INTRODUCTION TO ATMOSPHERIC CHEMISTRY

PART I Structure of the Atmosphere

09/09/2019 I ROBERT WEGENER

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or from: J. H. Seinfeld and S. N Pandis; "Atmospheric Chemistry and Physics", John Wileys & Sons, 1998.
Or from: IPCC Reports

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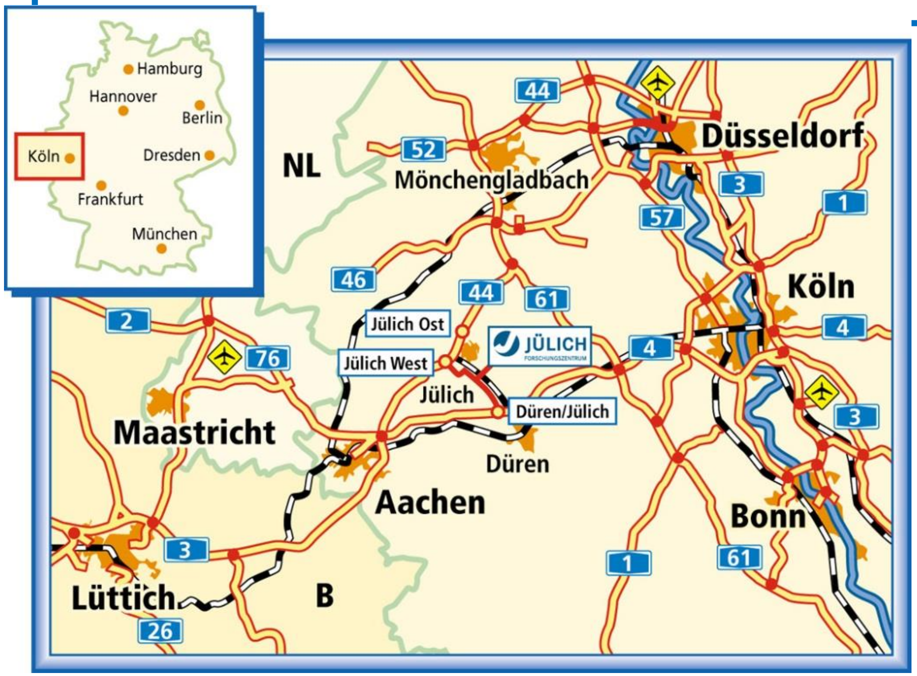

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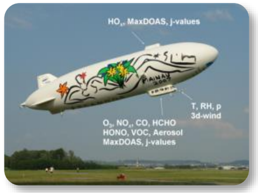
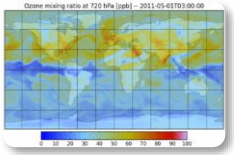
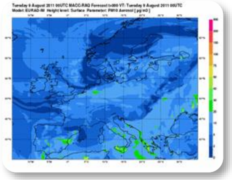
Examination of the physical and chemical Processes in the atmosphere necessary for the transformation, Distribution and removal of trace substances are responsible.

Lab studies	Field studies	simulations





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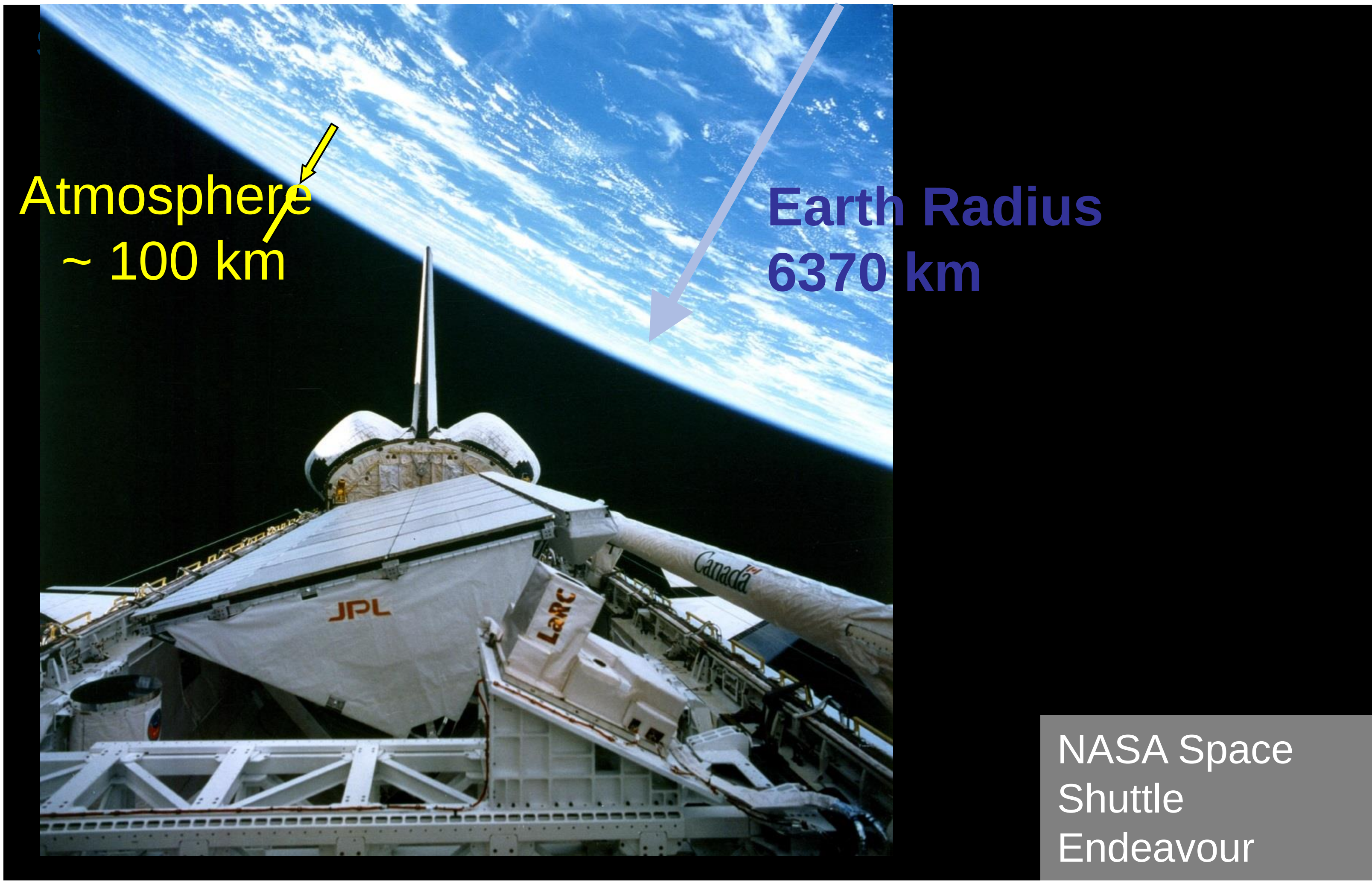
- Composition of the Atmosphere
- Vertical Structure
- Overview of Stratospheric and Tropospheric Chemistry

