Atmospheric Chemistry
Lecture 1: Chemical Principles and Stratospheric Ozone Chemistry

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Basic Chemical Concepts

- Chemical composition and units of measurement
- Reactants: molecules, radicals, ions
- Reactions: primary, binary, tertiary, chain reaction, catalysis
- Equilibrium
- Reaction Rates and Lifetimes
- Photochemistry
- Dry and wet deposition
The bulk composition of the air (99.997% by vol.) consists of mainly $\text{N}_2$, $\text{O}_2$, Ar, $\text{CO}_2$. These are stable species with little or no interesting chemistry!

About 99% of the mass of the atmosphere is located below 50 km, in the stratosphere and the troposphere.
Because we deal with such trace amounts of material, we have adopted special units of measure to describe the concentration of gas phase chemical compounds in the atmosphere.

- **Number Density** (molecules/cm³)

- **Mass Density** (kg/m³ or g/cm³).

- Frequently we use dimensionless volume mixing ratio:

  \[ \mu_i = \frac{n_i}{n_a} \]

  where \( n_i \) is the number density of species \( i \) and \( n_a \) is the air number density.

- and mass mixing ratio:

  \[ \tilde{\mu}_i = \frac{\rho_i}{\rho_a} \]

  where each now refers to the mass density of species \( i \) and of air.
Mixing ratios are usually volume mixing ratios unless indicated, and usually presented as follows:

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-6}$</td>
<td>parts per million (ppmv)</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>parts per billion (ppbv)</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>parts per trillion (pptv)</td>
</tr>
</tbody>
</table>

The “v” in the units refers to volume mixing ratios, which are used so much more frequently than mass mixing ratios that we often get lazy and leave the “v” off the units.

Going from one unit to the next is accomplished by approximating the atmosphere as an ideal gas and then using the ideal gas law:

$$pV = nRT$$

where $p$ is pressure, $V$ is volume, $n$ is number of moles, $R$ is the gas constant (0.0821 L-atm/(mol-K)).

You will also need to know Avogadro’s constant, which defines the mole as $6.022 \times 10^{23}$ molecules.
Basic Chemical Concepts

Reactants

- **Reactants** are individual chemical compounds that participate in reactions. Several types are important in atmospheric processes:

- **Free radicals**: neutral compounds containing an odd number of electrons. These are highly reactive. The most important free radical in the atmosphere is hydroxyl, which is the combination of oxygen and hydrogen atoms:

\[
:O\cdot \cdot H
\]

to form a complex with one unpaired electron that REALLY wants to find another electron:

\[
:O::H
\]

- **Ions**: an atom or molecule that carries a positive or negative electric charge as a result of having lost or gained one or more electrons. Ions are important:
  - in the upper reaches of the atmosphere (above 6km, from cosmic radiation),
  - in clouds (lightning from thunderstorms), and
  - in the liquid droplets themselves.
  - E.g., the dissolution of nitric acid in clouds or fog, and is one of the primary contributors (along with \(H_2SO_4\)) to “acid rain.”

\[
HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-\]
Basic Chemical Concepts

Reactions

- **unimolecular reaction** (reaction involving one species), e.g., photodissociation of ozone:
  \[
  O_3 + \hbar \nu \ (290 \ nm < \lambda < 350 \ nm) \rightarrow O + O_2 \quad (1)
  \]

  The oxygen atom reacts quickly with water to form 2 molecules of hydroxyl in a
  **bimolecular reaction** (reaction involving two reactants):
  \[
  O \ + \ H_2O \rightarrow 2 \ OH \quad (2)
  \]

  The net result of this sequence is the formation of OH from ozone photolysis:
  \[
  O_3 \ + \ h\nu \ + \ H_2O \rightarrow 2 \ OH \ + \ O_2
  \]

- Reactions 1 and 2 are **elementary reactions**, that is, they cannot be subdivided into
two or more simpler reactions. Together they form a **chain reaction**. Reaction 1 is the
one that started it up, and this is called the **initiation step**. Subsequent steps, such as
reaction 2 and others that may follow are called **propagation steps** in the reaction.

