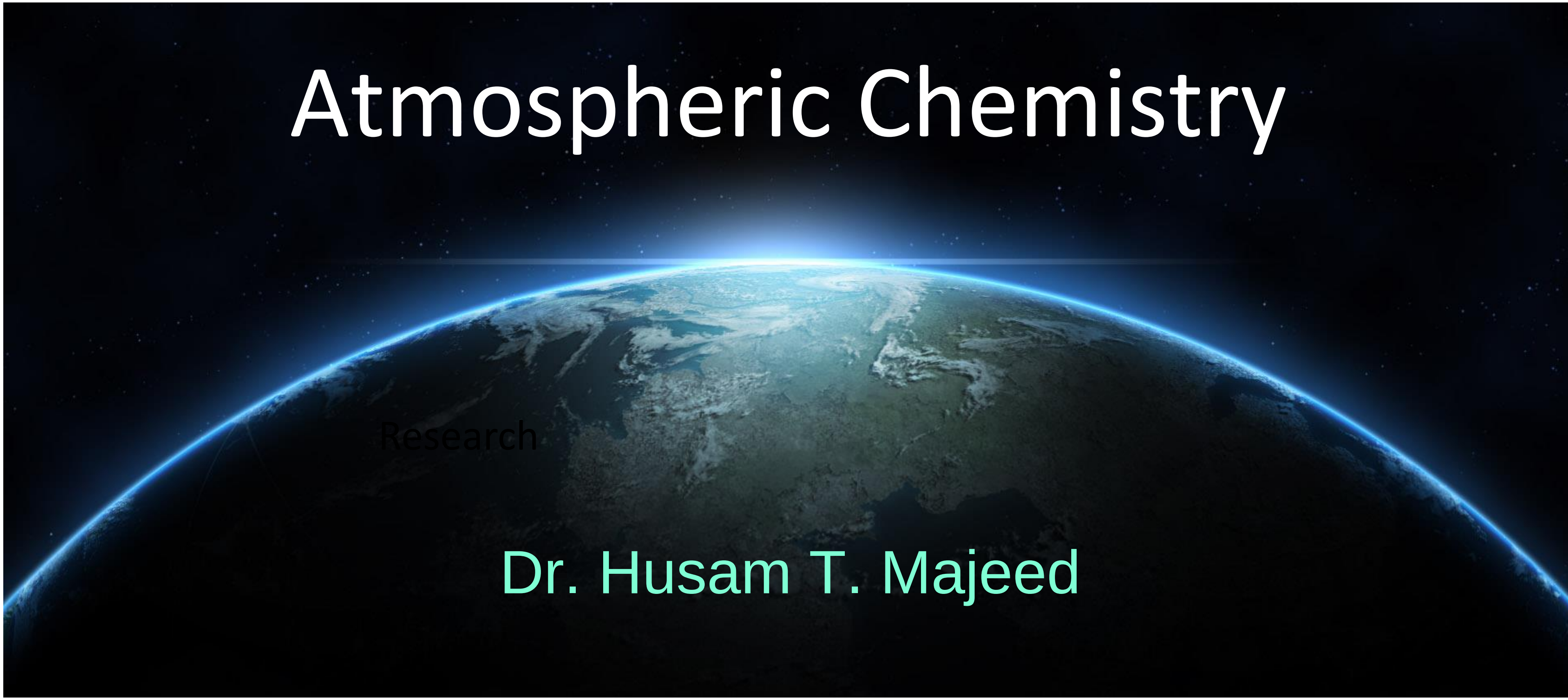

Atmospheric Chemistry

Research

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Department of Atmospheric Sciences