The Atmosphere

Subline

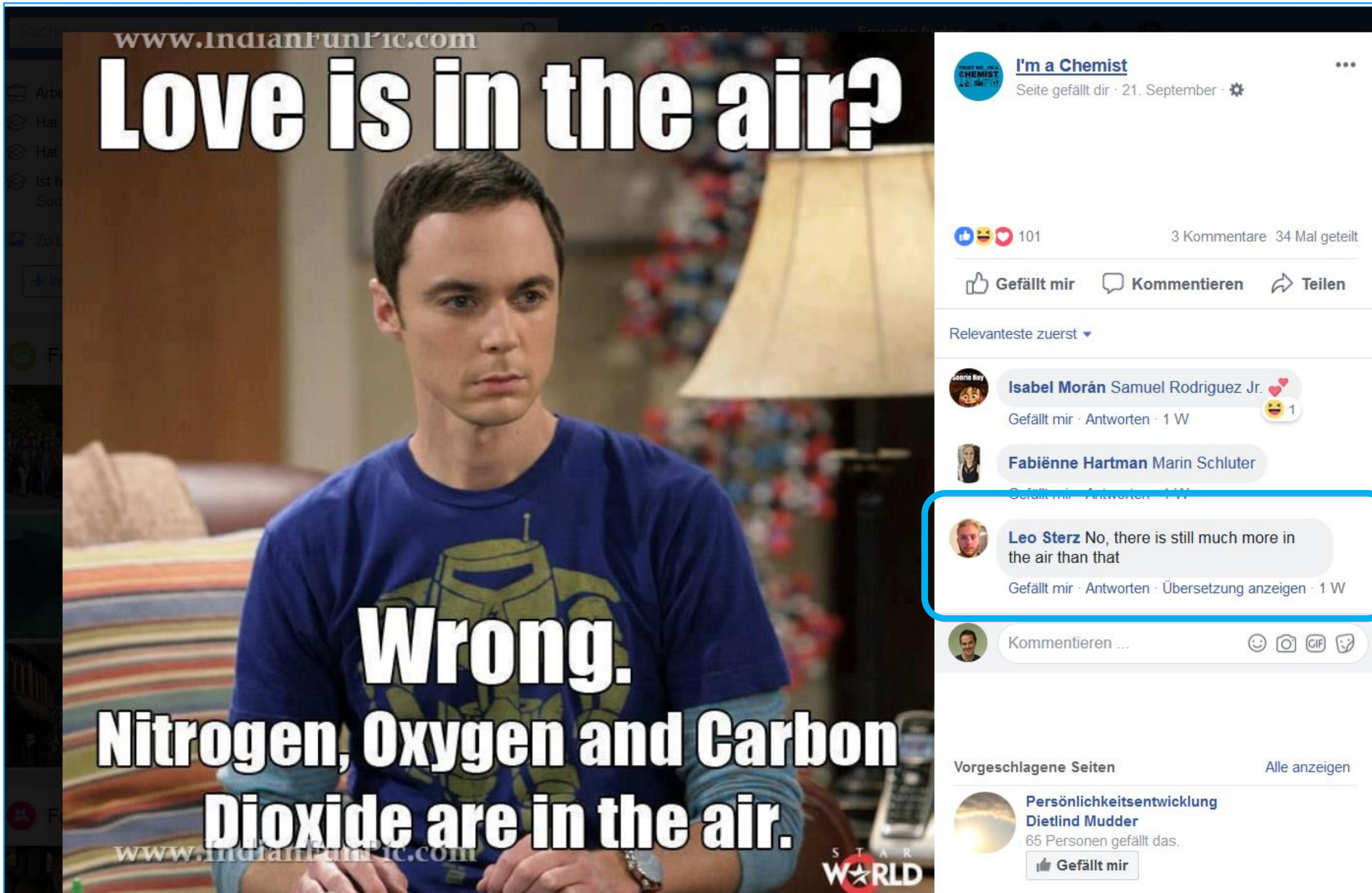
NASA

The Atmosphere

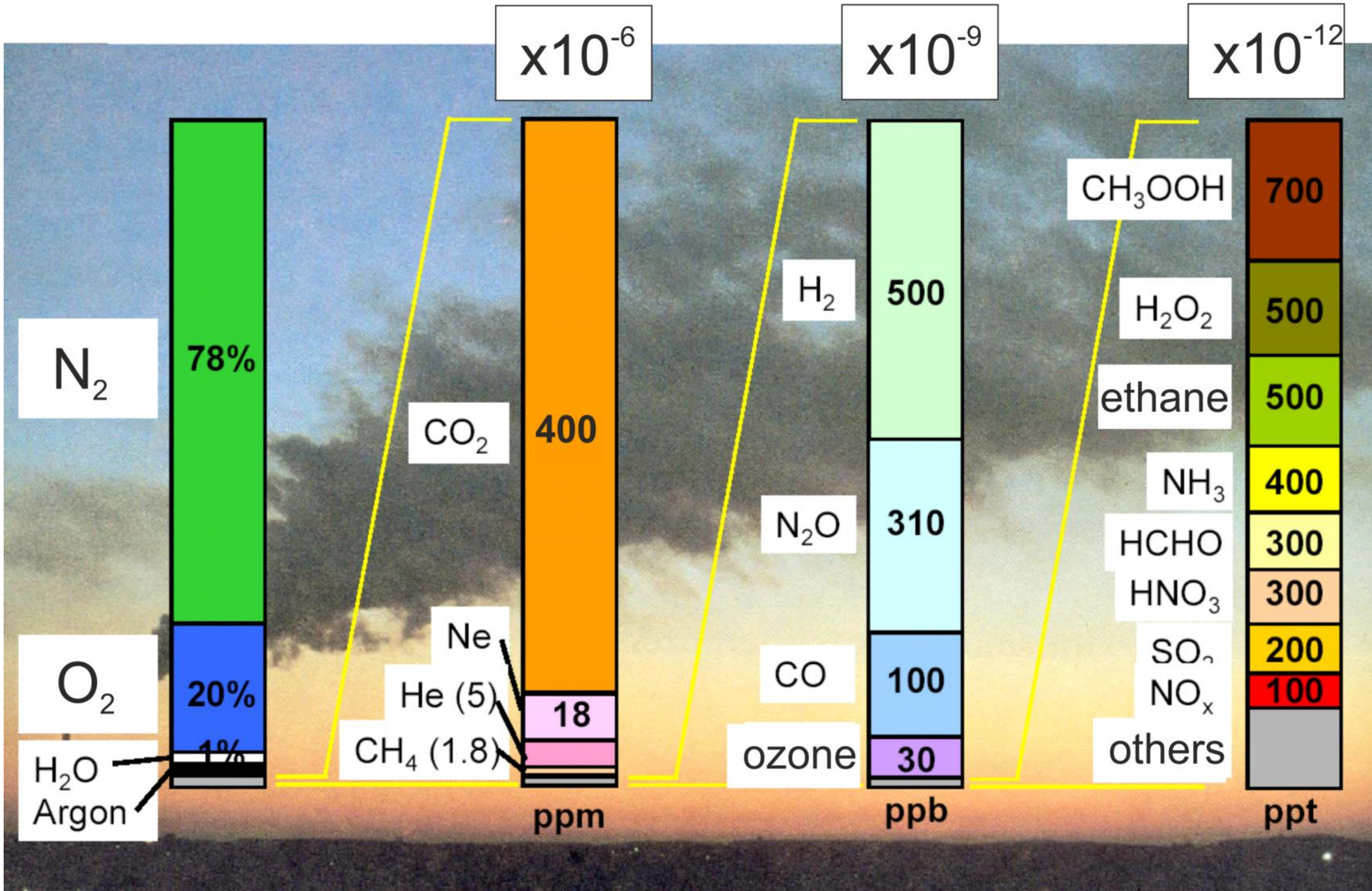


NASA Space Shuttle Endeavour

Gas Phase Composition of the Atmosphere



Gas Phase Composition of the Atmosphere



Atmospheric Composition

Present composition of the atmosphere:

- ***Permanent gases*** (remain essentially constant)

Nitrogen 78.1%
Oxygen 20.9%

Argon 0.9%
Neon 0.002%
Helium 0.0005%
Krypton 0.0001%
Hydrogen 0.00005%

- ***Variable gases*** (changing concentrations over a finite period of time).

Water vapor 0 to 4%

Carbon Dioxide 0.04%
Methane 0.0002%
Ozone 0.000004%

Atmospheric Composition

Definitions + terms

- NO_x — $NO + NO_2$
- NO_y — NO_x + all N(oxidation state ≥ +II) containing compounds, *e.g., NO_3, HONO, HNO_3, N_2O_5, PAN, nitrates, …*
