

EWCE 105

ENVIRONMENTAL CHEMISTRY

Lecture – 4

Lecture Outlines

- Evolution of Earth's Atmosphere
- Atmospheric Structure
- Atmospheric Composition

Evolution of Earth's Atmosphere

Atmosphere

- The atmosphere consists of the thin layer of mixed gases covering the earth's surface.

Evolution of Earth's Atmosphere

- Atmosphere of Earth and other planets are thought to have formed as **a result of the release of trapped volatile compounds from the planet itself.**



Evolution of Earth's Atmosphere

- The early atmosphere of Earths is believed to have been **a mixture of CO_2, N_2, Water vapor (H_2O), with trace amounts of H_2.**
- Most of the **water vapor that out-gassed** from the Earth's interior **condensed out gradually to form the oceans**; where the first life forms developed (Algae and bacteria). Algae started producing oxygen which increased the concentration of oxygen in the Atm.

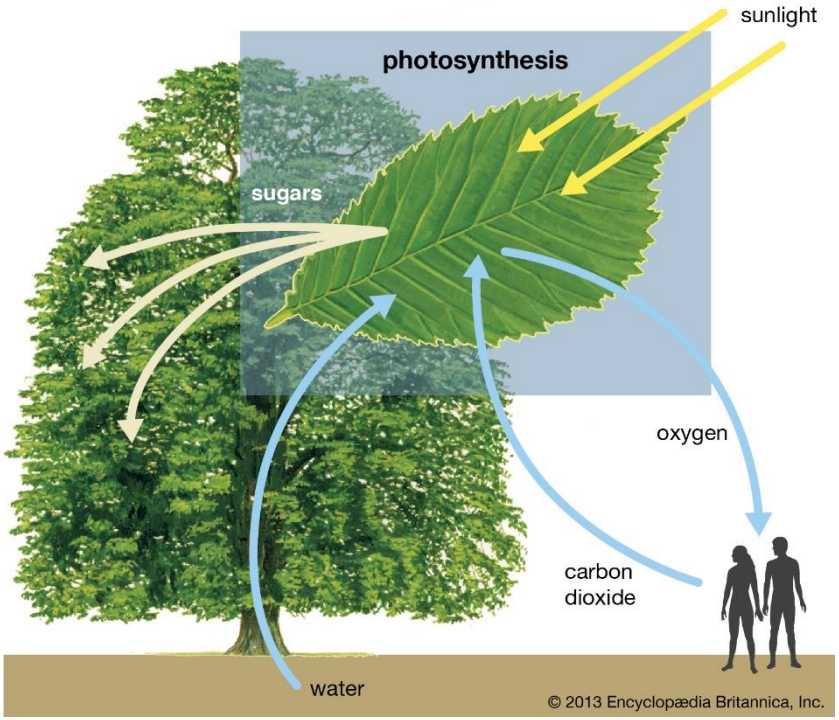
  *Out-gassed - The release of a gas that was dissolved, trapped, frozen, or absorbed in some material.

- Since **N_2** is **chemically inert**, has **low water solubility**, and **non-condensable**, most of the out-gassed **N_2 accumulated** in the atmosphere to become the **most abundant of the atmosphere**.

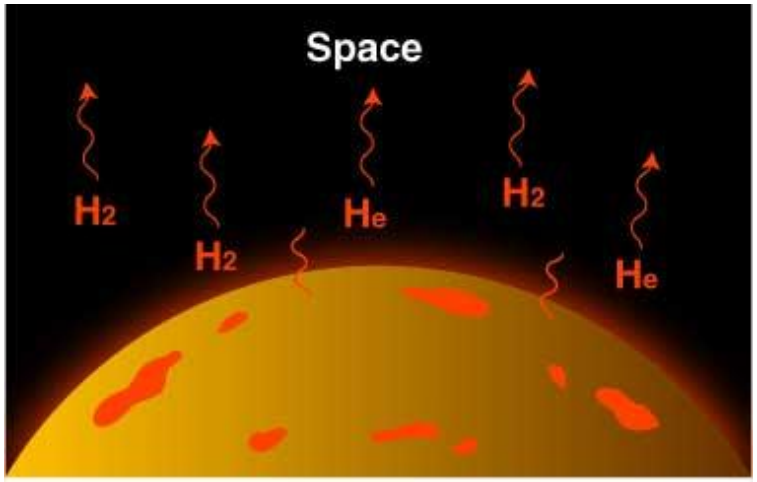
Evolution of Earth's Atmosphere

- The **dramatic rise of O_2** as an atmospheric constituent over time was the **result of the production of O_2** as **a by-product of photosynthetic activity.**

