EUROPEAN UNION
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Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

ATMOSPHERIC CHEMISTRY

Lecture No.: 1

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Organisation of study

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  e-learning:
  https://e-learning.vscht.cz/course/view.php?id=106
- Scale of subject: winter semester
  14 lectures, 14 weeks, 2 hours/week
- Classification: Exam - written + oral form (depending on result of the test)

Syllabus of subject

- Lecture 1. Atmosphere as basic component of natural environment
- Lecture 2. History of Earth's atmosphere
- Lecture 3. Environmental information systems
- Lecture 4. Physical rules in atmospheric processes
- Lecture 5. Basic reactions in the atmosphere, homogeneous and heterogeneous reactions
- Lecture 6. Introduction to the problematics of greenhouse gases
- Lecture 7. Characterisation of the main greenhouse gases
- Lecture 8. Selected atmospheric pollutants – acidic substances
- Lecture 9. Selected atmospheric pollutants – toxic substances

Syllabus of subject

- Lecture 10. Reactions of oxygen and water, formation of clouds and precipitations
- Lecture 11. Reactions of ozone, chemistry of the background troposphere, hydroxyl radical, hydroperoxyl radical, stratospheric damaging of ozone layer
- Lecture 12. Worldwide evolution in the field of air protection and important international agreements
- Lecture 13. Power industry as the main contributor to air pollution – London-type smog
- Lecture 14. Road transport as a contributor to air pollution – photochemical smog

Scope of lecture 1

Atmosphere as basic component of natural environment

- Definition of atmosphere, its borders and distribution of weight
- Atmospheric stratification according to altitude
- Physical characterisation of atmosphere and its overall chemical composition
- Detailed description of the most important atmospheric layers
- Influence of magnetic field on the atmosphere
- Atmosphere as a radiation filter

Basic properties of atmosphere

- The approximate height of measurable concentrations of the atmosphere is 560 km (the precise altitude is not available, however, a part of thermosphere and the whole exosphere are situated faraway)
- The overall weight of the atmosphere is only estimated and the value is 5.15×10^{18} kg

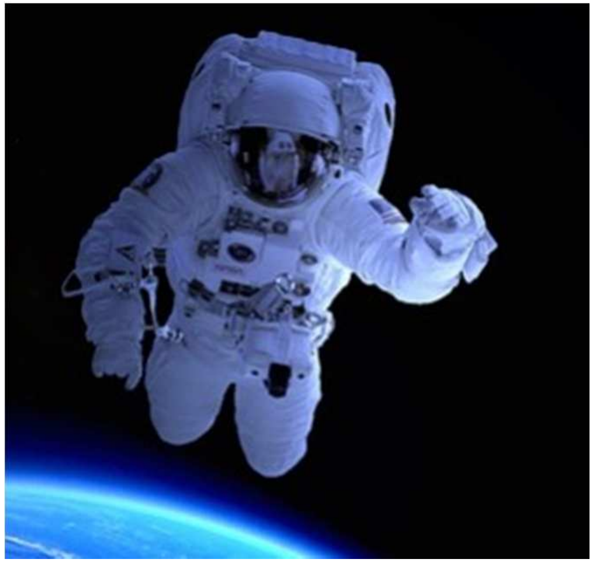
  (Source: American National Center for Atmospheric Research)
- The weight of the atmosphere distributed according to the altitude is following:

  ca. 50 % height up to 5.6 km (above the sea level)
  ca. 75 % height up to 11 km
  ca. 90 % height up to 16 km
  99.99997 % height up 100 km

Basic properties of atmosphere

- The border of the outer space is 100 km according to Féderátion Aéronautique Internationale (FAI) = International Aeronautical Federation
- The practical consequence of the so called Kármán line (KL = 100 km): the term „pilot“ is used for flights under this line and astronaut for flights over the KL
- but NASA defines the space border line to 50 miles = 80 km.
- Up to KL we speak about altitude, over KL about distance from Earth.

