The Atmospheric Chemistry and Physics of Ammonia

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Photo from UMD Aztec, 2002
Talk Outline

I. Fundamental Properties
   Importance
   Reactions
   Aerosol formation
   Thermodynamics
   Role as ccn

II. Local Observations
   Observed concentrations
   Impact on visibility
   Box Model results
   New Detection Technique

III. Fun Stuff – if there’s time.
Atmospheric Ammonia, NH₃
I. Fundamental Properties

Importance
• Only gaseous base in the atmosphere.

• Major role in biogeochemical cycles of N.

• Produces particles & cloud condensation nuclei.
  • Haze/Visibility
  • Radiative balance; direct & indirect cooling
  • Stability wrt vertical mixing.
  • Precipitation and hydrological cycle.

• Potential source of NO and N₂O.
Fundamental Properties, continued

Thermodynamically unstable wrt oxidation.

\[
\text{NH}_3 + 1.25\text{O}_2 \rightarrow \text{NO} + 1.5\text{H}_2\text{O}
\]

\[
\Delta H^\circ_{\text{rxn}} = -53.93 \text{ kcal mole}^{-1}
\]

\[
\Delta G^\circ_{\text{rxn}} = -57.34 \text{ kcal mole}^{-1}
\]

But the kinetics are slow:

\[
\text{NH}_3 + \text{OH} \cdot \rightarrow \text{NH}_2 + \text{H}_2\text{O}
\]

\[
k = 1.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad \text{(units: (molec cm}^{-3}\text{)}^{-1} \text{ s}^{-1})
\]

Atmospheric lifetime for [OH] = 10^6 cm^{-3}

\[
\tau_{\text{NH}_3} = (k[\text{OH}])^{-1} \approx 6 \times 10^6 \text{ s} = 72 \text{ d.}
\]

Compare to \( \tau_{\text{H}_2\text{O}} \approx 10 \text{ d.} \)
Fundamental Properties, continued

Gas-phase reactions:

\[
\begin{align*}
\text{NH}_3 + \text{OH}\cdot & \rightarrow \text{NH}_2\cdot + \text{H}_2\text{O} \\
\text{NH}_2\cdot + \text{O}_3 & \rightarrow \text{NH}, \text{NHO}, \text{NO} \\
\text{NH}_2\cdot + \text{NO}_2 & \rightarrow \text{N}_2 \text{ or N}_2\text{O (} + \text{H}_2\text{O)}
\end{align*}
\]

Potential source of atmospheric NO and N\textsubscript{2}O in low-SO\textsubscript{2} environments.

Last reaction involved in combustion “deNO\textsubscript{x}” operations.
Fundamental Properties, continued

Aqueous phase chemistry:

\[ \text{NH}_3(g) + \text{H}_2\text{O} \leftrightarrow \text{NH}_3\cdot\text{H}_2\text{O}_{(aq)} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \]

Henry’s Law Coef. = 62 M atm\(^{-1}\)

Would not be rained out without atmospheric acids.

Weak base: \( K_b = 1.8 \times 10^{-5} \)
Formation of Aerosols

**Nucleation** – the transformation from the gaseous to condensed phase; the generation of new particles.

H$_2$SO$_4$/H$_2$O system *does not* nucleate easily.

NH$_3$/H$_2$SO$_4$/H$_2$O system *does* (e.g., Coffman & Hegg, 1995).
Formation of aerosols, continued:

\[ \text{NH}_3(g) + \text{H}_2\text{SO}_4(l) \rightarrow \text{NH}_4\text{HSO}_4(s, l) \] (ammonium bisulfate)

\[ \text{NH}_3(g) + \text{NH}_4\text{HSO}_4(l) \rightarrow (\text{NH}_4)_2\text{SO}_4(s, l) \] (ammonium sulfate)

Ammonium sulfates are stable solids, or, at most atmospheric RH, liquids.

**Deliquescence** – to become liquid through the uptake of water at a specific RH (~40% RH for \( \text{NH}_4\text{HSO}_4 \)).

**Efflorescence** – the become crystalline through loss of water; *literally to flower*.

We can **calculate** the partitioning in the \( \text{NH}_4/\text{SO}_4/\text{NO}_3/\text{H}_2\text{O} \) system with a thermodynamic model; see below.
**FIGURE 9.4** Diameter change of \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{HSO}_4\), and \(\text{H}_2\text{SO}_4\) particles as a function of relative humidity. \(D_{p0}\) is the diameter of the particle at 0% RH.
Formation of aerosols, continued

\[
\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{s})
\]

\[\Delta G_{\text{rxn}}^\circ = -22.17 \text{ kcal mole}^{-1}\]

\[
K_{\text{eq}} = \frac{[\text{NH}_4\text{NO}_3]}{[\text{NH}_3][\text{HNO}_3]} = \exp \left( -\frac{\Delta G}{RT} \right)
\]

\[K_{\text{eq}} = 1.4 \times 10^{16} \text{ at } 25^\circ \text{C}; \quad = 1.2 \times 10^{19} \text{ at } 0^\circ \text{C}\]

Solid ammonium nitrate (\text{NH}_4\text{NO}_3) is unstable except at high [\text{NH}_3] and [\text{HNO}_3] or at low temperatures. We see more \text{NH}_4\text{NO}_3 in the winter in East.
Ammonium Nitrate Equilibrium in Air = f(T)

\[
\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{s})
\]

\[-\ln(K) = 118.87 - 24084 - 6.025\ln(T) \text{ (ppb)}^2\]

\[
\frac{1}{K_{eq}} 298K = [\text{NH}_3][\text{HNO}_3] \text{ (ppb)}^2 = 41.7 \text{ ppb}^2
\]

\[
\left(\sqrt{41.7} \approx 6.5 \text{ ppb each}\right)
\]

1/\(K_{eq}\) 273K = 4.3x10\(^{-2}\) ppb\(^2\)

*Water* in the system shifts equilibrium to the right.
**Radiative impact on stability:** Aerosols reduce heating of the Earth’s surface, and can increase heating aloft. The atmosphere becomes more stable wrt vertical motions and mixing – inversions are intensified, convection (and rain) inhibited (e.g., Park et al., *JGR.*, 2001).
Additional Fundamental Properties

• Radiative effects of aerosols can accelerate photochemical smog formation.