- A chain reaction will end with the formation of stable products (called the **termination
step**):
  \[
  OH \ + \ NO_2 \ + \ M \rightarrow HNO_3 \ + \ M
  \]

In this reaction, nitric acid is formed in a **termolecular reaction** (a reaction involving
three reactants). M is commonly N\textsubscript{2} or O\textsubscript{2} and stabilizes the product through collisions.
Without such collisions, the nitric will have so much internal energy that is will fall apart
as soon as it is formed.
A **catalytic cycle** is one in which a molecule significantly changes or enables a reaction cycle without being altered by the cycle itself. The example that we will see later today is the catalytic destruction of stratospheric ozone, which is carried out by the following mechanism:

\[
\begin{align*}
X \cdot + O_3 & \longrightarrow XO\cdot + O_2 \\
O_3 + hv & \longrightarrow O + O_2 \\
O + XO\cdot & \longrightarrow X \cdot + O_2 \\
\text{Net:} & \quad 2 O_3 + hv \longrightarrow 3 O_2
\end{align*}
\]

Here, the radical X (which can be Cl, NO, Br, etc.) **catalyzes** the destruction of ozone and is regenerated in the process, thus allowing for the cycle to repeat over and over … “a little goes a long way”!
Many chemical reactions occur in both directions such that the products are able to re-form the reactants. The result is that equilibrium will be established between products and reactants. In the example:

\[ \text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^- \]

Equilibrium can be described by:

\[ K = \frac{[\text{H}^+][\text{NO}_3^-]}{[\text{HNO}_3]} = 15.4 \text{M} \]

Note that all reactions have an equilibrium constant associated with them. In the gas phase reaction:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

The equilibrium constant is about $10^{140}$. Most gas phase reactions are like this, that is, they are irreversible.
Basic Chemical Concepts

Reaction Rate Laws

- The speed of a chemical reaction is called the reaction rate. The science that deals with reaction rates is called chemical kinetics. A basic understanding of chemical kinetics is crucial to atmospheric chemistry.

- In chemical kinetics-speak, unimolecular reactions are part of a class of reactions called first-order reactions:

\[
\begin{align*}
  & A \quad \xrightarrow{k} \quad \text{products} \\
  & - \frac{d\left[A\right]}{dt} = k \cdot \left[A\right].
\end{align*}
\]

- We define k as the reaction rate constant, which is a constant of proportionality between the rate at which A is depleted and the concentration of A, defined as:

\[
- \frac{d\left[A\right]}{dt} = k \cdot [A].
\]

- If we look at the rate at which A is depleted, the solution to the above differential equation is:

\[
\left[A\right] = \left[A\right]_o \exp\left(-kt\right)
\]

- Where \([A]_o\) is the initial concentration of A. In this process, A will have a chemical lifetime that can be characterized by:

\[
\tau = \frac{1}{k}
\]
Most reactions in the atmosphere are bimolecular, and we call these reactions **second-order reactions**. In the reaction:

\[ aA + bB \xrightarrow{k} \ldots + cC + \ldots \]

the rate coefficient is defined as:

\[
- \frac{1}{a} \frac{d[A]}{dt} = k \cdot [A]^a \cdot [B]^b = \frac{1}{c} \frac{d[C]}{dt}.
\]

Analogous to the case of first order reactions, the chemical lifetime of A is defined as:

\[ \tau_A = \frac{1}{k [B]^b} \]