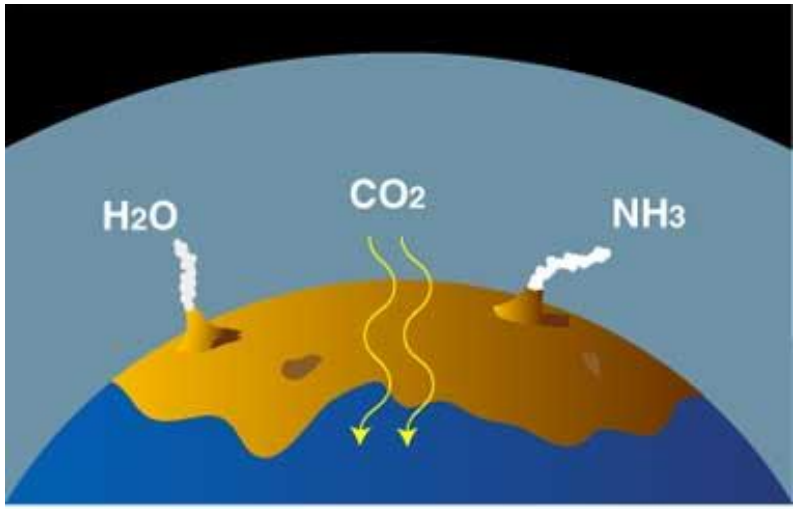
- The present **level of O_2 is maintained** by a **balance between** production by **photosynthesis** and removal through **respiration.**



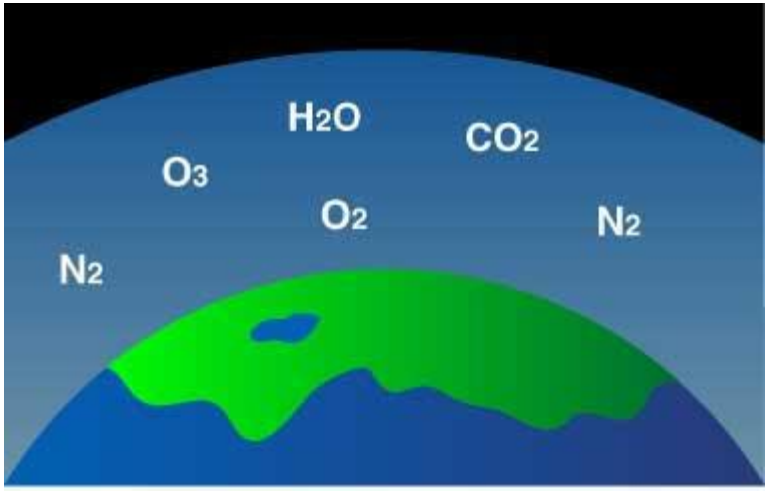
Evolution of Earth's Atmosphere



Atmosphere #1



Atmosphere #2



Atmosphere #3

Atmospheric Composition

- Atmosphere is dynamic system. Here,
- Gases are produced by:
  - Chemical processes within atmosphere,
  - Biological activities,
  - Volcanic eruption,
  - Radioactive decay, &
  - Anthropogenic (industry, transportation) activities.
- Gases are removed by:
  - Chemical reaction within atmosphere
  - Biological activities
  - Physical processes within atmosphere (e.g., particle formation)
  - Deposition and uptake by ocean and earth.