- HCs — hydrocarbons
- VOCs — volatile organic hydrocarbons
  NMHC: non-methane HC
- CFCs — chloro-fluoro hydrocarbons
  HCFC's: CFC's containing H-atom(s)

- HO_x — $OH + HO_2$
- XO_x — ClO, OClO, BrO, OBrO

Vertical Profiles of Pressure and Temperature

Ideal Gas Law

Assumption: gas is infinite compressible

Air can be treated as an ideal gas and hence follows the ideal gas law:

$$PV = nRT, \qquad \text{(A)}$$

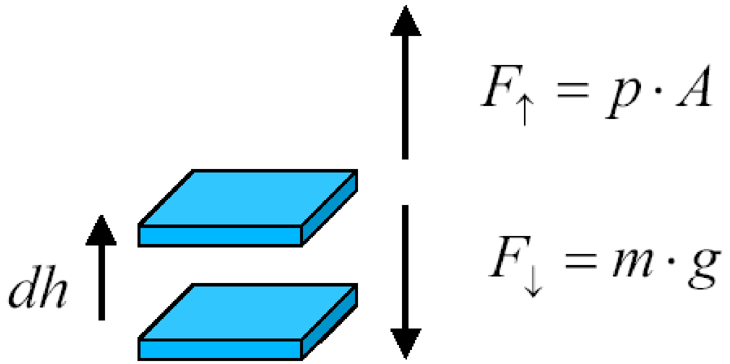
where P is the air pressure, n the number of moles of gas in the air parcel, and T the temperature (in

R : universal gas constant

R = 8.314 J mol^{-1} K^{-1}

Vertical Profiles of Pressure and Temperature

Hydrostatic Equilibrium -- Barometric Height Equation



The air pressure is due to the weight, i.e., gravitational force, of the column of air above it

