Module 7: Combustion and Environment

Lecture 36: Atmosphere

The Lecture Contains:

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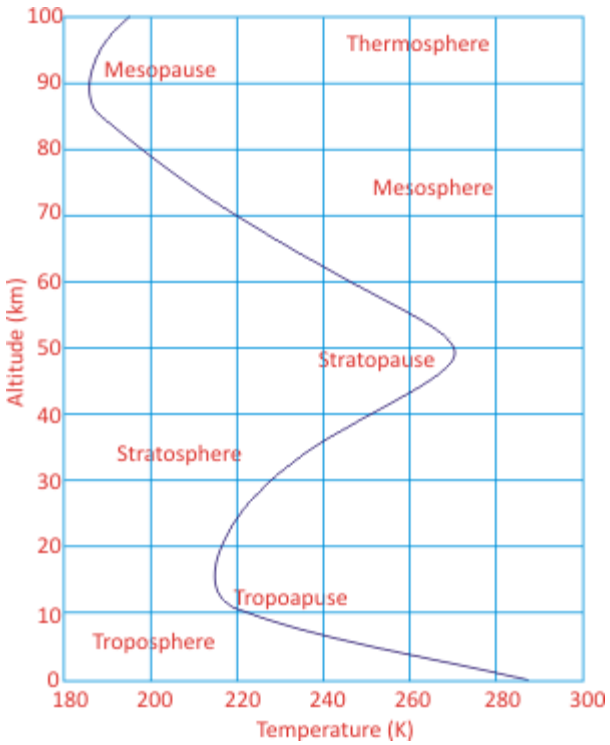
Atmosphere

Figure 1: Variation of temperature with altitude



(Figure 35.3)

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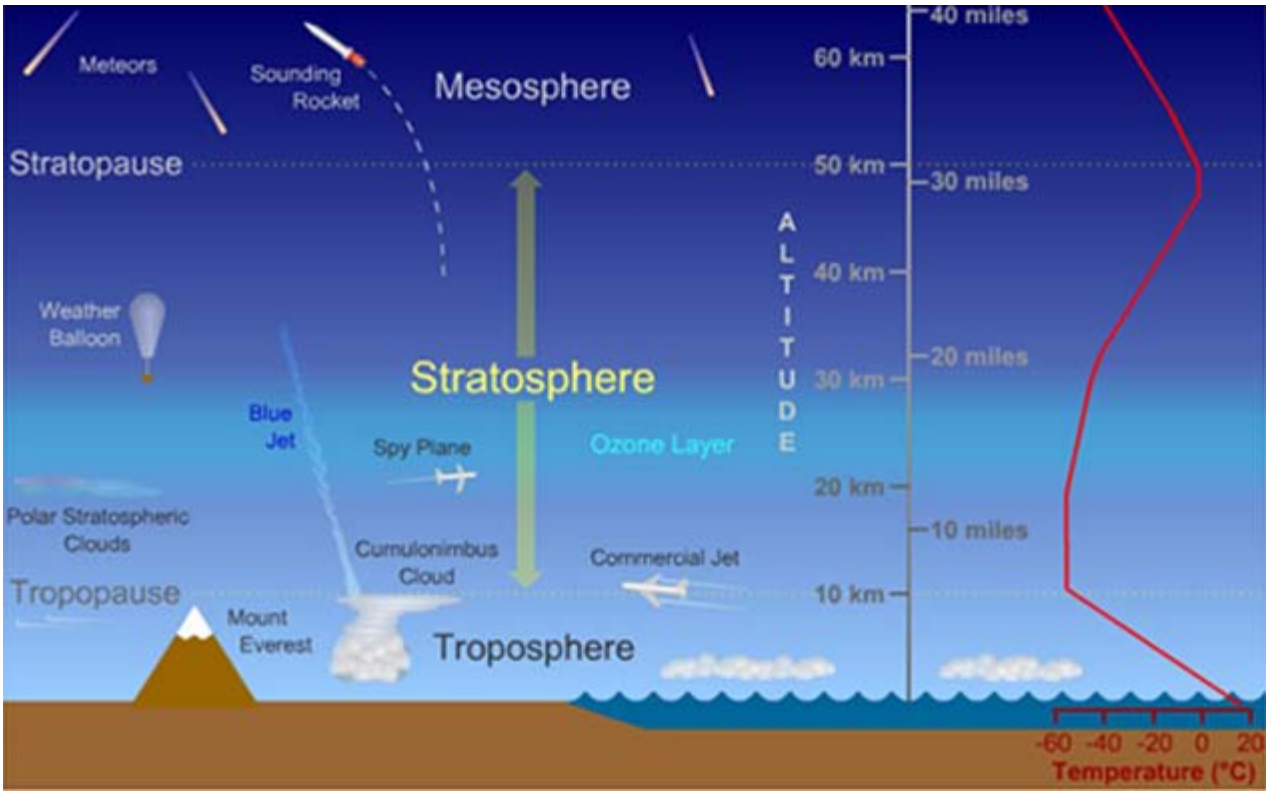
Atmosphere



Source: http://www.theresilientearth.com/files/images/stratosphere_diagram.jpg

(Figure 36.1)

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Atmosphere (Contd..)