Atmospheric Composition

Dry air within several kilometers of ground level consists of two **major components**

- Nitrogen, 78.08 % (by volume)
- Oxygen, 20.95 %

two minor components

- Argon, 0.934 %
- Carbon dioxide, 0.036 %

in addition to argon, four more noble gases,

- Neon, 1.818 x 10-3 %
- Helium, 5.24 x 10-4 %
- Krypton, 1.14 x 10-4 %
- Xenon, 8.7 x 10-6 %

Atmospheric Composition (Trace Gases)

Table 9.1. Atmospheric Trace Gases in Dry Air Near Ground Level

Gas or species	Volume percent[1]	Major sources	Process for removal from the atmosphere
CH_4	1.6×10^{-4}	Biogenic[2]	Photochemical[3]
CO	$\sim 1.2 \times 10^{-5}$	Photochemical, anthropogenic[4]	Photochemical
N_2O	3×10^{-5}	Biogenic	Photochemical
NO_x[5]	10^{-10}-10^{-6}	Photochemical, lightning, anthropogenic	Photochemical
HNO_3	10^{-9}-10^{-7}	Photochemical	Washed out by precipitation
NH_3	10^{-8}-10^{-7}	Biogenic	Photochemical, washed out by precipitation
H_2	5×10^{-5}	Biogenic, photochemical	Photochemical
H_2O_2	10^{-8}-10^{-6}	Photochemical	Washed out by precipitation
HO·[6]	10^{-13}-10^{-10}	Photochemical	Photochemical
HO_2·[6]	10^{-11}-10^{-9}	Photochemical	Photochemical
H_2CO	10^{-8}-10^{-7}	Photochemical	Photochemical
CS_2	10^{-9}-10^{-8}	Anthropogenic, biogenic	Photochemical
OCS	10^{-8}	Anthropogenic, biogenic, photochemical	Photochemical
SO_2	$\sim 2 \times 10^{-8}$	Anthropogenic, photochemical, volcanic	Photochemical
I_2	0-trace	—	—
CCl_2F_2[7]	2.8×10^{-5}	Anthropogenic	Photochemical
H_3CCCl_3[8]	$\sim 1 \times 10^{-8}$	Anthropogenic	Photochemical

[1] Levels in the absence of gross pollution
[2] From biological sources
[3] Reactions induced by the absorption of light energy as described later in this chapter and in Chapters 10-14
[4] Sources arising from human activities
[5] Sum of NO, NO_2, and NO_3, of which NO_3 is a major reactive species in the atmosphere at night
[6] Reactive free radical species with one unpaired electron, described later in Chapters 12 and 13; these are transient species whose concentrations become much lower at night
[7] A chlorofluorocarbon, Freon F-12
[8] Methyl chloroform

Atmospheric Composition (Trace Gases- Overview)

- **Trace gases** comprising less that 1% of the atmosphere play a crucial role in the earth's radiative balance and in the chemical properties of the atmosphere.

Radiative balance - The relationship between the amount of energy reaching an object (or a portion of it) and the amount leaving it. A good example of this is our Earth receiving energy from the sun, and giving off The energy.

- The **trace gas concentrations** have **changed** dramatically over the last **two decades**.

Atmospheric Composition (Trace Gases- Overview)

- Atmosphere composed primarily of N_2, O_2 and several 'noble gases', the concentrations of which have remained remarkably fixed over time.
- Also present are small number of gases (water vapor, CO_2, O_3) that occur in relatively small and sometimes highly variable amounts. The common urban air pollutants (e.g., CO, SO_2, NO_2) also fall in this category.

Terms related to Atmospheric Composition

- Atmosphere - comprised of a mixture of invisible **permanent** and **variable gases** as well **as suspended microscopic particles** (both liquid and solid).
- Permanent Gases – Form a constant proportion of the total atmospheric mass.
- Variable Gases – Distribution and concentration **varies in space and time**.
- Aerosols – is a **suspension** of **fine solid particles** or **liquid droplets**, in air or another gas. Aerosols can be natural or anthropogenic..