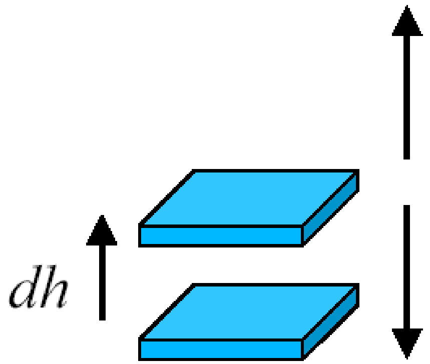
$$P = F/A = mg/A = \rho V g/A$$

m is the mass of air of density in a column of air of area *A* and volume *V*

Vertical Profiles of Pressure and Temperature

Hydrostatic Equilibrium -- Barometric Height Equation

$$P = F/A = mg/A = \rho V g/A$$



$$F_{\uparrow} = p \cdot A$$

$$F_{\downarrow} = m \cdot g$$

$$\frac{dp}{dh} = -g \cdot \rho$$

Considering the ideal gas law:

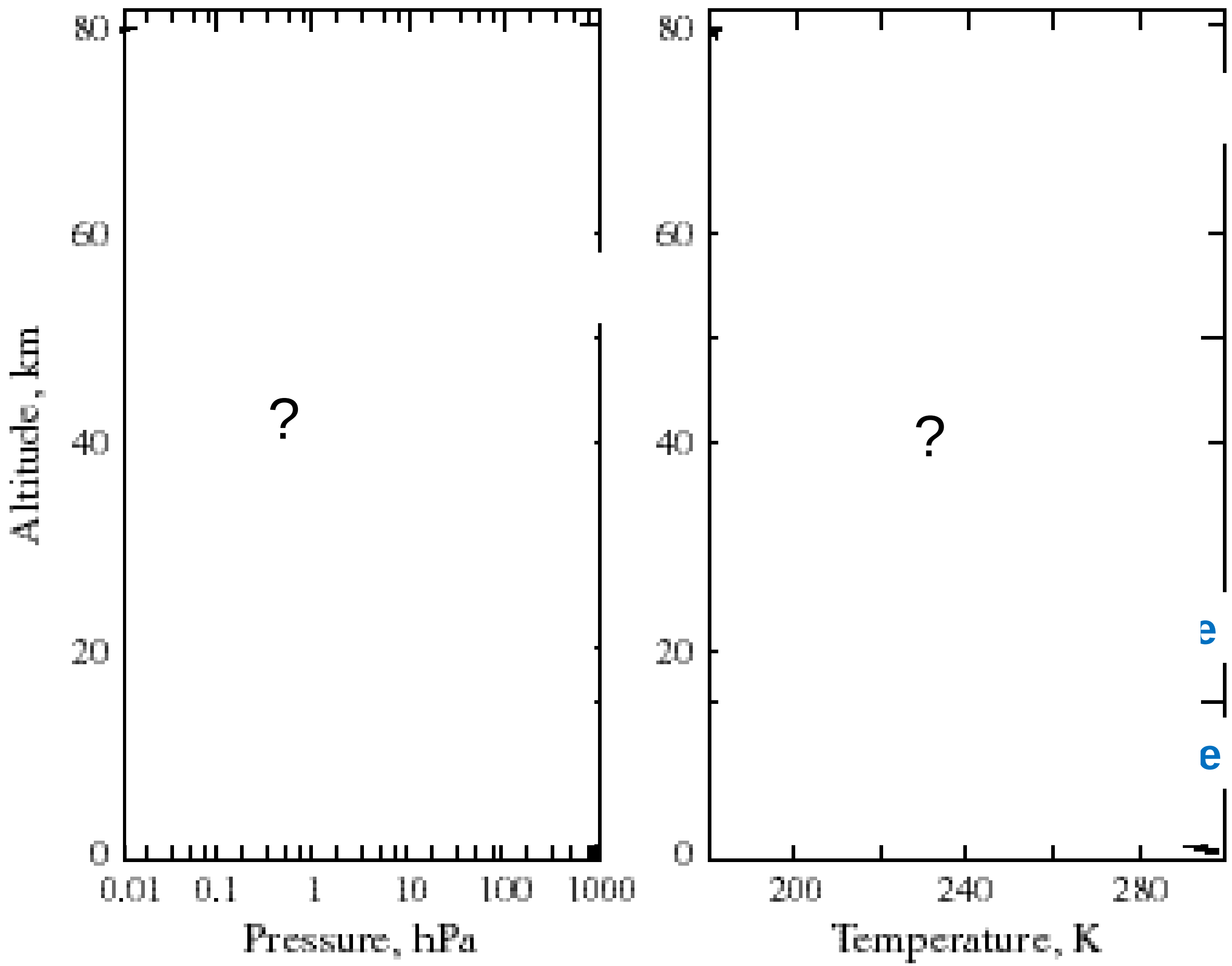
$$\frac{dp}{dh} = -\frac{g}{R \cdot T} p$$

Integration yields the <u>barometric height equation</u>:

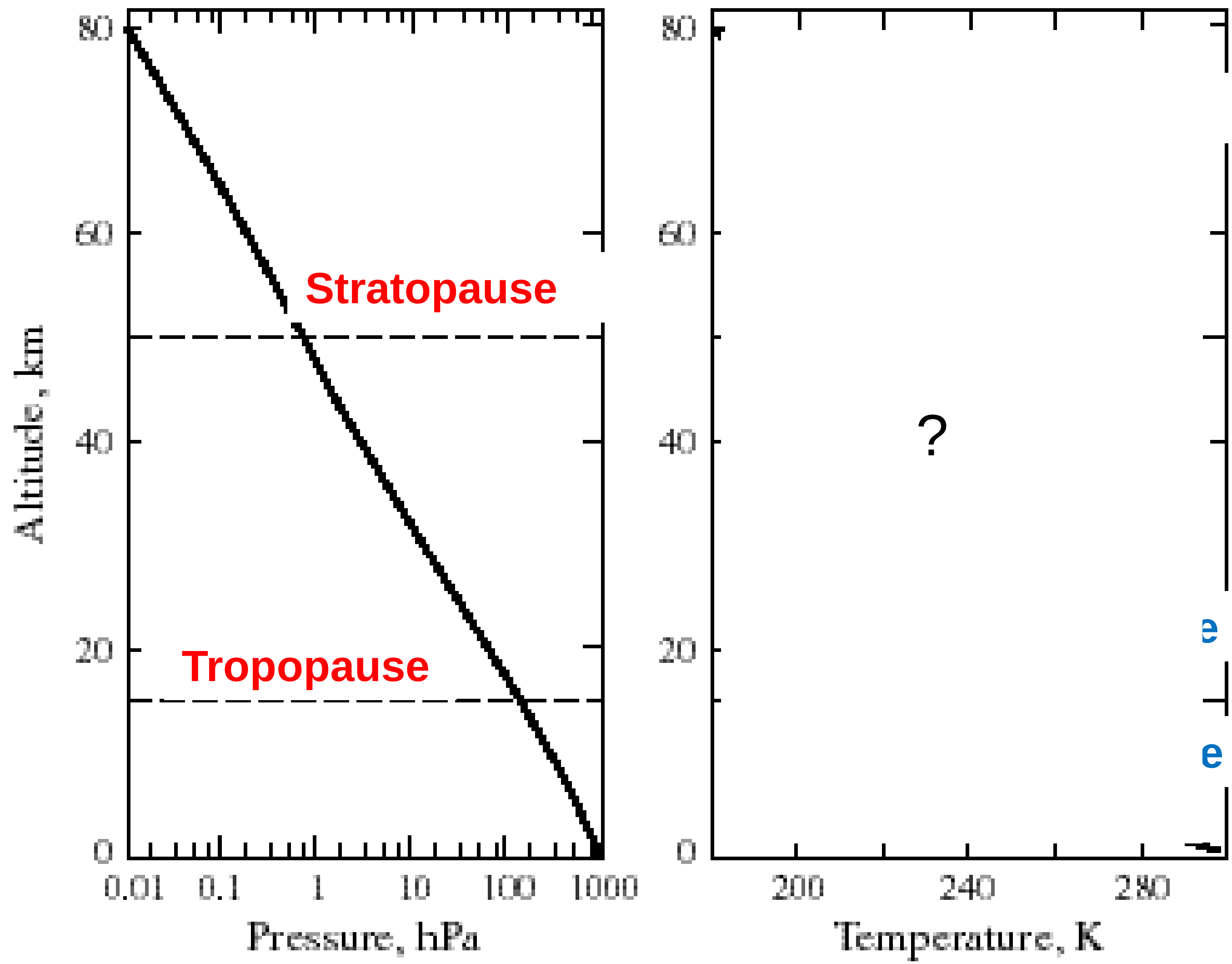
$$p = p_0 \exp(-h/H)$$

$H = RT/g$ scale height

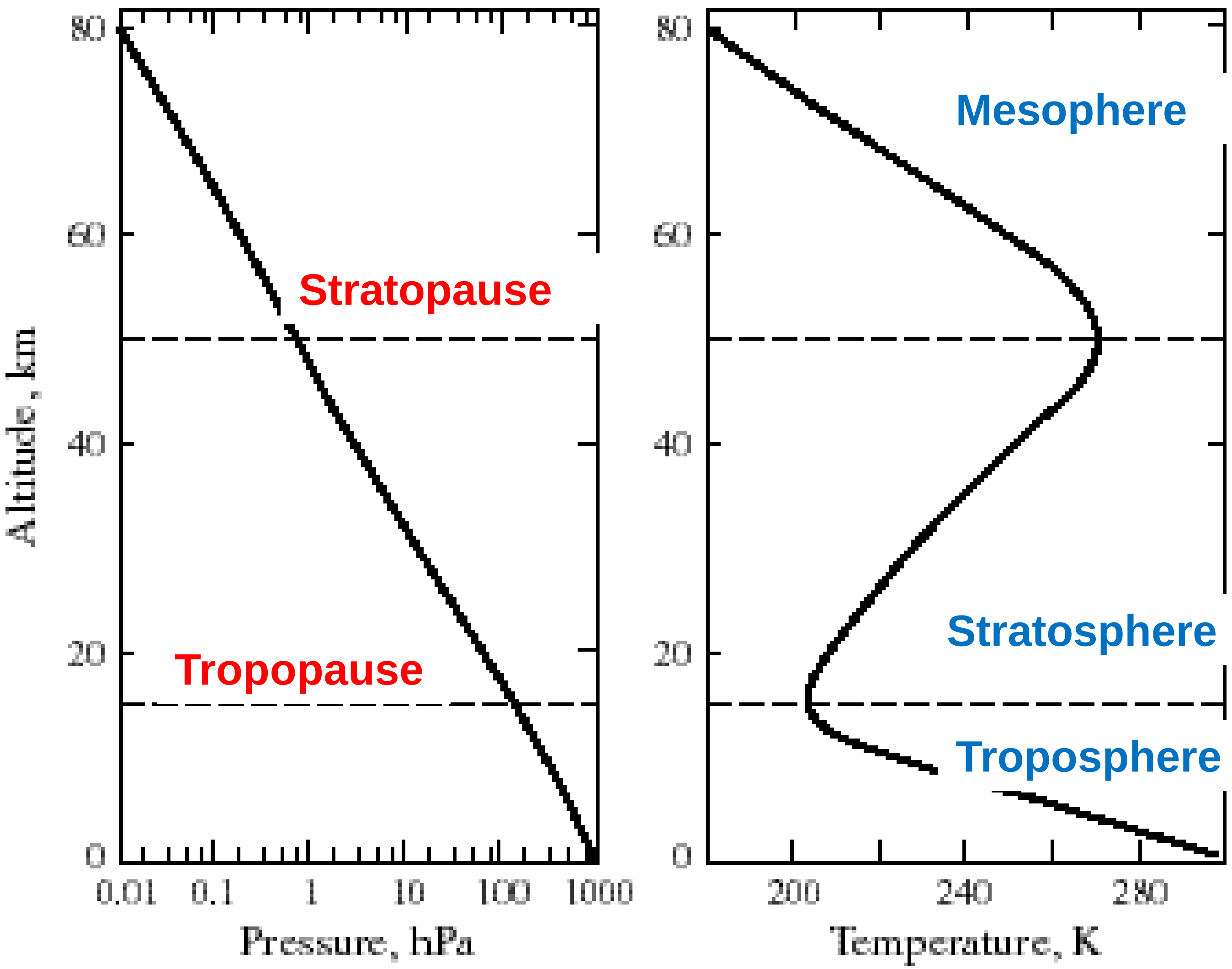
Vertical Profiles of Pressure and Temperature