Troposphere

- Region where we are living.
- Contains 90% of the mass of the atmosphere.
- Starts at ground level with 228 K and ends at 18 km (200 K) with 6 K drop in temperature per km altitude.
- Beyond 18 km, temperature rises. This inflection point is called "Tropopause".
- Tropopause divides troposphere from stratosphere.
- Atmospheric boundary layer - 2 km from the ground level.
- Combustion byproducts instantly affects this region.

Photochemical chain reaction begin with dissociation of ozone as given below

$$O_3 + \text{UV Sunlight}(h\lambda) \rightarrow O_2 + O(1_D) \text{ for } \lambda < 320\ nm \qquad \text{--------(1)}$$

The atomic oxygen $O(1_D)$ reacts with water vapor to form hydroxyl radical

$$O(1_D) + H_2O \rightarrow 2\,OH \qquad \text{--------(2)}$$

The OH radical reacts with CO and initiates other chain reactions as below

$$OH + CO \rightarrow H + CO_2 \qquad \text{--------(3)}$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{--------(4)}$$

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Atmosphere (Contd..)

The peroxy radicals HO_2 are recycled to OH by the following reaction:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad \text{----------(5)}$$

Cycling of OH and HO_2 is turned off by several reactions involving OH, HO_2 and NO_2

$$OH + NO_2 \rightarrow HNO_3 \quad \text{----------(6)}$$

NO and NO_2 pair is produced via the following chain reactions.

$$HO_2 + NO \rightarrow OH + NO_2 \quad \text{----------(7)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{----------(8)}$$

$$NO_2 + UV(sunlight) \rightarrow NO + O \quad \text{----------(9)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{--------(10)}$$

Concentration of ozone and NO_x can also be influenced by non-photolytic reactions during night time.

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Atmosphere (Contd..)

Stratosphere

- Region between tropopause (18 km) and stratopause (50 km).
- Contains 9.5% of atmospheric mass.
- The temperature increases from tropopause (220 K) to stratopause (280 K).
- The chemicals from troposphere that are not destroyed are dissociated in this region.
- CFC is converted into CO_2, HF and mixture of CI compounds.
- The photochemistry in the stratosphere is strongly affected by ozone layer.
- The short wavelength $(\lambda_{UV} < 290nm)$ cannot reach below 25 km due to the photochemistry.
- This is how we are protected from the harmful UV rays.
- Stratospheric O_3 column is the major absorber of solar UV between 220 and 320 nm.
- Depletion of ozone layer will change the tropospheric chemistry in two ways
    i. Lowers the flux of O_3 into troposphere
    ii. Enhances the production of OH

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Chemical Emission From Combustion

Most of the fossil fuels can be depicted by the following chemical equation

$$C_xH_{2y} + \left(x + \frac{y}{2}\right)(O_2 + 3.76N_2) \rightarrow y\,H_2O + xCO_2 + 3.76\left(x + \frac{y}{2}\right)N_2$$

Fuels contain sulphur , oxygen, nitrogen and certain heavy metals.

Air contains large amount of nitrogen.

Combustion process leads to the formation of $NO_x, SO_x, CO_x, UHC\ etc$

The quantities are sufficient enough to affect the quality of atmospheric air.

Total amount of fossil fuel burnt was around 6.2 Gt/Yr.

Another source of pollutant emission from combustion process is the biomass.

Total amount of biomass fuel burnt was around 3 to 5 Gt/Yr.

The combustion conditions for biomass combustion leads to higher emissions.

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Chemicals From Combustion (Contd..)

Emission of CO, CO_2, O_2

- It has been observed that there is an imbalance in the atmospheric carbon-oxygen cycle.
- CO is released directly into the atmosphere by incomplete combustion.
- About 40% of CO in the atmosphere is contributed by the burning of fossil fuel.
- CO level in southern hemisphere in around 50 ppb and in northern hemisphere it is 120 ppb.
- Is the major portions CO produced form combustion?
  NO! from the oxidation of methane generated by anaerobic bacteria in swamps and paddies.

Why there is a climate change?

- Due to the change in CO_2 level.
- Deforestation in recent days is the main cause for the accumulation of CO_2 in the biosphere.
- Changes in land used by human beings contribute around 1 Gt(C)/yr CO_2 to atmosphere.
- Global carbon cycle involves exchange of atmospheric CO_2 with carbon reservoir in ocean and biosphere in several time scales.
- It has been predicted that the freezing of current emissions would not really solve our problem immediately.
- CO_2 emission does not impact atmospheric chemistry directly but changes the temperature and circulation, which indirectly changes the chemistry and climate.

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