What if you have numerous reactions that compete in depleting A? How do we determine the lifetime of A? We sum up the individual contributions as follows:

\[ \tau^{-1} = \tau_a^{-1} + \tau_b^{-1} + \ldots \]
A plot of the lifetime of chemical compounds in the atmosphere shows a **wide variety**, from seconds (in the case of free radicals), to centuries (in the case of stable molecules). Also note that the chemical lifetime determines the spatial and temporal variability of the species. Long-lived gases such as CFCs are well mixed in the troposphere, whereas radicals exhibit much more temporal and spatial variability.
Lastly, many reactions are termolecular, or third-order, reactions. The example given above demonstrates one such reaction:

$$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$$

How do we deal with calculating the rates of such reactions? In most termolecular reactions, one compound is present at equal concentrations before, during, and after the reaction. In the example above, the species M is one of these compounds. Since M remains constant during the reaction, we can simplify the kinetics by representing it as a pseudo-second-order reaction:

$$-\frac{d[\text{NO}_2]}{dt} = k' \cdot [\text{OH}]$$

where \(k' = k[M]\)

All the rules of second order reactions thus apply!
Don’t forget, that in the case of a chain reaction:

\[ \text{A} \xrightarrow{k_1} \text{B} + \text{C} \]

\[ \text{B} + \text{D} \xrightarrow{k_2} \text{products} \]

you need to consider both the production and loss of B when you apply rate equations:

\[
\frac{d[B]}{dt} = k_1 \cdot [A] - k_2 \cdot [B][D]
\]

Another important concept is that, often, compounds are in **steady state**. If B were in steady state in the above example, then

\[
\frac{d[B]}{dt} = k_1 \cdot [A] - k_2 \cdot [B][D] = 0
\]
Basic Chemical Concepts

**Photochemistry**

ปาก One of the unique features of the “atmospheric chemical reactor” is that many reactions are initiated by the absorption of photons of solar radiation. We have already seen an example of this:

\[
O_3 + \text{hv} \ (290 \text{ nm} < \lambda < 350 \text{ nm}) \rightarrow O + O_2
\]

ปาก Just as we defined a rate constant for a chemical reaction, so too can we define a photodissociation rate constant \( J_i \) (sometimes in the vernacular you hear these referred to as “J-values,” given by:

\[
- \frac{d[O_3]}{dt} = J_{O_3} \cdot [O_3].
\]

ปาก Note the important difference between J values and regular rate constants. In the case of photochemistry, J is not constant but is a function of must be computed for each compound considering the time of day, and altitude. The expression for this is:

\[
J_i = \int_{\lambda_{\text{max}}}^{\lambda_{\text{min}}} \sigma_i(\lambda) \cdot \phi_i(\lambda) \cdot I(\lambda) \cdot d\lambda
\]

where \( \sigma_i(\lambda) \) is the absorption cross-section of compound \( i \) (often given in cm\(^2\)/molecule), \( I(\lambda) \) is the photon flux (units of photons/cm\(^2\)), and \( \Phi_i(\lambda) \) is the quantum yield of the reaction, which states the probability that the absorption of a photon will result in a reaction.
For many gases and for particles as well, deposition to surfaces competes with chemical reaction for the depletion of those species. We will consider **dry and wet deposition**.

**Dry deposition** refers to the flux into surfaces in the absence of precipitation (but the surface can be wet), whereas **wet deposition** applies to deposition into fogs, clouds, rain, or snow where the gas is incorporated in the bulk solution.

In both cases, the relationship between the concentration of species \( i \) and the vertical flux, \( \Phi_i \), to a surface is given by:

\[
\Phi_i = v_d [C_i]
\]

where \( v_d \) is deposition velocity of species \( i \) with units of, most commonly, cm/s. The deposition velocity is difficult to define by first principles, depending on:

- the type of surface (tree, grass, asphalt, etc)
- atmospheric conditions (temperature, pressure, wind)
- the reference height at which the concentration of species \( i \) is measured
Both can be a function of the solubility of the gas, so an important parameter that dictates the deposition velocity is the **Henry’s law constant**, $H_c$, for the gas. Henry’s law is the expression that defines the partitioning of a species between gas and solution phase:

$$[C_{soln}] = H_c [C_{gas}]$$

For solutions of water, molecules that dissolve readily are termed **hydrophilic**, whereas those that are sparingly soluable are termed **hydrophobic**.