Vertical Profiles of Pressure and Temperature



Vertical Profiles of Pressure and Temperature



Vertical Profiles of Pressure and Temperature

Scale Height

$$H = \frac{RT}{g} \approx 7.4 \text{ km } (T = 250 \text{ K})$$

Scale height is not constant ! Real application must include the temperature gradient (lapse rate) :

$\Gamma \approx -6.5 \text{ K km}^{-1}$	in the troposphere
$\Gamma \approx 0$	in the tropospause region
$\Gamma \approx +4 \text{ K km}^{-1}$	in the stratosphere

Vertical Profiles of Pressure and Temperature

Inversion

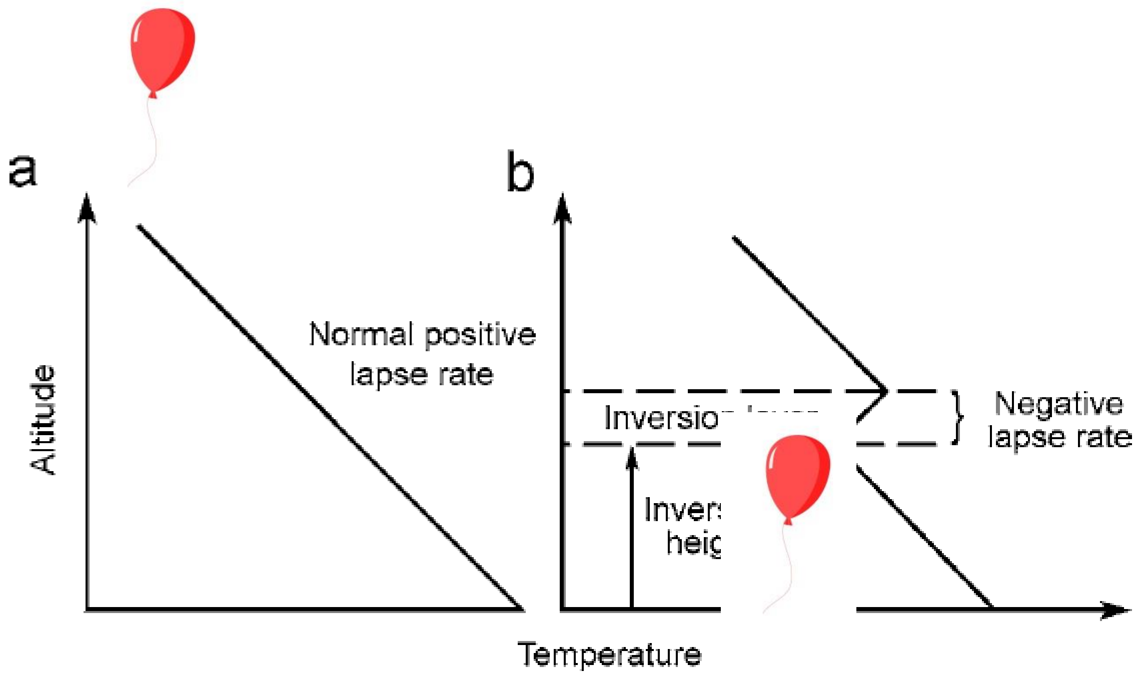
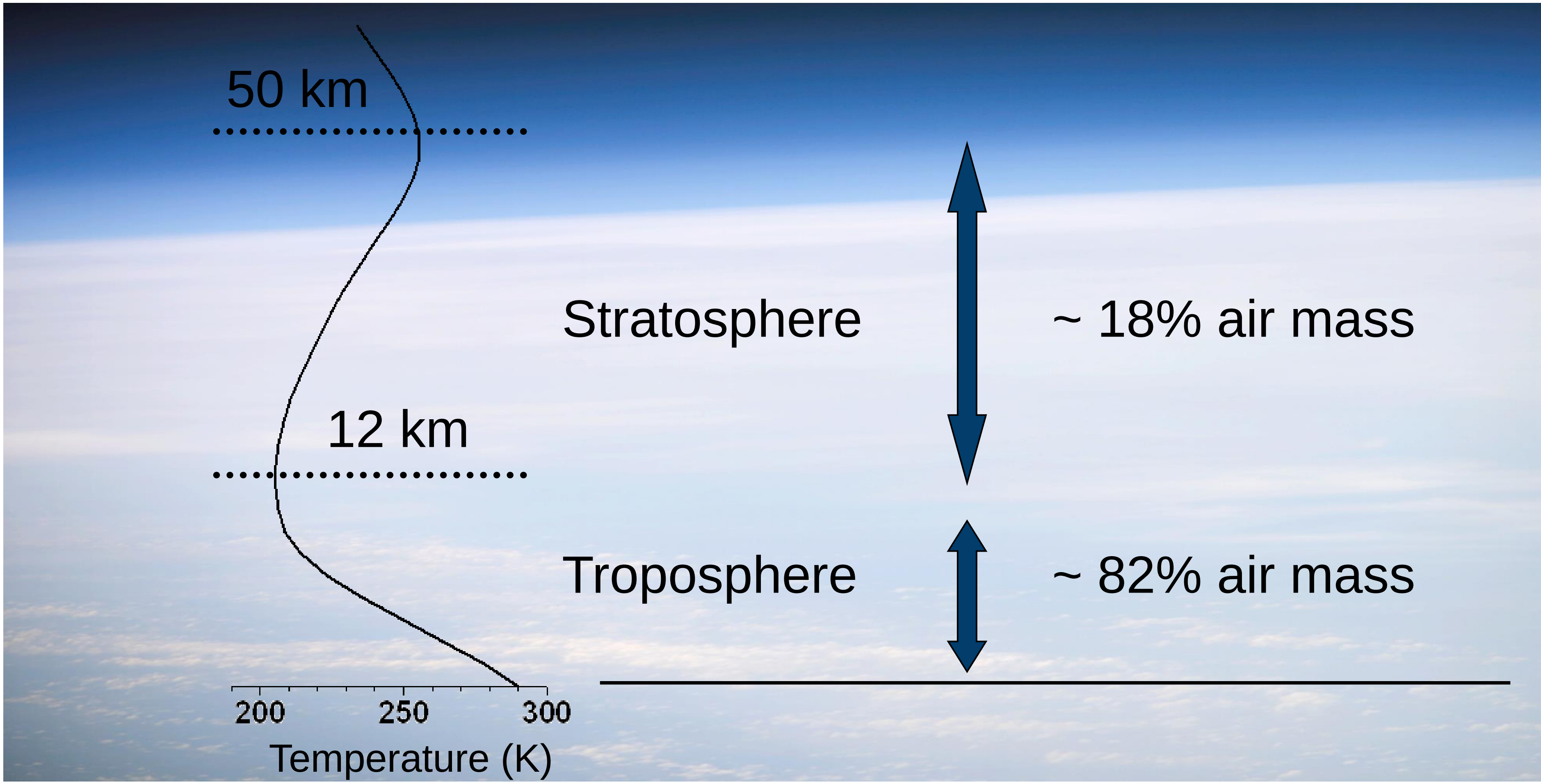