Terms related to Atmospheric Composition

Examples of natural aerosols are **fog, mist, dust etc.** Examples of anthropogenic aerosols are **haze, particulate air pollutants and smoke.**

Permanent Gases

- 78% Nitrogen (N_2)
- 21% Oxygen (O_2)
- <1% Argon (Ar)

Relative percentages of the **permanent gases remain constant up to 80-100km high** (~ 60 miles!)

Terms related to Atmospheric Composition

VARIABLE gases in the atmosphere and typical percentage values (by volume):

Variable Gases

typical percentage values (by volume):

- Water vapour (H_2O) - 0 to 4%
- Carbon Dioxide (CO_2) - 0.038%
- Methane(CH_4) - 0.00017%
- Ozone(O_3) - 0.000004%

Water vapor is the third most common molecule in Earth's atmosphere after nitrogen and oxygen.

Stratification of the Atmosphere

Layers in Atmosphere

- Vertical Structure of the Atmosphere commonly broken into layers.

- Four distinct layers in the atmosphere have been identified using thermal characteristics (temperature changes), chemical composition, movement, and density.
  1. Troposphere
  2. Stratosphere
  3. Mesosphere
  4. Thermosphere

Stratification of the Atmosphere

Troposphere

- Lower part of the atmosphere.
- This part of the atmosphere is the densest.
- Temperature generally decreases with height, at a global average of approximately 6.5°C/km (environmental lapse rate).
- Air circulations (weather) take place mainly here.
- Troposphere goes from surface to about 30,000 ft. (10 to 12 km).

Stratification of the Atmosphere

Stratosphere

- The ozone layer which absorbs and scatters the solar ultraviolet radiation, is in this layer.
- The temperature in this region increases gradually to -3^{o}C, due to the absorption of ultraviolet radiation.
- Boundary between troposphere and stratosphere is the tropopause.
- Compared to the troposphere, this part of the atmosphere is dry and less dense.
- Stratosphere goes from about 10 to 50 km above the surface.

Stratification of the Atmosphere

Mesosphere

- The stratopause separates the stratosphere from the next layer.
- In this region, the temperatures again fall as low as -93^{o}C with the increase in altitude.
- The chemicals are in an excited state, as they absorb energy from the Sun.
- Mesosphere extends from about 50 km to 85 km above the surface.