2nd Year Class

First Semester 2018-2019

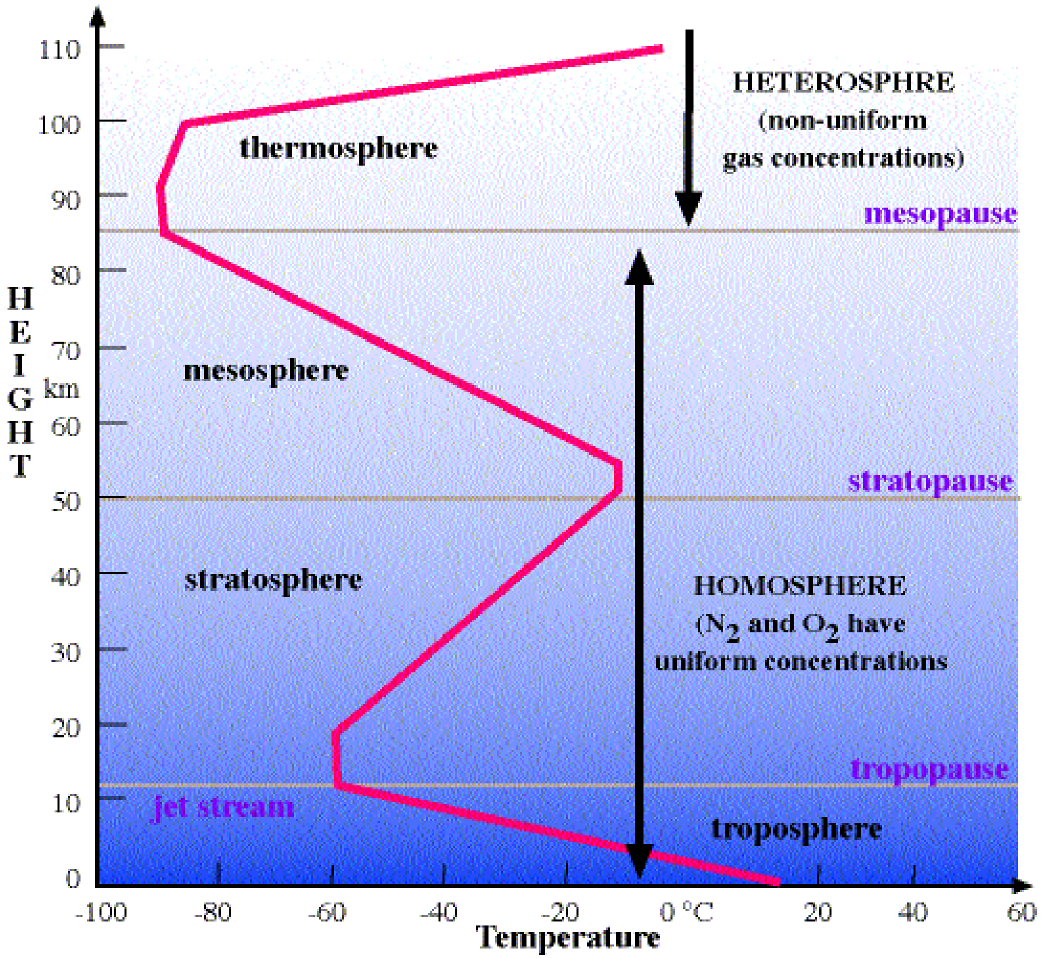
Course Syllabus

1. Introduction & Review

Atmospheric Chemistry

Box Models and Residence Times

2. Earths Atmosphere



Thermal structure and composition

Reactions and calculations in atmospheric chemistry

Chemical Kinetics

Biogeochemical cycling

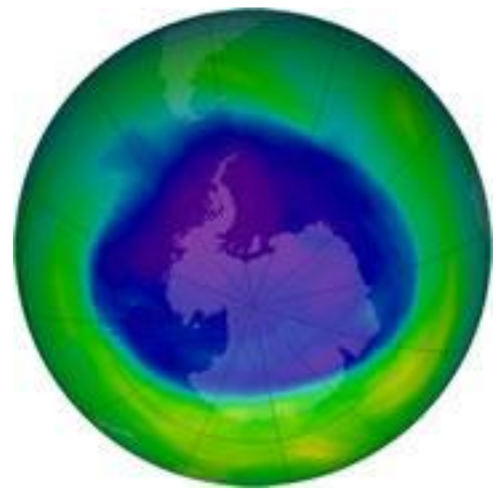
3. Stratospheric Chemistry - Ozone

The ozone layer and Chapmann reactions

Catalytic decomposition of ozone

Chlorofluorocarbon chemistry

Polar hole formation



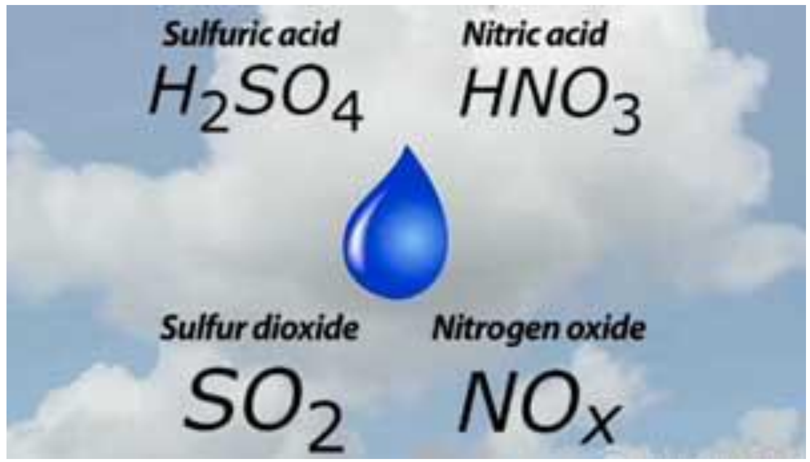
4. Tropospheric Chemistry - Smog

Photochemical smog formation

Hydroxyl radical chemistry

Internal combustion engine exhaust

5. Tropospheric Chemistry - Precipitation



Composition of rainwater
Atmospheric production of nitric and sulfuric acids
Rain, snow and fog chemistries
Short and long range acid transport
Control technologies for sulfur and nitrogen emissions

6. Atmospheric Aerosols

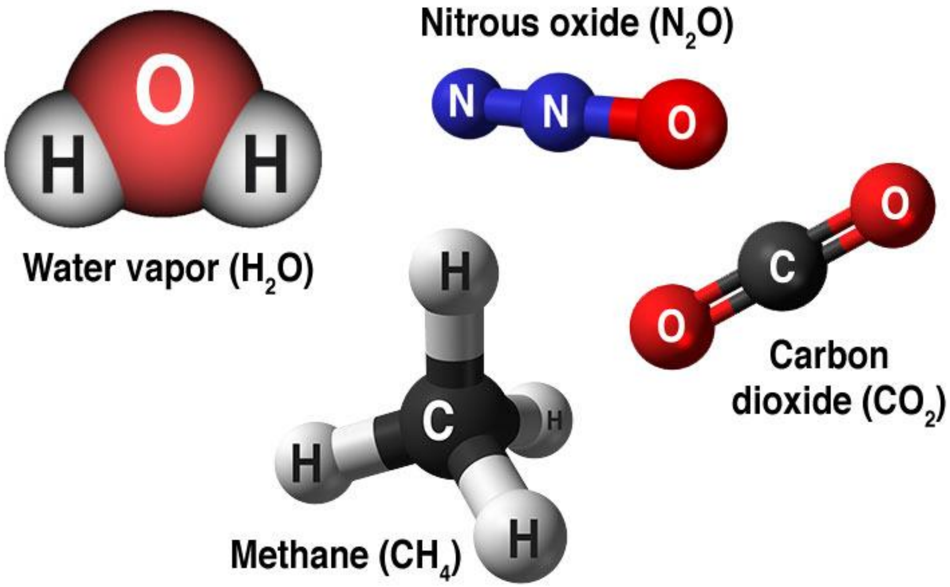
Sources, concentrations and atmospheric lifetimes
Abatement strategies for particulate emissions