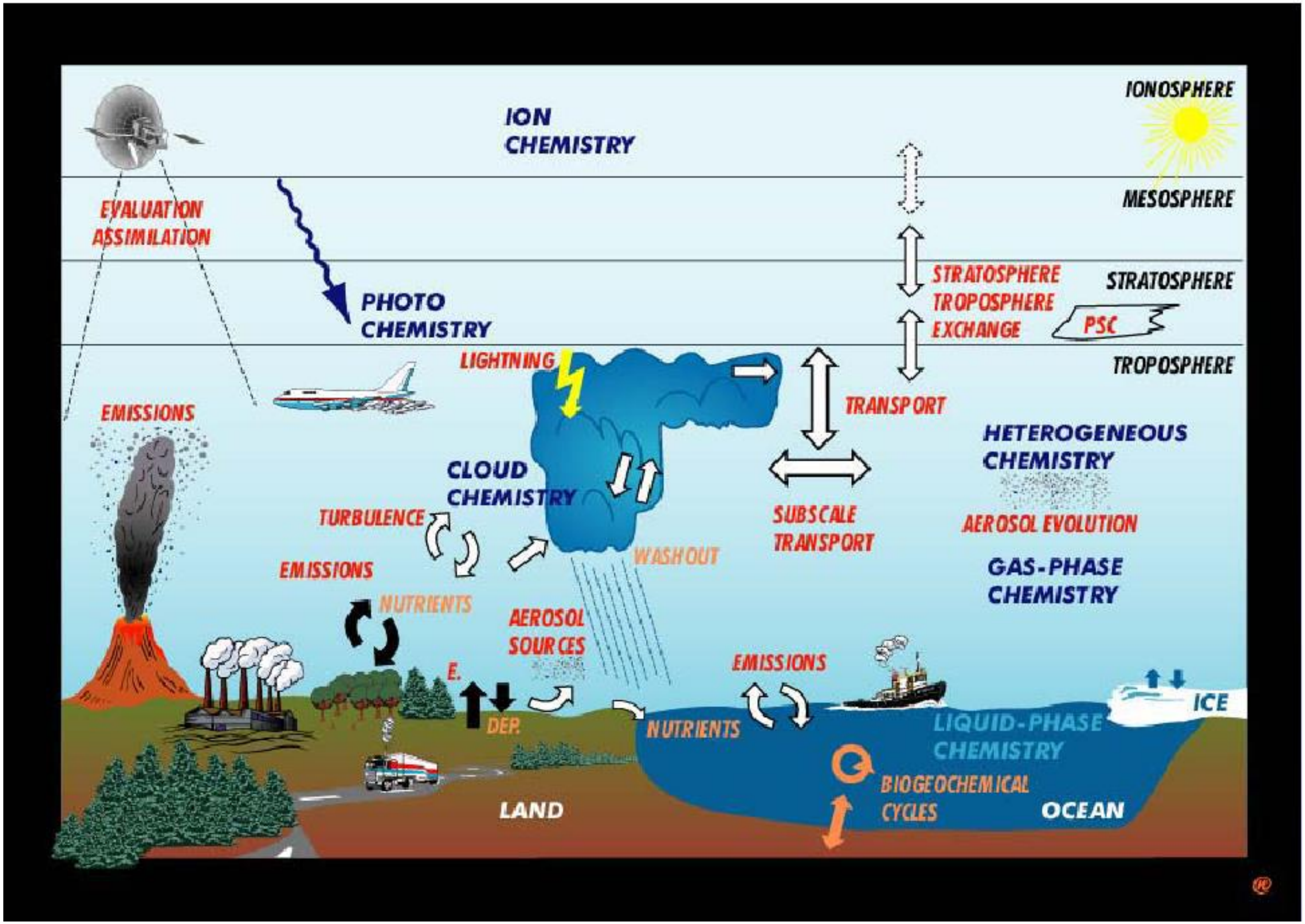
FIGURE 2.18 Variation of temperature with altitude within the troposphere: (a) normal lapse rate; (b) change in lapse rate from positive to negative, characteristic of a thermal inversion.

