	0040-0140	5.18	1270	10 ± 4	69	4 ^c
			0140-0410	5.40	969			
			0410-0620	5.33	1070			
Jan. 3, 1985	4	0000-0220	0000-0215	5.25	2080	11 ± 4	159	<7
Jan. 4, 1985	3	0020-0220	0015-0215	5.73	553	8 ± 3	42	<8
Jan. 4, 1985	1.5	0415-0810	0430-0630	6.14	519	16 ± 6	<17	<4

TABLE 3. (continued)

Date	Temperature, °C	HNO ₃ (g)/NH ₃ (g) Sampling Period, PST	Fog Water Sampling Periods	pH ^a	NH ₄ ⁺ , μeq L ⁻¹	NH ₃ (g) ^b Predicted, neq m ⁻³	NH ₃ (g) Observed, neq m ⁻³	HNO ₃ (g) Observed, neq m ⁻³
<i>Buttonwillow (continued)</i>								
Jan. 4, 1985	4	1930-2135	1930-2030	6.55	968	124 ± 33	79	N/A
Jan. 5, 1985	2.5	0220-0410	2030-2135	6.76	858			
Jan. 5, 1985	2	0415-0810	0205-0300	5.70	529	8 ± 2	102	<9
			0300-0400	5.87	483			
			0400-0500	6.16	456			
			0500-0615	6.78	683			
			0615-0700	6.89	582			
0700-0800	6.87	542	75 ± 21	145	<8			
<i>Visalia</i>								
Jan. 7, 1984	6	0145-0335	0120-0250	6.97	860	355 ± 90	592	<8
			0250-0430	7.23	678			

Measurement errors for NH₃(g) and HNO₃(g) were about 20%. Detection limits depended on filter run time [Jacob et al., this issue]. N/A = not analyzed.

^aFog water concentrations. Complete fog water analyses are reported by Jacob [1985a] for the January 1984 data and by Waldman [1986] for the December 1984 to January 1985 data.

^bAverage over time of NH₃(g) concentrations predicted from fog water concentrations and equation (2).

^cDetection limit.

measurable partial pressure of NH₃ contain alkalinity, and [H⁺] will not be conserved upon the mixing of alkalinity-containing droplets of different compositions in the sample. Further, (NH₃(g)) is proportional to 1/[H⁺], a quantity which is not properly averaged by measurement of pH in the collected sample. The resulting errors will depend on the extent of nonuniformity in the fog water composition and are difficult to estimate, but they could clearly account for most of the discrepancies. The large variations in pH often observed between two consecutive fog water samples (Table 3) are indicative of the variability in fog water composition.

The largest discrepancies were observed for four sampling periods at Buttonwillow when the fog water pH was in the range 5-6. In those four cases, equilibrium with fog water considerably underpredicted the observed NH₃(g) concentrations. Fog water at pH 5-6 scavenges most of the atmospheric NH₃ (Figure 1) but returns it to the gas phase upon evaporation [Jacob et al., this issue]. An explanation for the large discrepancies that were sometimes observed in this pH range is the existence within the fog of pockets of air undersaturated with respect to water vapor [Gerber, 1981]. These air pockets would support much larger concentrations of NH₃(g)

than the bulk foggy atmosphere and would correspondingly affect the measured NH₃(g) concentration. Further, sampling of undersaturated air may evaporate fog droplets previously collected on the aerosol prefilter and cause artifact NH₃(g).

Concentrations of HNO₃(g) in fogs were at or below the detection limit in fogs with pH > 5, but detectable HNO₃(g) concentrations (5-23 neq m⁻³) were found in fogs with lower pH. The presence of HNO₃(g) in acidic fog cannot be explained on the basis of equilibrium with fog water. However, the presence of HNO₃(g) can be explained by the substantial vapor pressure of HNO₃(g) over the acid precursor aerosol; undersaturated air pockets within the fog would support HNO₃(g) at equilibrium. An additional explanation is that detectable HNO₃(g) concentrations may subsist for some time in the fog because of the slow rate of HNO₃(g) diffusion to the droplets. Chameides [1984] reports that scavenging of HNO₃(g) by diffusion to the fog droplets proceeds on a time scale of a few minutes, but this time may be longer if organic films form at the surface of the droplets [Gill et al., 1983].

CONCLUSION

Concentrations of HNO₃(g) and NH₃(g) were determined in the field under both foggy and nonfoggy conditions, simultaneously with aerosol and fog water composition. Observed concentrations were compared to predictions from thermodynamic models.

Measurements under nonfoggy, cool, and humid conditions (temperatures 3°-13°C, relative humidities 60-100%) were compared to predictions from the Bassett and Seinfeld [1983] model for the H₂SO₄-HNO₃-NH₃-H₂O system. The observed products of HNO₃ and NH₃ vapor pressures were of the same magnitude as those predicted by the model; however, the model predictions were consistently too low. The agreement between observations and model was slightly improved by assuming that SO₄²⁻ and NO₃⁻ were present in different phases (external mixture).

Concentrations of NH₃(g) were below the detection limit of 17-30 neq m⁻³ in fogs with pH < 5, and this is consistent with thermodynamic predictions. Substantial NH₃(g) concentrations were observed in fogs with higher pH; the observed concentrations were usually within a factor of 2 of those predicted at equilibrium with the fog water, but some

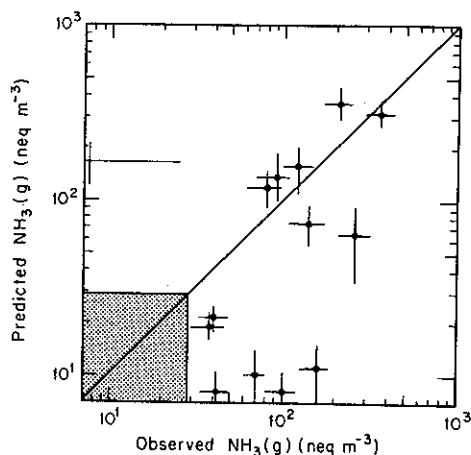


Fig. 3. NH₃(g) concentrations at equilibrium with fog water versus observed NH₃(g) concentrations. Both were below the detection limit for 13 of the points (shaded area). Line represents 1:1 agreement between predictions and observations.

important discrepancies were noted. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the presence of pockets of undersaturated air within the fog.

Concentrations of HNO₃(g) were at or below the detection limit of 4–8 neq m⁻³ in fogs with pH > 5; but detectable concentrations (5–23 neq m⁻³) were often found in fogs with lower pH. Because HNO₃(g) should not be present at equilibrium with fog water, we attribute our observations to the presence of undersaturated air within the fog or to the slow rate of HNO₃(g) diffusion to the fog droplets.

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