7. Chemistry of Urban and Indoor Air

Pollutants in urban atmospheres

Indoor air quality, airborne contaminants and exposure

8. Chemistry of Global Climate



Thermal structures revisited and the solar energy balance
IR absorption spectra, greenhouse gases and aerosols
Relative importance of greenhouse gases
Carbon based fuels and alternative energy supplies

Atmospheric Chemistry: Definitions

- **Contaminant** - a substance present in greater than the usual (normal) concentration.
- **Pollutant** - a contaminant which has a detrimental effect upon its environment (or something of value within it). A pollutant can be anthropogenic (human made) or from a natural source.
- **Source** - every pollutant originates from a source. Identifying the source is very important since the most efficient remediation can usually be achieved at this location. Point sources are often easy to identify as they are often associated with a specific industry or activity. Non-point sources give rise to a more diffuse pollutant loading and can be more difficult to identify and remediate.

- **Receptor** - anything that the pollutant acts upon.
- **Reservoir or Compartment** - a region or unit within the environment in which a substance resides and mixes. The atmosphere, oceans and other water bodies are reservoirs for many substances. When the concentration of a substance within a reservoir does not appear to change, the rate of inflow = rate of outflow and the situation is said to have reached a steady-state.
- **Sink** - a longer term reservoir in which a substance is essentially immobilized. Such a repository may be natural or human-made. The oceans and ocean sediments are a sink for many of the dissolved species present in freshwater.
- **Residence time** – is the average amount of time a substance spends in a particular compartment or reservoir. It is defined numerically as the steady-state amount of material in a reservoir divided by its total rate of inflow (or outflow).

$$\text{Residence time} = \frac{\text{steady-state amount of substance in the reservoir}}{\text{rate of inflow to (or outflow from) reservoir}}$$

- The numerator of this equation will have units expressing amount, such as grams, moles per liter, m^3 or tons while the denominator will have units of amount per time, such as grams per second, moles per liter per minute, m^3 per day or tons per year. The units should be chosen to be compatible, so that the amount of substance cancels and the final quantity has units of time.

SIMPLE MODELS

- The concentrations of chemical species in the atmosphere are controlled by four types of processes:
- **Emissions**: Chemical species are emitted to the atmosphere by a variety of sources. Some of these sources, such as fossil fuel combustion, originate from human activity and are called *anthropogenic*. Others, such as photosynthesis of oxygen, originate from natural functions of biological organisms and are called *biogenic*. Still others, such as volcanoes, originate from non-biogenic natural processes.
- **Chemistry:** Reactions in the atmosphere can lead to the formation and removal of species.

- **Transport:** Winds transport atmospheric species away from their point of origin.
- **Deposition**: All material in the atmosphere is eventually deposited back to the Earth's surface. Escape from the atmosphere to outer space is negligible because of the Earth's gravitational pull. Deposition takes two forms: *"dry deposition"* involving direct reaction or absorption at the Earth's surface, such as the uptake of CO2 by photosynthesis; and *"wet deposition"* involving scavenging by precipitation.