or



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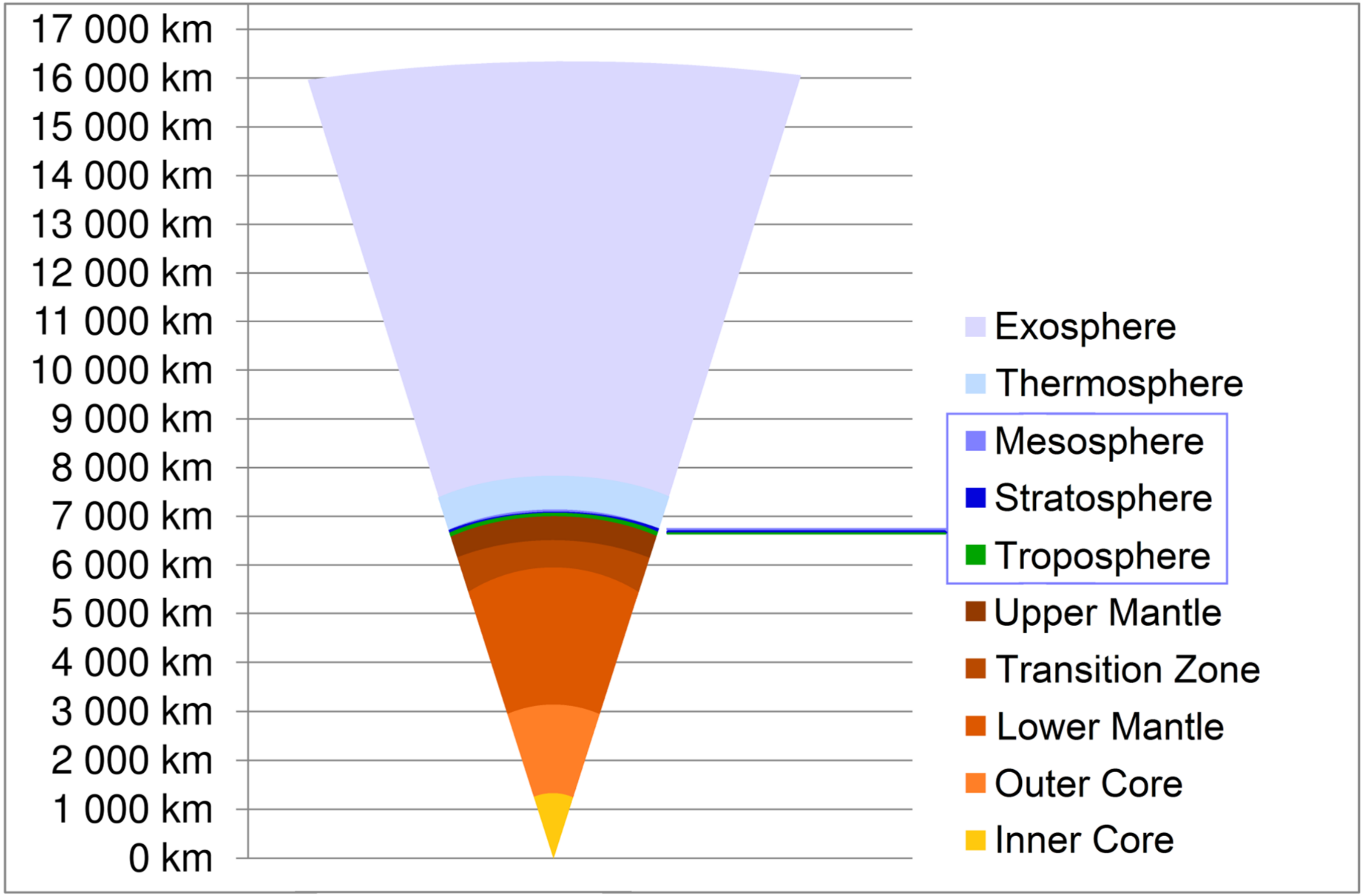
Basic properties of atmosphere

- Participation of atmosphere on the total weight of Earth, which is 8.62×10^{-5} % (it means < one millionth of the Earth's weight 5.972×10^{24} kg)



Stratification of atmosphere

- The atmosphere can be stratified according to various criteria: (Source: Kleczek, J. Toulky Vesmírem)

- According to temperature:
  - Troposphere
  - Stratosphere
  - Mesosphere
  - Thermosphere

- According to chemical properties:
  - Ecosphere
  - Troposphere
  - Stratosphere
  - Chemosphere
  - Ozonosphere
  - Ionosphere
  - Mesosphere