• Condensed–phase chemistry tends to inhibit smog production.

• Too many ccn may decrease the average cloud droplet size and inhibit precipitation.

• Dry deposition of NH$_3$ and HNO$_3$ are fast; deposition of particles is slow.
II. Local Observations
Annual mean visibility across the United states
(Data acquired from the IMPROVE network)
Fort Meade, MD
Summer: Sulfate dominates.

Winter: Nitrate/carbonaceous particles play bigger roles.
- Seasonal variation of 24-hr average concentration of NO$_y$, NO$_3^-$, and NH$_4^+$ at FME.
ISORROPIA Thermodynamic Model (Nenes, 1998; Chen 2002)

Inputs: Temperature, RH, T-$\text{SO}_4^{2-}$, T-$\text{NO}_3^-$, and T-$\text{NH}_4^+$

Output: $\text{HNO}_3$, $\text{NO}_3^-$, $\text{NH}_3$, $\text{NH}_4^+$, $\text{HSO}_4^-$, $\text{H}_2\text{O}$, etc.
ISORROPIA Thermodynamic Model (Nenes, 1998; Chen, 2002)

Inputs: Temperature, RH, T-SO$_4^{2-}$, T-NO$_3^-$, and T-NH$_4^+$

Output: HNO$_3$, NO$_3^-$, NH$_3$, NH$_4^+$, HSO$_4^-$, H$_2$O, etc.
Comparison of PM$_{2.5}$ at FME and visibility at BWI

\[ y = 0.0084x + 0.0589 \]

\[ R^2 = 0.4752 \]

(Data acquired in July 1999)
Comparison of PM$_{2.5}$ at FME and visibility at BWI

\[ y = 0.0084x + 0.0589 \]
\[ R^2 = 0.4752 \]

\[ y = 0.0074x + 0.0377 \]
\[ R^2 = 0.6851 \]

(Water amount estimated by ISORROPIA)
Interferometer for NH$_3$ Detection

Schematic diagram detector based on heating of NH$_3$ with a CO$_2$ laser tuned to 9.22 µm and a HeNe laser interferometer (Owens et al., 1999).
Linearity over five orders of magnitude.
Response time (base e) of laser interferometer ~ 1 s.
TABLE 2.7 Estimated Global Ammonia Emissions

<table>
<thead>
<tr>
<th>Source of Ammonia</th>
<th>Emission (Tg(N) yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ANTHROPOGENIC</strong></td>
<td></td>
</tr>
<tr>
<td>Dairy cattle</td>
<td>5.5</td>
</tr>
<tr>
<td>Beef cattle/buffalo</td>
<td>8.7</td>
</tr>
<tr>
<td>Pigs</td>
<td>2.8</td>
</tr>
<tr>
<td>Horses</td>
<td>1.2</td>
</tr>
<tr>
<td>Sheep/goats</td>
<td>2.5</td>
</tr>
<tr>
<td>Poultry</td>
<td>1.3</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>6.4</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td><strong>30.4</strong></td>
</tr>
<tr>
<td><strong>NATURAL</strong></td>
<td></td>
</tr>
<tr>
<td>Wild animals</td>
<td>2.5</td>
</tr>
<tr>
<td>Vegetation</td>
<td>5.1</td>
</tr>
<tr>
<td>Ocean</td>
<td>7.0</td>
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<tr>
<td><strong>Subtotal</strong></td>
<td><strong>14.6</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>45.0</strong></td>
</tr>
</tbody>
</table>

*Source: Dentener and Crutzen (1994).*

*Emissions from vehicles can be important in urban areas.*
Summary:

- Ammonia plays a major role in the chemistry of the atmosphere.
- Major sources – agricultural.
- Major sinks – wet and dry deposition.
- Positive feedback with pollution – thermal inversions & radiative scattering.
- Multiphase chemistry
  - Inhibits photochemical smog formation.
  - Major role in new particle formation.
  - Major component of aerosol mass.
  - Thermodynamic models can work.
- Rapid, reliable measurements will put us over the top.

Go Terps!
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EPRI
The End.
MODIS: August 9, 2001

Highest Ozone of the Summer

“Visible” Composite

Aerosol Optical Depth at 550 nm

Robert Levy, NASA
Donora, PA Oct. 29, 1948
Madonna
Harten Castle
Germany: Ruhr area
Portal figure
Sandstone
Sculptured 1702
Photographed 1908
Madonna
Harten Castle
Germany: Ruhr area
Portal figure
Sandstone
Sculptured 1702
Photographed 1969
<table>
<thead>
<tr>
<th>Salt</th>
<th>DRH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>84.2 ± 0.3</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>84.2 ± 0.4</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>80.0</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>79.9 ± 0.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>75.3 ± 0.1</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>74.3 ± 0.4</td>
</tr>
<tr>
<td>(NH₄)₃H(SO₄)₂</td>
<td>69.0</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>61.8</td>
</tr>
<tr>
<td>NaHSO₄</td>
<td>52.0</td>
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<tr>
<td>NH₄HSO₄</td>
<td>40.0</td>
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