One-box model for an atmospheric species X

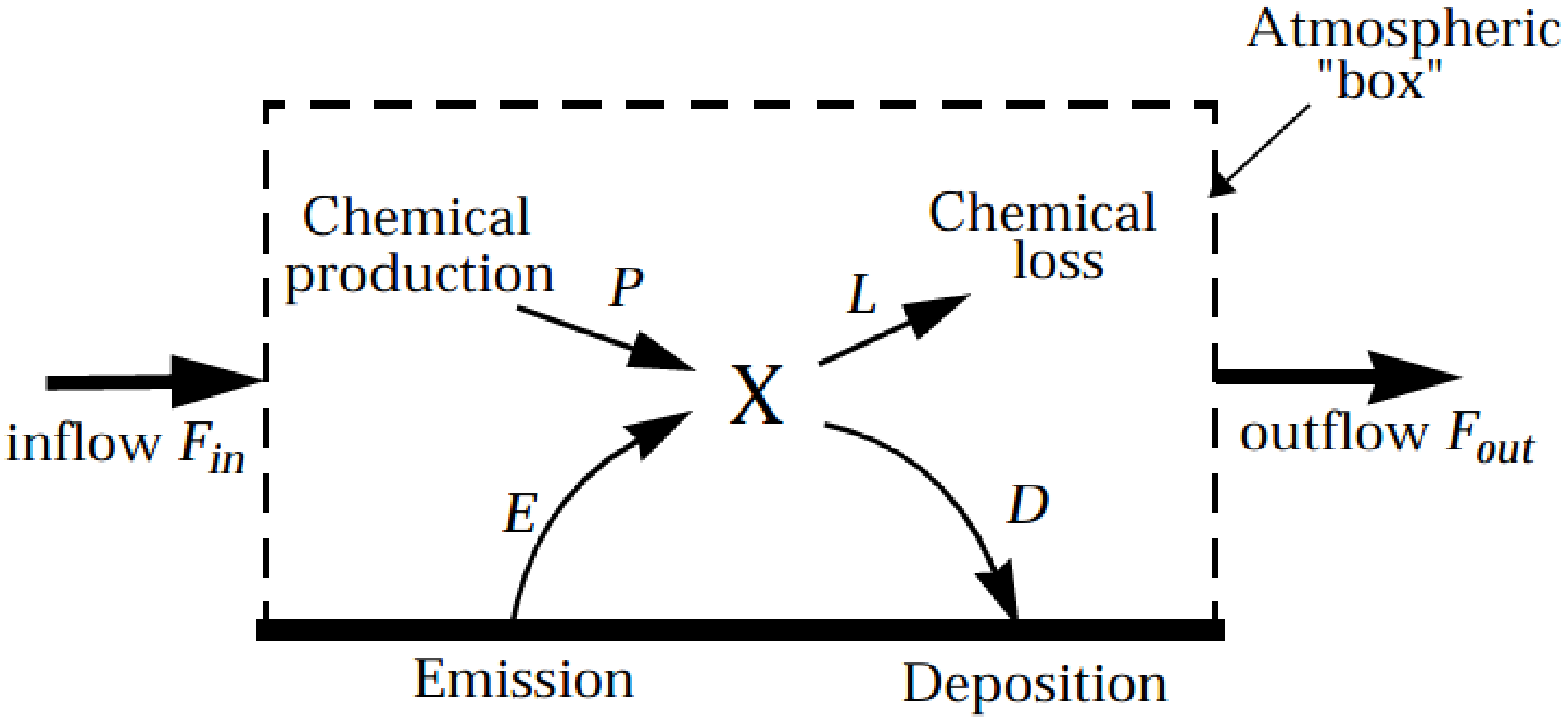
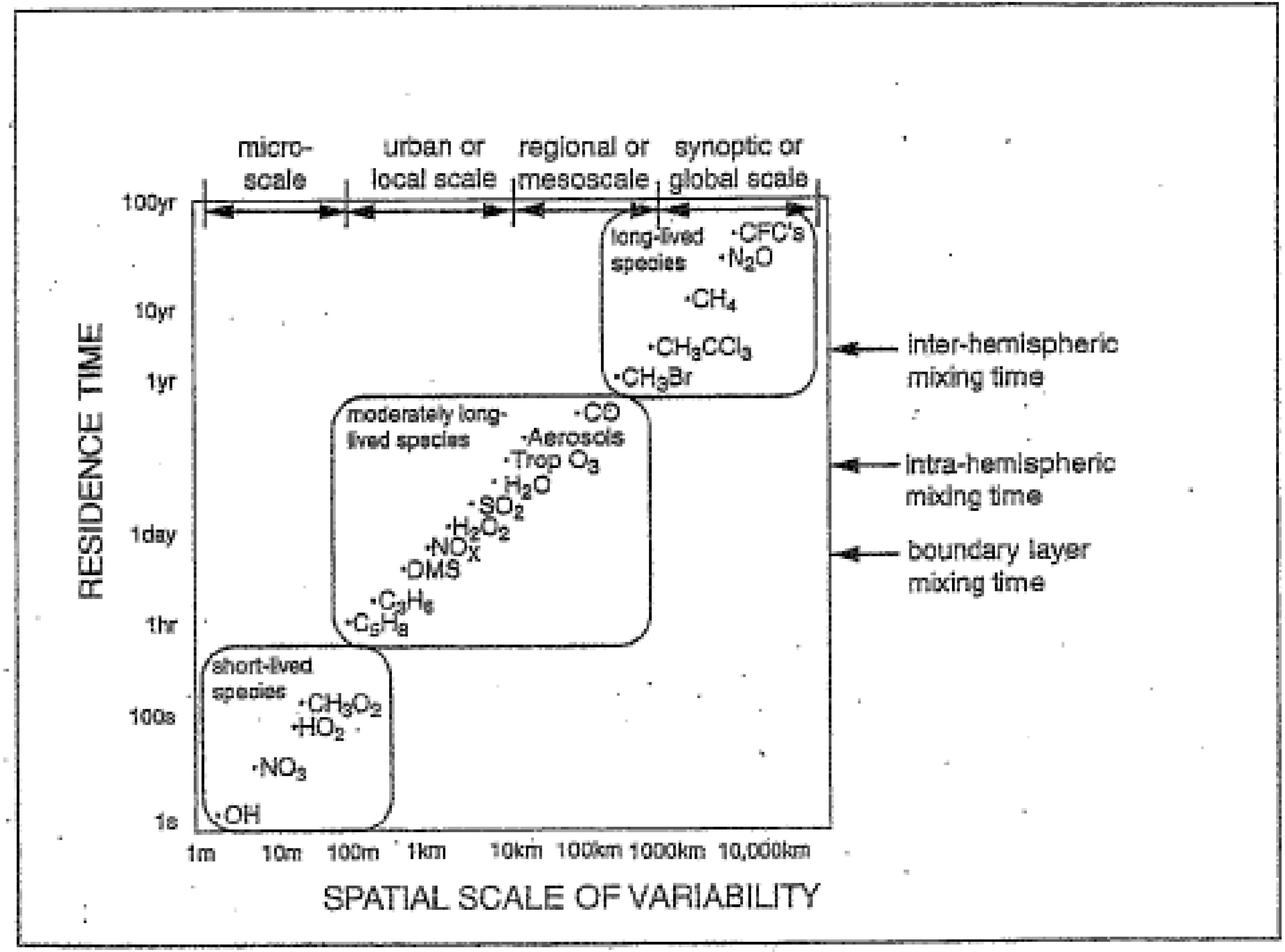
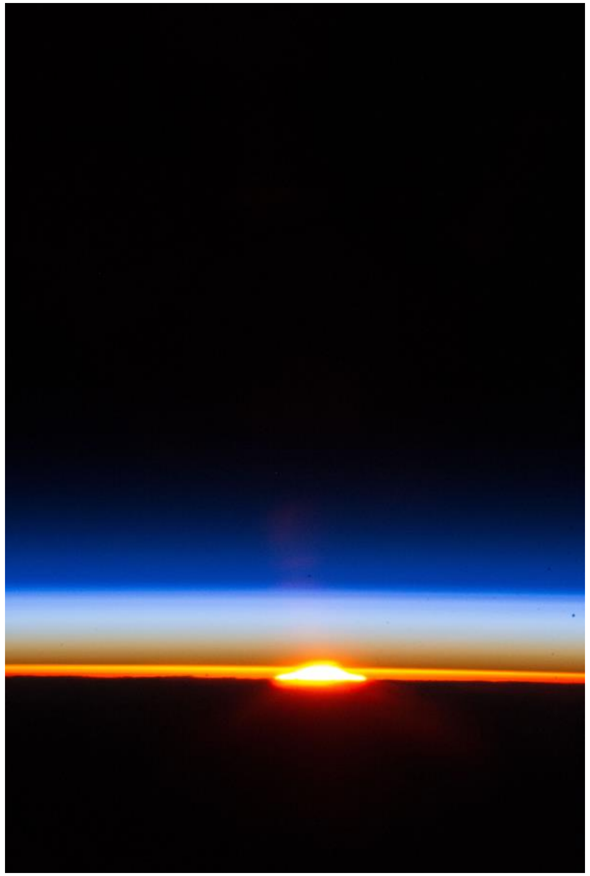