- Examples of hydrophilic compounds, for which wet deposition or dry deposition onto wetted surfaces is a significant loss mechanism include the agents of acid rain, $H_2SO_4$ and $HNO_3$, and ammonia.
- Examples of hydrophobic compounds are hydrocarbons such as the alkanes, e.g., methane.
Stratospheric Ozone Chemistry: Origins

**Chapman Mechanism**

- Ozone is produced by the photodissociation of $O_2$ by solar UV radiation:
  \[
  O_2 + h\nu (\lambda < 242 \text{ nm}) \rightarrow O + O
  \]
  \[
  2 \left[ O + O_2 + M \rightarrow O_3 + M \right]
  \]
  \[
  \text{Net:} \quad 3O_2 + h\nu \rightarrow 2O_3
  \]

- The following reaction sequence then recycles ozone back into $O_2$:
  \[
  O_3 + h\nu \rightarrow O + O_2
  \]
  \[
  O + O_3 \rightarrow 2O_2
  \]
  \[
  \text{Net:} \quad 2O_3 + h\nu \rightarrow 3O_2
  \]

- Ozone in the stratosphere is maintained as a result of a dynamic balance between these formation and destruction processes. From 1930 to 1975, this was the basis for our understanding of the ozone layer. We now know that the loss mechanism from the Chapman scheme accounts for only 20% of ozone loss.
Stratospheric Ozone Chemistry

Catalytic Ozone Destruction Cycle: Chlorine

(Rowland and Molina, 1975)

1. **ULTRAVIOLET LIGHT**
   **CHLOROFLUOROCARBON MOLECULE**
   
   **ULTRAVIOLET LIGHT BREAKS OFF A CHLORINE ATOM FROM A CHLOROFLUOROCARBON MOLECULE**

2. **CHLORINE ATOM**
   **OZONE MOLECULE**
   
   **THE CHLORINE ATTACKS OZONE BREAKING IT APART**

3. **CHLORINE MONOXIDE**
   **OXYGEN MOLECULE**
   
   **AN OXYGEN MOLECULE AND CHLORINE MONOXIDE ARE FORMED**

4. **CHLORINE ATOM**
   **OXYGEN MOLECULES**
   
   **AFTER AN OXYGEN ATOM BREAKS UP CHLORINE MONOXIDE, THE CHLORINE IS FREE TO BEGIN THE PROCESS AGAIN (2)**
Catalytic Ozone Destruction Cycle: Chlorine

(Rowland and Molina, 1975)

\[
\begin{align*}
\text{ClO} + \text{ClO} + M & \rightarrow \text{Cl}_2\text{O}_2 + M \\
\text{Cl}_2\text{O}_2 + h\nu & \rightarrow \text{Cl} + \text{ClO}_2 \\
\text{ClO}_2 + M & \rightarrow \text{Cl} + \text{O}_2 + M \\
\text{then:} \quad 2 \times (\text{Cl} + \text{O}_3) & \rightarrow 2 \times (\text{ClO} + \text{O}_2) \\
\text{net:} \quad 2 \text{O}_3 & \rightarrow 3 \text{O}_2
\end{align*}
\]

Termination Steps

\[
\begin{align*}
\text{ClO} + \text{NO}_2 + M & \rightarrow \text{ClONO}_2 + M \\
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3
\end{align*}
\]
Predicted ozone loss (%) vs. year calculation was made

Measured ozone loss (DU) over Antarctica ... showing a nosedive in the 1970s.
Stratospheric Ozone Chemistry

View this movie at:
http://www.atm.ch.cam.ac.uk/tour/anim_toms.html

TOMS Ozone measurements
The good news (sort of): Proved chlorine chemistry is causing ozone destruction!