Vertical Profiles of Pressure and Temperature

Mass Distribution



Processes in the Atmosphere



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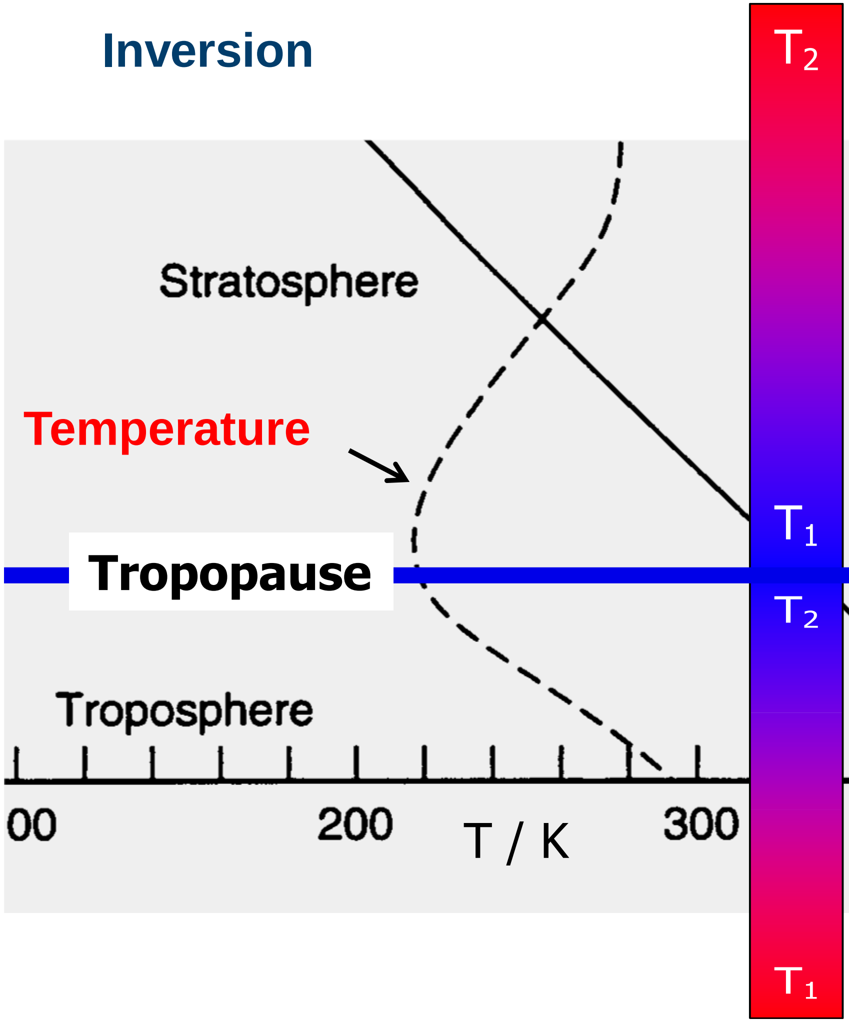
Vertical Profiles of Pressure and Temperature



Stratospheric Chemistry

- Laminar (diffusion)
- Low water content
- Inorganic chemistry (+CH_4)

Tropospheric chemistry

- Turbulent mixing
- High water content
- Inorganic + organic chemistry

Vertical Profiles of Pressure and Temperature

Stratosphere [10 – 40 km]

- ***Slow vertical mixing*** (“inversion layer”)
- Laminar (layered) flow, ***diffusion controlled***
- H_2O mixing ratios in the *ppmV* regime (!)
- CH_4 *the single carbon species* present in higher concentrations
- Prevailing presence of *CFC’s*

Vertical Profiles of Pressure and Temperature

Stratosphere [10 – 40 km]

'Inorganic' photochemistry
O_x, NO_x, HO_x, XO_X- cycles

Heterogeneous reactions:

Stratospheric surfaces: H_2SO_4 aerosol, PSC's

- Liquid phase (→ H_2SO_4/H_2O
  → $H_2SO_4/HNO_3/H_2O$)
- Solid phase (→ NAT, SAT, ice)

Vertical Profiles of Pressure and Temperature

Troposphere [0 – 10 km]

- ***Contains 80% of the total mass of the 'atmosphere'***
- ***Air moves vertically and turbulent***
- ***Decreasing temperature with increasing height, in response to the local pressure***
- ***Is directly in contact with earth's surface which is source and sink (≤ 1000 m 'boundary layer', BL)***
- ***Contains up-to 4% by volume gaseous H_2O***
- ***Variety of organic compounds present, many with a ≥ C4 body.***

Vertical Profiles of Pressure and Temperature

Troposphere [0 – 10 km]

Complex 'organic', sulfur and nitrogen oxides gas phase photochemistry

- Heterogeneous reactions:
- Surfaces within the troposphere:

→ Aerosols (air+particles)

- Liquid particles (→ Clouds, fog, sea salt,…)
- Solid particles (→ soot, dust, ice…)

→ Ground surfaces (→ liquid water, ice, soil,…)

END OF 1ST PART

- End of 1st part

Questions ??

Vertical Profiles of Pressure and Temperature

Atmospheric Mass (ma)

$$p_b = \frac{m_a\, g}{A}$$

Radius of Earth: 6378 km

Average Pressure at Ground: 984 hPa

$$m_a = \frac{4\pi R^2\, p_b}{g} = 5.2 \times 10^{18}\ \text{kg}$$

Total mole number of air in the atmosphere

$$N_a = \frac{m_a}{M_a} = 1.8 \times 10^{20}\ \text{moles}$$

Molar Mass of Air

M_a = 28.6 g/mol