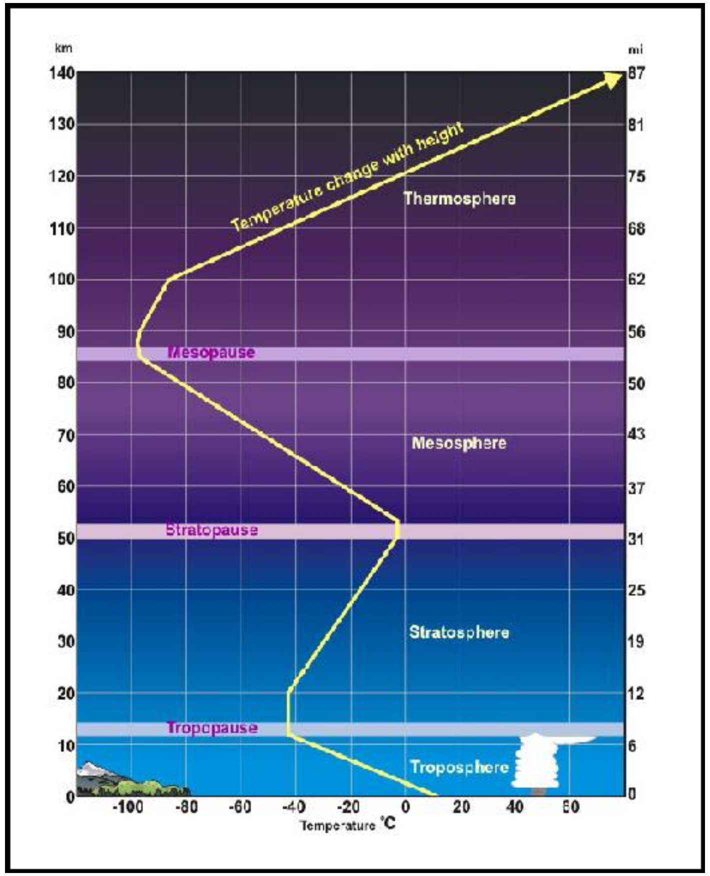
Figure 3-1 One-box model for an atmospheric species X