The bad news: ClO levels were 100 times higher than predicted by gas-phase models ... something was missing in the models...
Stratospheric Ozone Chemistry

Polar Stratospheric Clouds
The polar winter leads to the formation of the polar vortex which isolates the air within it.

Cold temperatures form inside the vortex; cold enough for the formation of Polar Stratospheric Clouds (PSCs). As the vortex air is isolated, the cold temperatures and the PSCs persist.
How Polar Stratospheric Clouds Help Chlorine Destroy Ozone

**Without Clouds**

Ultraviolet light from the sun breaks chlorofluorocarbons (CFCs) apart. The resulting chlorine (Cl) exists either as chlorine monoxide (ClO), formed in a reaction with ozone (O₃), or as free chlorine. Gases in the atmosphere, such as nitrogen dioxide (NO₂) and methane (CH₄), react with ClO and Cl to trap the chlorine in inert chemical reservoirs of chlorine nitrate (ClONO₂) and hydrochloric acid (HCl). Ozone depletion is minimal.

**With Clouds**

Polar stratospheric clouds, however, initiate chemical reactions that free molecular chlorine (Cl₂) from the reservoirs. The ClO-ClO catalytic cycle begins once sunlight breaks Cl₂ apart. The Cl atoms react with ozone, forming ClO and oxygen (O₂). ClO forms its dimer (Cl₂O₂), which is quickly broken by sunlight into Cl and O₂. Chlorine then attacks ozone again. PSCs also prevent reservoirs from forming by removing nitrogen from the atmosphere through the precipitation of nitric acid (HNO₃). Bromine will also destroy ozone in catalytic reaction with ClO (not shown).
Recall the termination steps for the Chlorine catalytic cycle:

\[
\text{ClO} + \text{NO}_2 + M \rightarrow \text{ClONO}_2 + M
\]

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3
\]

Once the PSCs form, heterogeneous reactions take place and convert the inactive chlorine reservoirs to more active forms of chlorine.

\[
\text{HCl} + \text{ClONO}_2 \rightarrow \text{HNO}_3 + \text{Cl}_2
\]

\[
\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}
\]

\[
\text{HCl} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{Cl}_2
\]

\[
\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{HNO}_3 + \text{ClONO}
\]

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\ \text{HNO}_3
\]

No ozone loss occurs until sunlight returns to the air inside the polar vortex and allows the production of active chlorine and initiates the catalytic ozone destruction cycles. Ozone loss is rapid. The ozone hole currently covers a geographic region a little bigger than Antarctica and extends nearly 10km in altitude in the lower stratosphere.
The largest eruption of the 20th Century

20 million tons of SO$_2$ emitted into the stratosphere, which rapidly forms H$_2$SO$_4$ aerosols.
Stratospheric Ozone Chemistry

Stratospheric aerosols following Pinatubo eruption as measured by SAGE II (Aerosol optical depth indicated)

Before

During

0.5-1 $\mu m^2/cm$

18 mos. after

Core after 5 mos.

35 cm$^2/cm$

Avg: 20 $\mu m^2/cm$
Stratospheric Ozone Chemistry

Following the Pinatubo eruption, 1992-93 levels of ozone were at record lows.

- Observations from various stations recorded a reduction in stratospheric Ozone of between 6-30%.
- Pinatubo aerosols may have been responsible for the loss of 10% of Antarctic ozone "before" the Antarctic ozone hole formed in the winter of 1992.
- Over the Antarctic ozone was 50% lower than normal between 13-16 km altitude and was totally absent between 16-18 km.
- Ozone hole appeared over Europe for the 1st time.
Equitorial Ozone following Pinatubo eruption as measured by TOMS (from NASA/Goddard Space Flight Center Scientific Visualization Studio)

View this movie at:
http://svs.gsfc.nasa.gov/vis/a000000/a002100/a002183/