Chapter 18: Atmosphere & Environment

Read: BLB 18.1–4
HW: BLB 18.9,11,15,29, 69; Sup 18:1–3

Know:
Types of Chemical reactions in the atmosphere
Ozone cycle
Ozone depletion and the ozone hole
Greenhouse effect, gases involved
Effect of CFC's
Global Warming
Pollution in the troposphere
  sulfur compounds & acid rain
  nitrogen oxides & smog

Atmospheric Profiles

Temperature profile of atmosphere
  At high temperature is the average KE of molecules high or low?

Pressure profile of atmosphere
  Low pressure means few molecular collisions
  Do Chemical reactions occur more or less frequently?
Composition of the Atmosphere

**TABLE 18.1 Composition of Dry Air Near Sea Level**

<table>
<thead>
<tr>
<th>Component*</th>
<th>Content (mole fraction)</th>
<th>Molar Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.78084</td>
<td>28.013</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.20948</td>
<td>31.998</td>
</tr>
<tr>
<td>Argon</td>
<td>0.00934</td>
<td>39.948</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.000375</td>
<td>44.0099</td>
</tr>
<tr>
<td>Neon</td>
<td>0.00001818</td>
<td>20.183</td>
</tr>
<tr>
<td>Helium</td>
<td>0.00000524</td>
<td>4.003</td>
</tr>
<tr>
<td>Methane</td>
<td>0.000002</td>
<td>16.043</td>
</tr>
<tr>
<td>Krypton</td>
<td>0.00000114</td>
<td>83.80</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0000005</td>
<td>2.0159</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>0.0000005</td>
<td>44.0128</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.00000087</td>
<td>131.30</td>
</tr>
</tbody>
</table>

*Ozone, sulfur dioxide, nitrogen dioxide, ammonia, and carbon monoxide are present as trace gases in variable amounts.

Describe as:

**mole fraction**  \[ x_i = \frac{\text{moles of } i}{\text{total moles}} \]

**Report in parts per million (ppm):**

\[ 1 \text{ ppm} = x_i \times 10^6 \]

**Example:** Neon  \[ x_{Ne} = 0.00001818 \]

**How many ppm?**

**Report partial pressures of components:**

*Use barometric pressure for total P*

**Example:** If \( P_{BAR} = 0.987 \text{ atm} \), What is \( P_{Ne} \)?

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**Photochemical Reactions in the Atmosphere**

**Definition:**

**Photoexcitation:**

\[ \text{NO}_2(g) + h\nu \rightarrow \text{NO}_2^*(g) \]

**Photodissociation:**

\[ \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \]

**Example:** What is the maximum wavelength photon that has sufficient energy to photodissociate the \( \text{O}_2 \) bond? (Bond energy for \( \text{O}_2 \) = 495 kJ/mol)

**Photoionization:**

\[ \text{N}_2 + h\nu \rightarrow \text{N}_2^+ + e^- \]

**Requires** \( E \geq \) Ionization potential
Importance of Atmospheric Ozone ($O_3$)

\[ \text{O}_3 \overset{\text{resonance forms}}{\rightleftharpoons} \text{O} = \text{O} \]

**Structure**
- How many resonance forms?
- Molecular geometry is ______, bond angle = ______
- Bond Order is _____ \(\Rightarrow\) bond length = 1.28 Å (bond length in $O_2$ is 1.21 Å; agrees with VSEPR predictions)

**Properties:**
- Light blue gas
- Pungent odor (smell near electrical discharges)
- \(\Delta H_f^\circ = 142 \text{kJ/mol}\) (reactive... less stable than $O_2$)

**Atmospheric Concentration:**
- In the **troposphere**: $O_3$ is an irritant (smog)
- In the **stratosphere**: $O_3$ is essential; peak concentration at \(\sim 25 \text{ km}\); \([O_3] \sim 10 \text{ ppm}\)

Why is ozone essential in the stratosphere?
$O_3$ in stratosphere blocks most radiation with \(\lambda = 240-320 \text{ nm}\) by undergoing photochemistry

Why is blocking this range of light important?