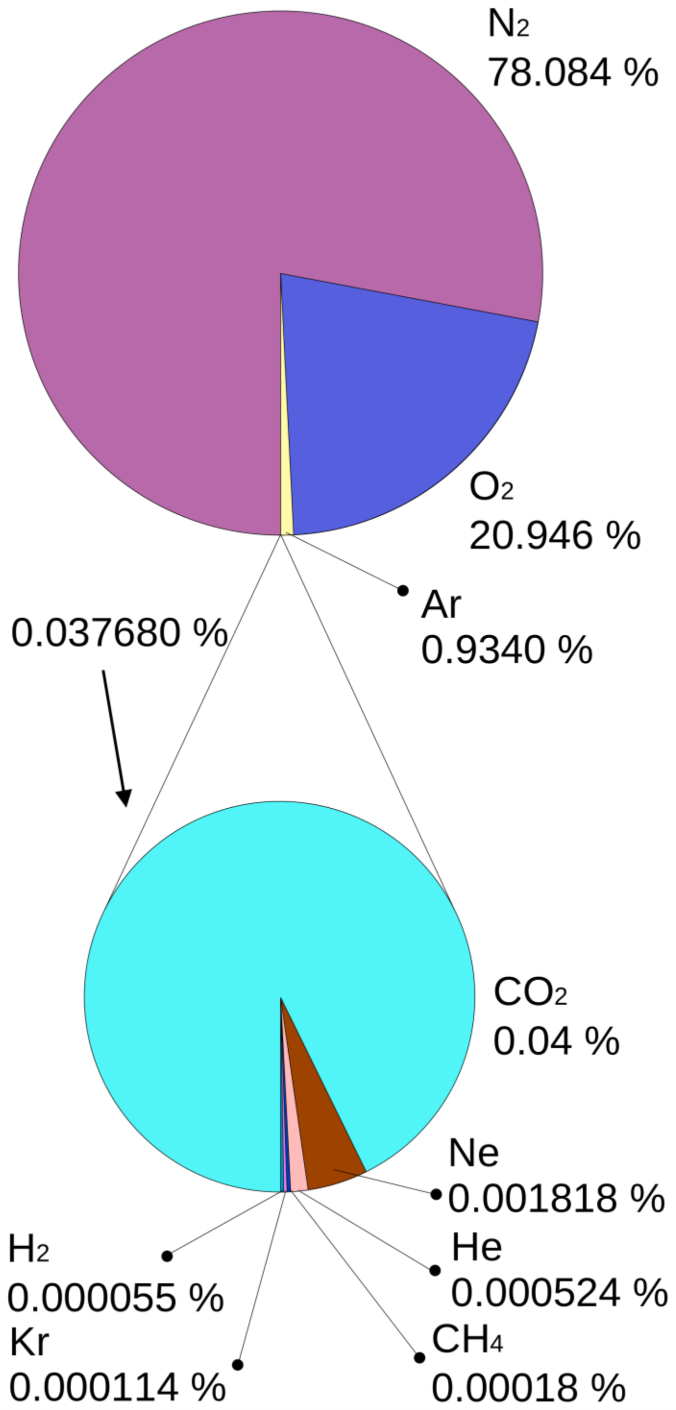


micro-scale
urban or local scale
regional or mesoscale
synoptic or global scale
100yr
10yr
1yr
1day
1hr
100s
1s
RESIDENCE TIME
long-lived species
·CFC's
·N_2O
·CH_4
·CH_3CCl_3
·CH_3Br
moderately long-lived species
·CO
·Aerosols
·Trop O_3
·H_2O
·SO_2
·H_2O_2
·NO_X
·DMS
·C_3H_6
·C_5H_8
short-lived species
·CH_3O_2
·HO_2
·NO_3
·OH
1m
10m
100m
1km
10km
100km
1000km
10,000km
SPATIAL SCALE OF VARIABILITY
inter-hemispheric mixing time
intra-hemispheric mixing time
boundary layer mixing time

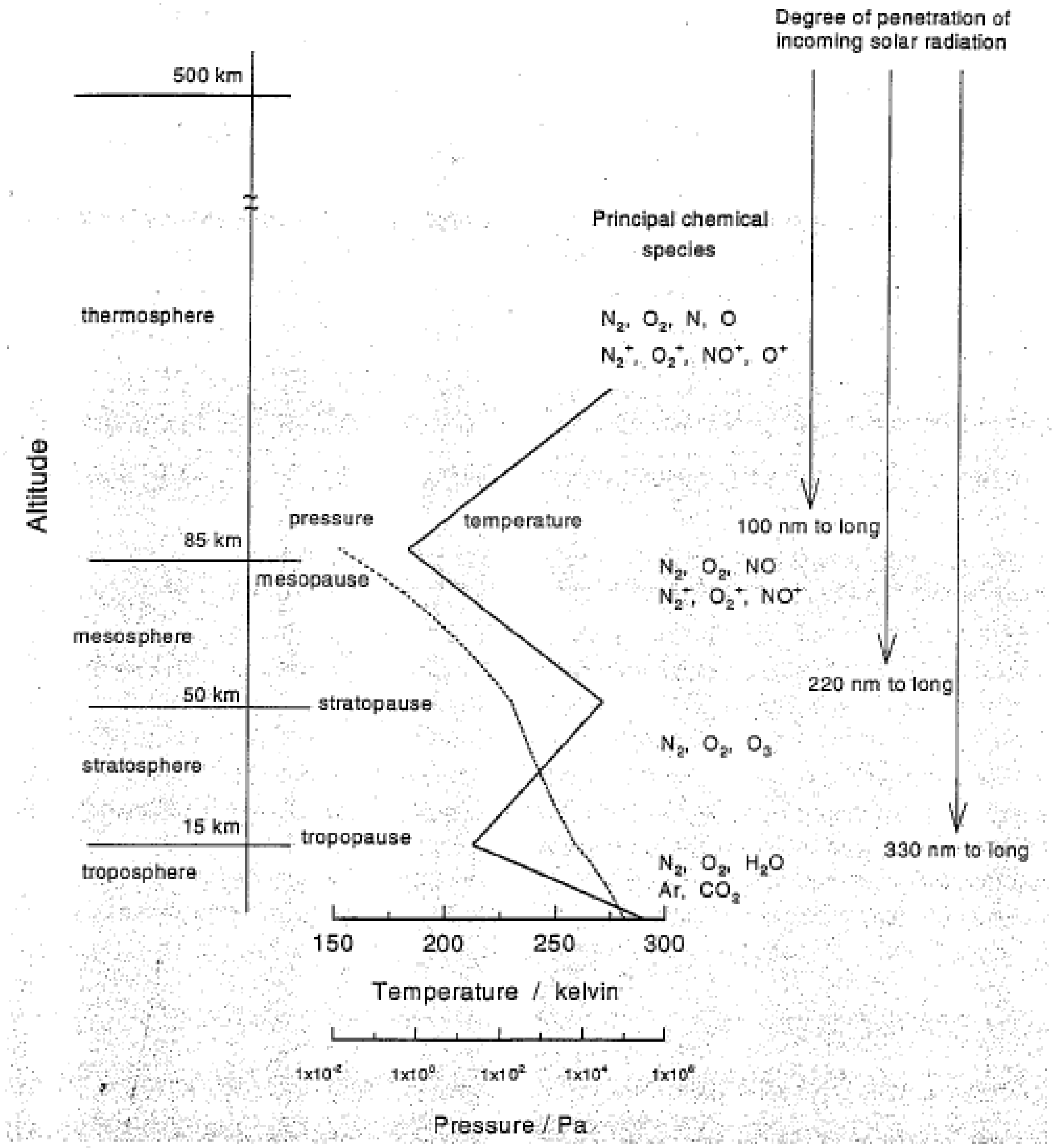
Structure and Composition of Earth's Atmosphere