Stratification of the Atmosphere

Thermosphere

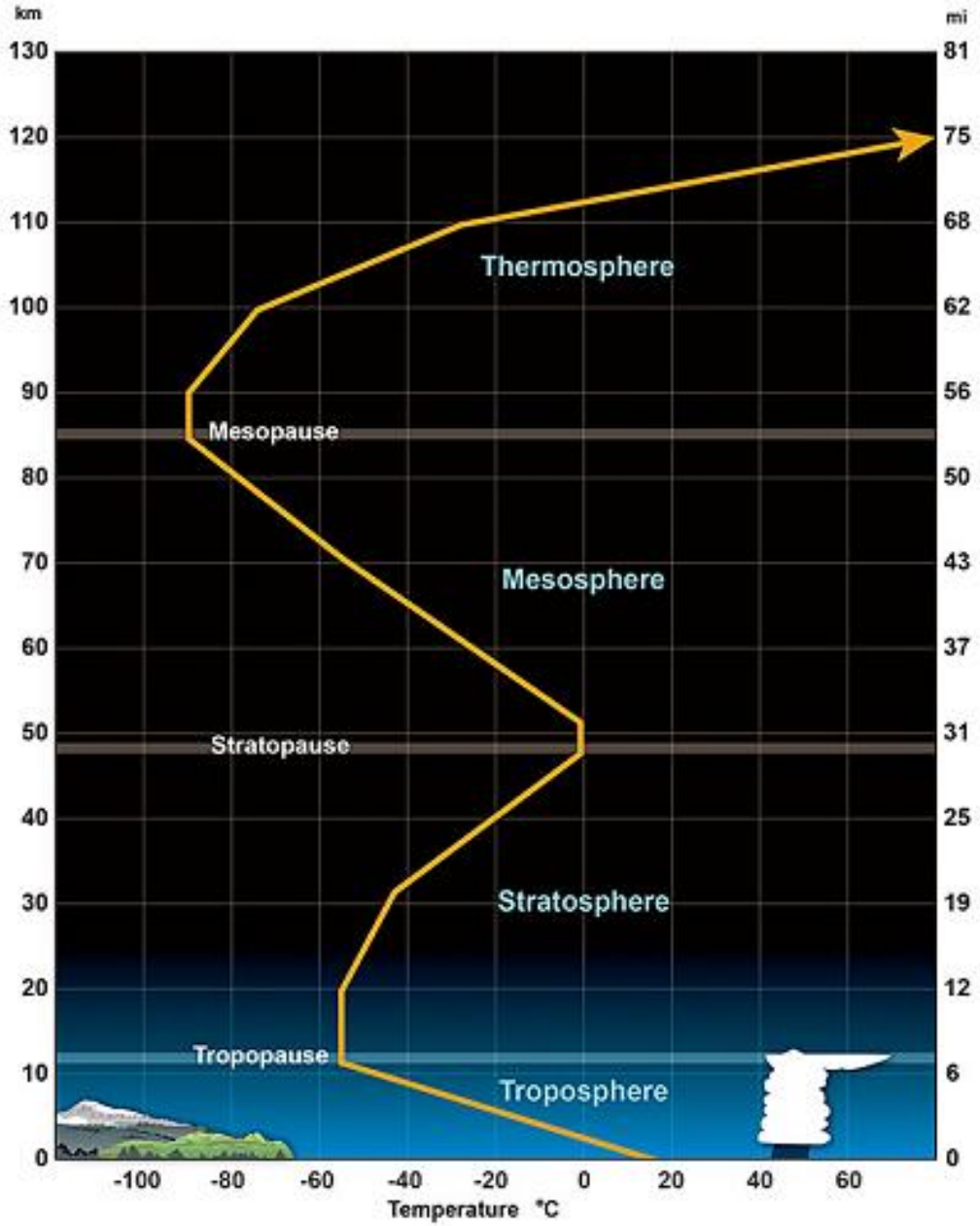
- Extends to 600 kilometers high.
- The temperatures go up as you increase in altitude due to the Sun's energy. Temperatures in this region can go as high as 1,727^{o}C.
- Chemical reactions occur much faster here than on the surface of the earth.
- This layer is known as the upper atmosphere.
- Absorbed energy causes increase of temperature with height.
- The pressure is very low at these heights.

Stratification of the Atmosphere

Temperature Layers of the Atmosphere:

Please draw the **temperature profile of atmosphere** representing different layers. (Hints : Y-axis represents Altitude; X-axis represents Temperature in °C

Temperature profile of atmosphere



Atmospheric Pressure

- Atmospheric pressure is a direct result of the total weight of the air above the point at which the pressure is measured. This means that air pressure varies with location and time, because the amount (and weight) of air above the earth varies with location and time.

- Atmospheric pressure decreases with height, dropping by 50% at an altitude of about 5.6 km (18,000 ft). Equivalently, about 50% of the total atmospheric mass is within the lowest 5.6 km.

- This pressure drop is approximately exponential.

Atmospheric Pressure

- 50% of the atmosphere by mass is below an altitude of 5.6 km.
- 90% of the atmosphere by mass is below an altitude of 16 km.
- 99.99997% of the atmosphere by mass is below 100 km (almost all of it).

Importance of the Atmosphere

- The atmosphere is a protective blanket that nurtures life on the Earth and protects it from the hostile environment of outer space.
- The atmosphere is the source of carbon dioxide for plant photosynthesis and of oxygen for respiration.
- It provides the nitrogen which is an essential component of life molecules.
- As a basic part of the hydrologic cycle, the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still.

Importance of the Atmosphere

An unwanted property

- The atmosphere serves as a dumping ground for many pollutant materials—ranging from sulfur dioxide to refrigerant Freon—a practice that causes damage to vegetation and materials, shortens human life, and alters the characteristics of the atmosphere itself.

Lecture Summary

- Evolution of Earth's Atmosphere
- Atmospheric Structure
- Atmospheric Composition

The End