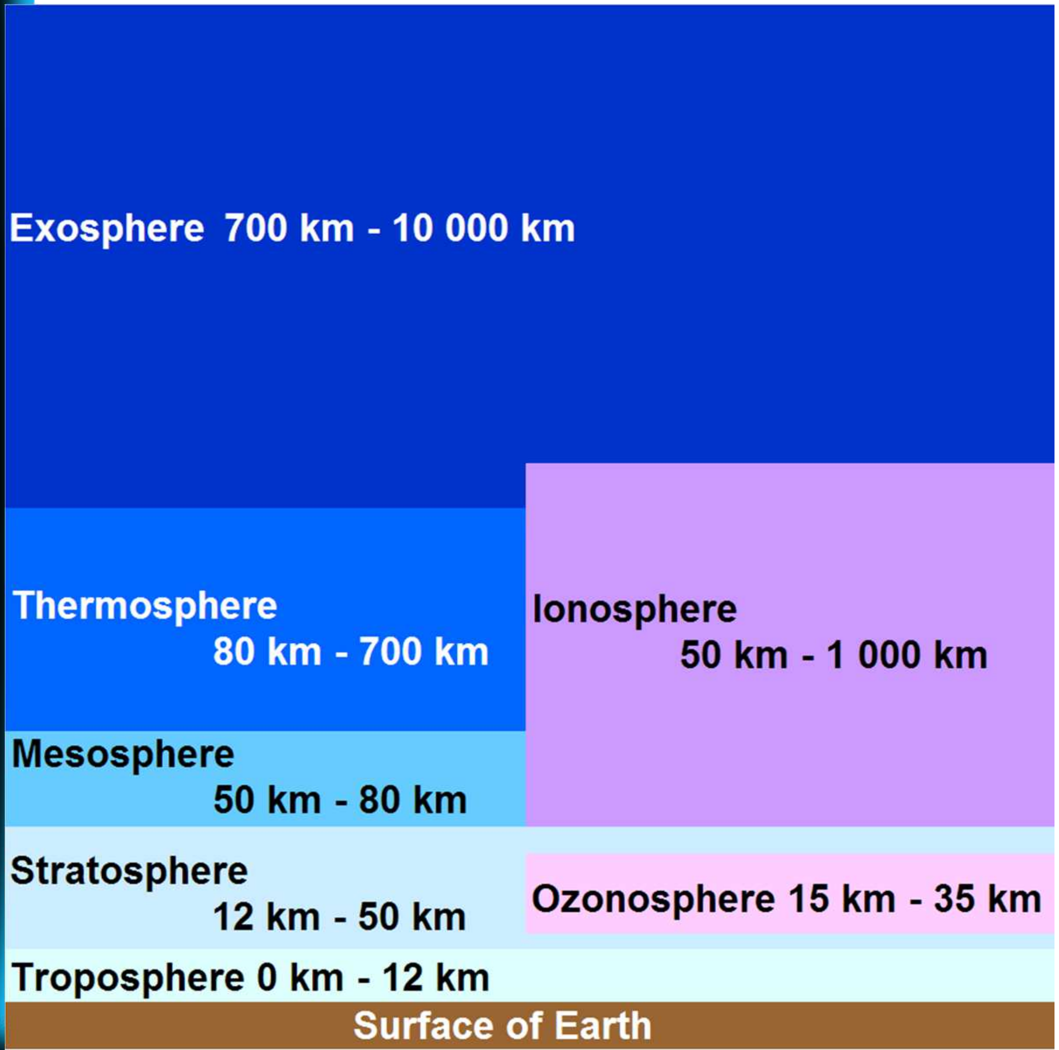
Stratification of atmosphere

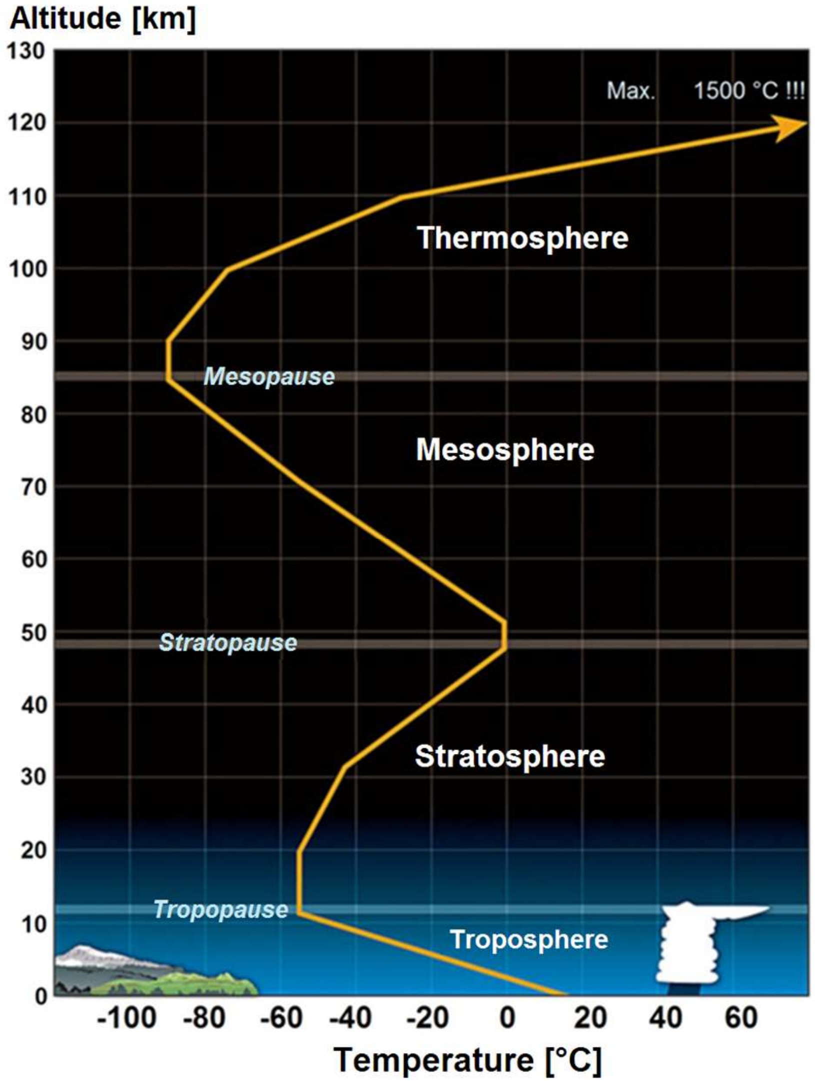
- The atmosphere can be stratified according to various criteria: (Source: Kleczek, J. Toulky Vesmírem)

- According to electrical properties
  - Neutrosphere
  - Ionosphere
- Accroding to movements
  - Troposphere
  - Stratosphere
- According to uniformity of composition
  - Homosphere
  - Heterosphere
- The most important and most frequently used stratification is according to the dependence of temperature and density upon altitude (seen on the next slide).

Stratification of atmosphere

Atmospheric layers and temperatures (by NASA and National Weather Service)





Relation altitude - parameters

- Expression of pressure in meteorology:

By SI permitted only:	Pascal	[Pa] = [N.m^{-2}]