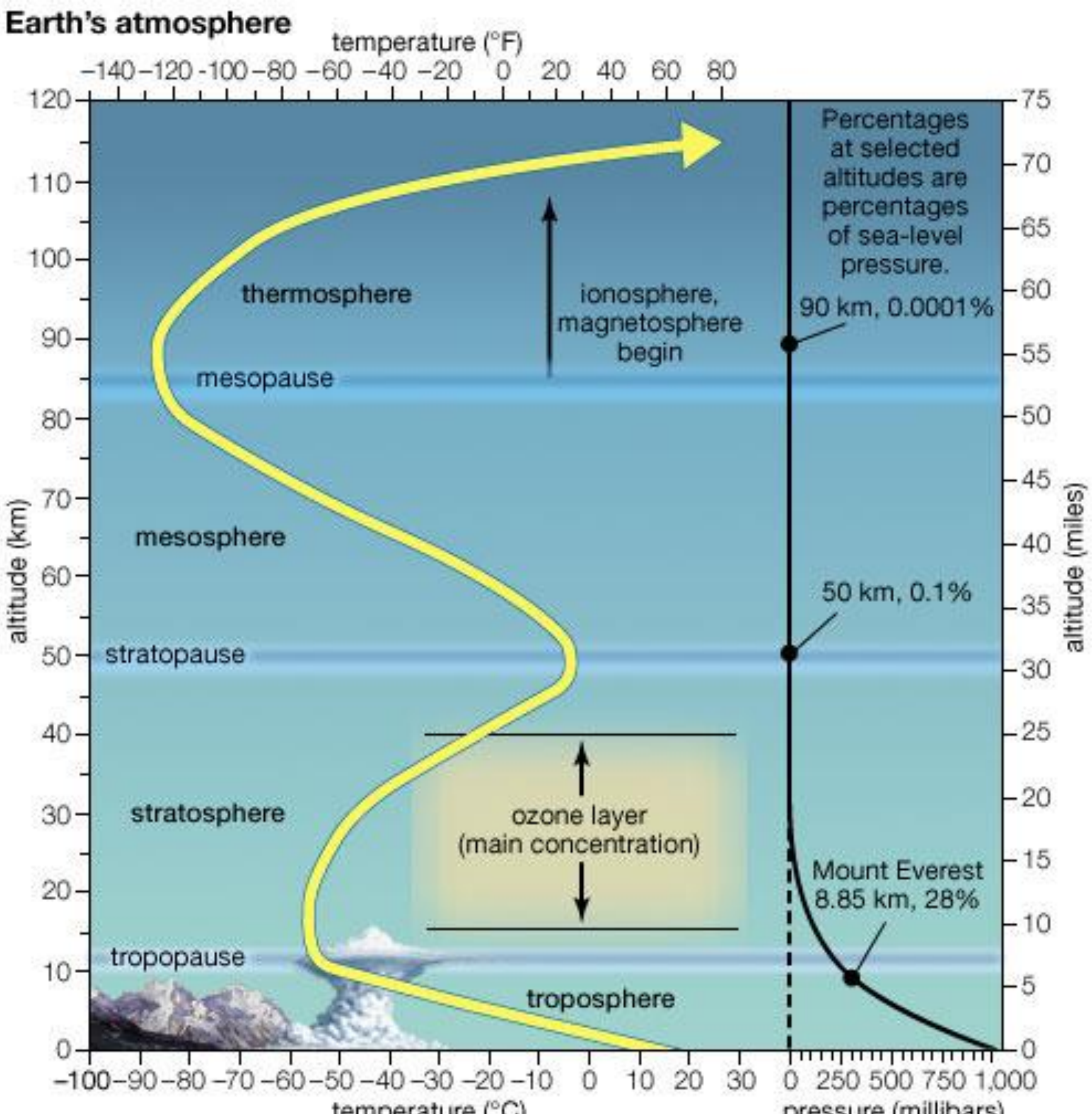




N_2
78.084 %
O_2
20.946 %
Ar
0.9340 %
0.037680 %
CO_2
0.04 %
Ne
0.001818 %
He
0.000524 %
CH_4
0.00018 %
H_2
0.000055 %
Kr
0.000114 %