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**The Natural Ozone Cycle**

- **Formation of $O_3$**
  \[ O_2 + h \nu \rightarrow 2O \quad \lambda < 242 \text{nm} \]
  \[ O + O_2 \rightarrow O_3 \]

- **UV-blocking by $O_3$**
  \[ O_3 + h \nu \rightarrow O_2 + O \quad \lambda < 320 \text{nm} \]

The (small) amount of $O_3$ in the stratosphere reflects the delicate balance between creation of $O_3$ and destruction of $O_3$. 

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http://www.theozonehole.com
CFC’s react with ozone; upset the cycle

\[ \text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl}^\cdot + \text{Cl}^\cdot \quad (\lambda < 240\text{nm}) \]

\[ 2\text{Cl}^\cdot + 2\text{O}_3 \rightarrow 2\text{ClO}^\cdot + 2\text{O}_2 \]

\[ \text{ClO}^\cdot + \text{ClO}^\cdot \rightarrow \text{ClOOCl} \]

\[ \text{ClOOCl} + h\nu \rightarrow \text{ClOO}^\cdot + \text{Cl}^\cdot \]

\[ \text{ClOO}^\cdot + h\nu \rightarrow \text{Cl}^\cdot + \text{O}_2 \]

NET: \[ 2\text{O}_3 \rightarrow 3\text{O}_2 \]

- Cl atom from CFC catalyzes O\(_3\) destruction
- 1 Cl atom destroys ~2 million O\(_3\) molecules

Dramatic Seasonal Loss of Ozone over South Pole

- Complex reactions related to presence of polar stratospheric clouds
- Nearly complete loss of ozone at some altitudes near the poles, ~50% total reduction at other latitudes near the poles.
- Away from the poles, depletion is not as great and is seasonal (~10% over Australia in 1987).
- Global concentration of O\(_3\) has been on the decline since 1980.

You can sunburn in < 7 min. in Chile & Argentina; population of Australia has 6% lethal skin cancer vs. 0.3% general world population ⇒ bring your sunblock
The Greenhouse Effect

Earth absorbs, then radiates heat (infrared)
- $\text{H}_2\text{O}$ and $\text{CO}_2$ absorb certain wavelengths of IR radiation, which traps ~84% of this energy
- UV and visible radiation escape through atmosphere, but IR is absorbed: Greenhouse Effect
- Without the greenhouse effect, Earth would be ~33° colder (water → ice)

Global Temperatures are Rising

Projections:
- $\text{CO}_2$ levels are expected to double in 25 years.
  - 1.5–4.5 change in global T (?)
  - 1–5m rise in ocean levels (but then more $\text{CO}_2$ dissolves!)
  - shift in climate and crop production

Solutions:
1. Reduce fossil fuel consumption
2. Reforestation (decrease $\text{CO}_2$)
Chemistry and Pollution in the Troposphere

Acid Rain:

Chemistry of S in the atmosphere:

\[ \text{2SO}_2(g) + \text{O}_2(g) \rightarrow \text{2SO}_3(g) \]
\[ \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4 \]

Sources:
- bacterial decay of organic matter
- volcanic gases
- forest fires
- fossil fuels combustion
- industrial processes

http://www.epa.gov/airmarkets/cmap/mapgallery/mg_so2.html
Acid Rain

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1999

Natural Rain pH ≈ 6
Acid Rain pH of 4 to 4.5
- affects pH of soil and water
- corrodes metals (Fe)
- dissolves stone (marble, limestone)

CaCO₃(s)+H₂SO₄(aq)→CaSO₄(aq)+CO₂(g)+H₂O(ℓ)

http://upload.wikimedia.org/wikipedia/commons/thumb/5/54/-Acid_rain_damaged_gargoyle_.jpg/800px--Acid_rain_damaged_gargoyle_.jpg

Chemistry and Pollution in the Troposphere

Photochemical Smog:
- primary pollutants +hv→ secondary pollutants

In auto engines:
N₂ + O₂→ 2NO ∆H = 181kJ

In air:
1) 2NO + O₂→ 2NO₂
   NO₂ + hν→ 2NO + O ∆H = –400nm
   O + O₂ + R→O₃ + R⁺ R = molecule
2) NO₂ + H₂O→ HNO₃ (What does this do to your eyes?)

Why is ozone not good in the troposphere?
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http://en.wikipedia.org/wiki/Smog