Traditionally used also:	Torr	[Torr]
	Bar	[bar]
	Conventional mm of Mercury	[mm Hg]
	Conventional mm of water	[mm H_2O]
	Physical atmosphere	[atm]
Multiples in meteorology:	Millibar	[mbar]
	Hectopascal	[hPa]

	Torr	Pa	hPa	bar	mbar	mm Hg	mm H_2O	atm
1 Torr =	1	133.322	1.333	0.001	1.333	1	13.595	0.001
1 Pa =	0.008	1	0.01	1E-05	0.01	0.008	0.102	9.869E-06
1 hPa =	0.750	100	1	0.001	1	0.750	10.197	9.869E-04
1 bar =	750.064	100 000	1 000	1	1 000	750.064	10196.798	0.987
1 mbar =	0.750	100	1	0.001	1	0.750	10.197	9.869E-04
1 mm Hg =	1	133.322	1.333	1.333E-03	1.333	1	13.595	1.316E-03
1 mm H_2O =	0.074	9.807	0.098	9.807E-05	0.098	0.074	1	9.679E-05
1 atm =	760.002	101 325	1013.25	1.013	1013.25	760.002	10331.906	1

Relation altitude - parameters

- Calculation of pressure dependence on the height above sea level (Source: The Engineering ToolBox)