Degree of penetration of incoming solar radiation
500 km
Principal chemical species
thermosphere
N_2, O_2, N, O
N_2^+, O_2^+, NO^+, O^+
Altitude
pressure
temperature
100 nm to long
85 km
mesopause
N_2, O_2, NO
N_2^+, O_2^+, NO^+
mesosphere
220 nm to long
50 km
stratopause
N_2, O_2, O_3
stratosphere
15 km
tropopause
330 nm to long
troposphere
N_2, O_2, H_2O
Ar, CO_2
150
200
250
300
Temperature / kelvin
Pressure / Pa



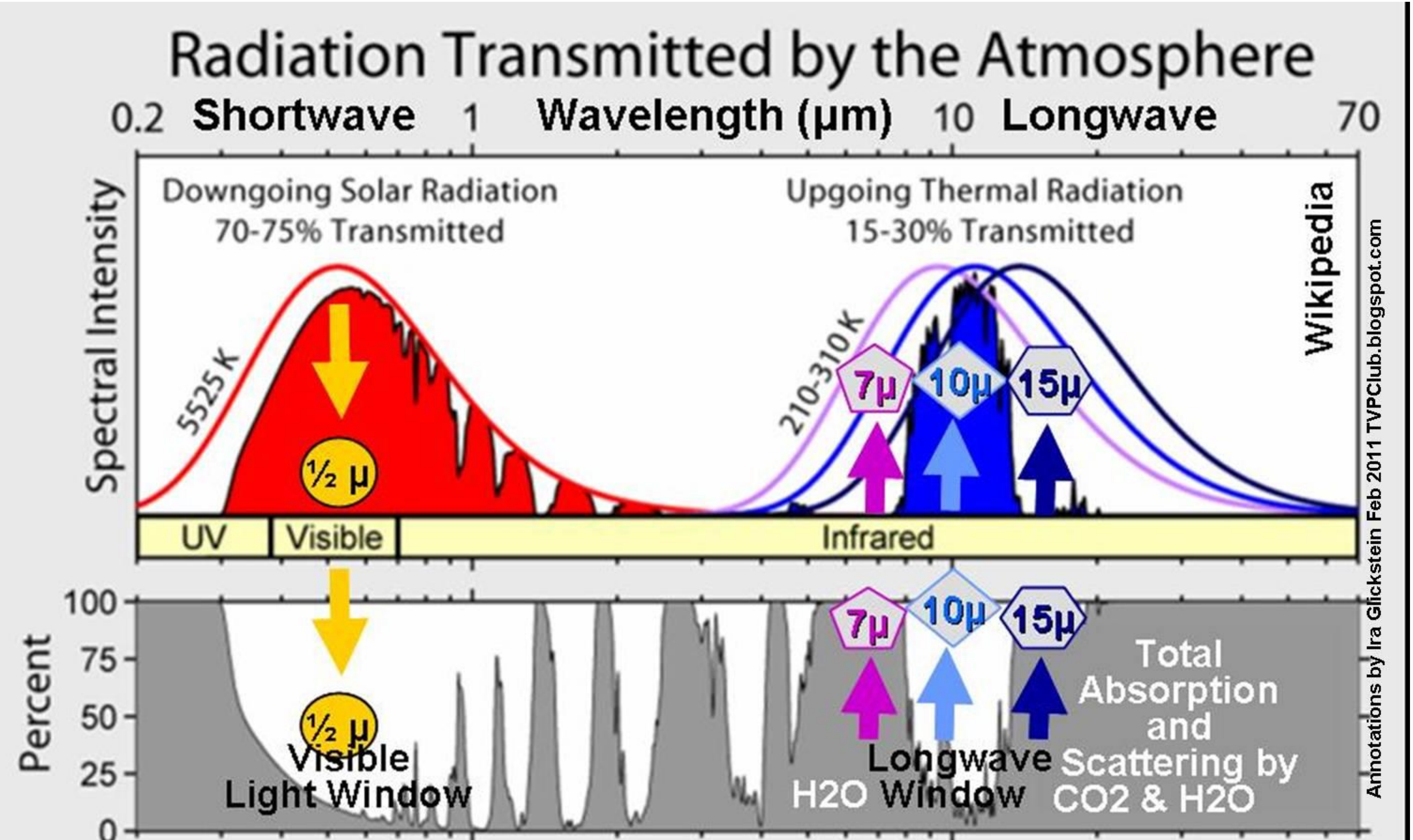
Thermal Structure

<u>Radiative Energy Balance</u>

Energy in (absorbed from Sun) =
Energy out (emitted by Earth)

Blackbody radiation depends only on temperature of emitter

Sun ~ 6000 K
Earth ~ 255 K



Radiation Transmitted by the Atmosphere
0.2 Shortwave 1 Wavelength (μm) 10 Longwave 70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
Wikipedia
½ μ
7μ
10μ
15μ
UV
Visible
Infrared
Percent
100
75
50
25
0
Visible
Light Window
Longwave
H2O Window
Total
Absorption
and
Scattering by
CO2 & H2O
Annotations by Ira Glickstein Feb 2011 TVPClub.blogspot.com

Fig. 1.2. A comparison between (*a*) the electromagnetic spectrum for black bodies at 6000 and 255 K and (*b*) the absorption spectrum of gases in the Earth's atmosphere. Note that the atmosphere is practically transparent to black body radiation emitted at temperatures typical of the sun.