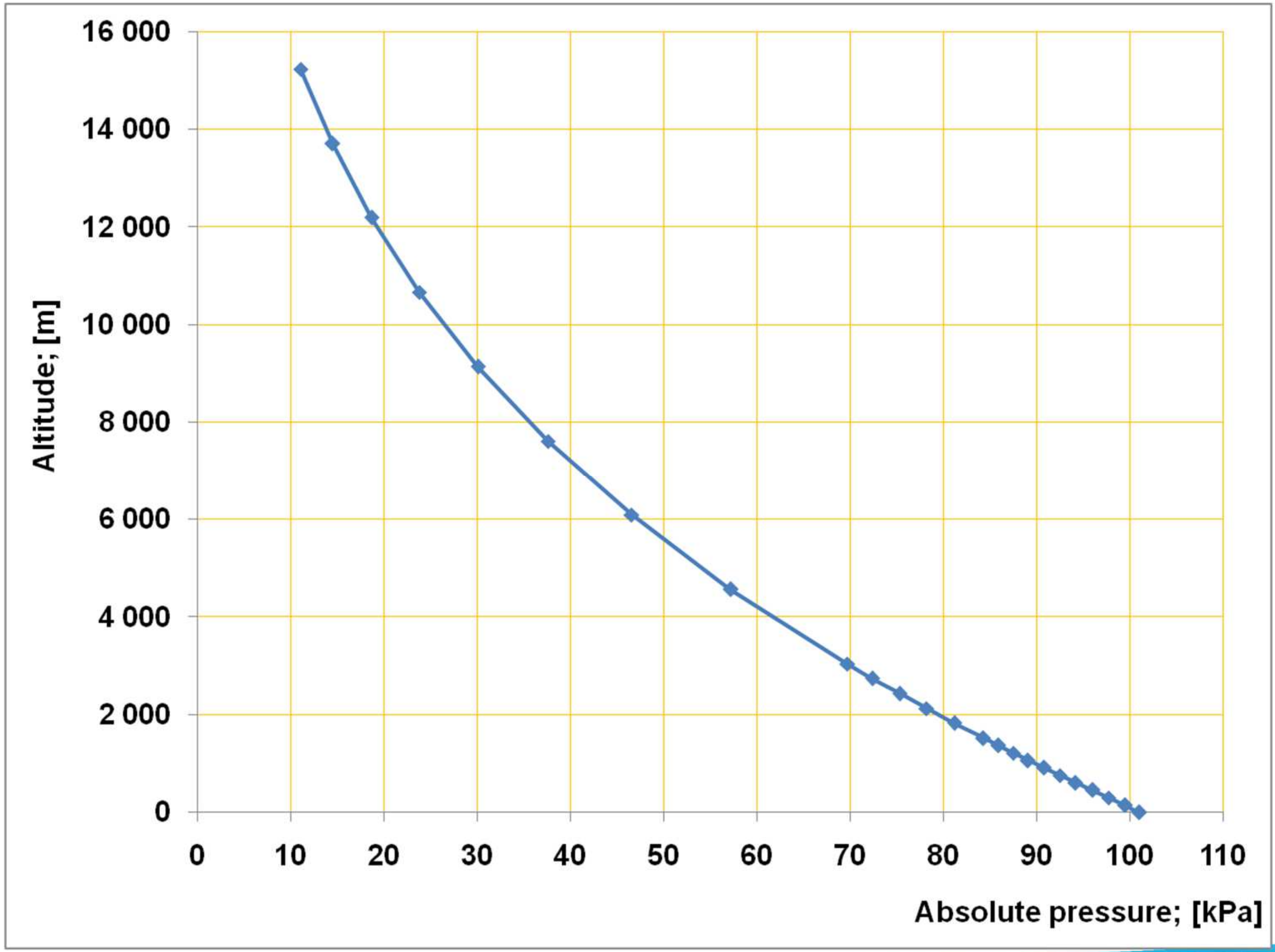
  Simple empirical model used: $p = 101\,325 \cdot (1 - 2.25577 \cdot 10^{-5} \cdot h)^{5,25588}$

Where:

p … pressure [Pa]

h … altitude [m]

(Applicable only up to 20 km)



Relation altitude - parameters

- Common dependence of p a T on altitude (Source: Engineering Smart Technology Products)

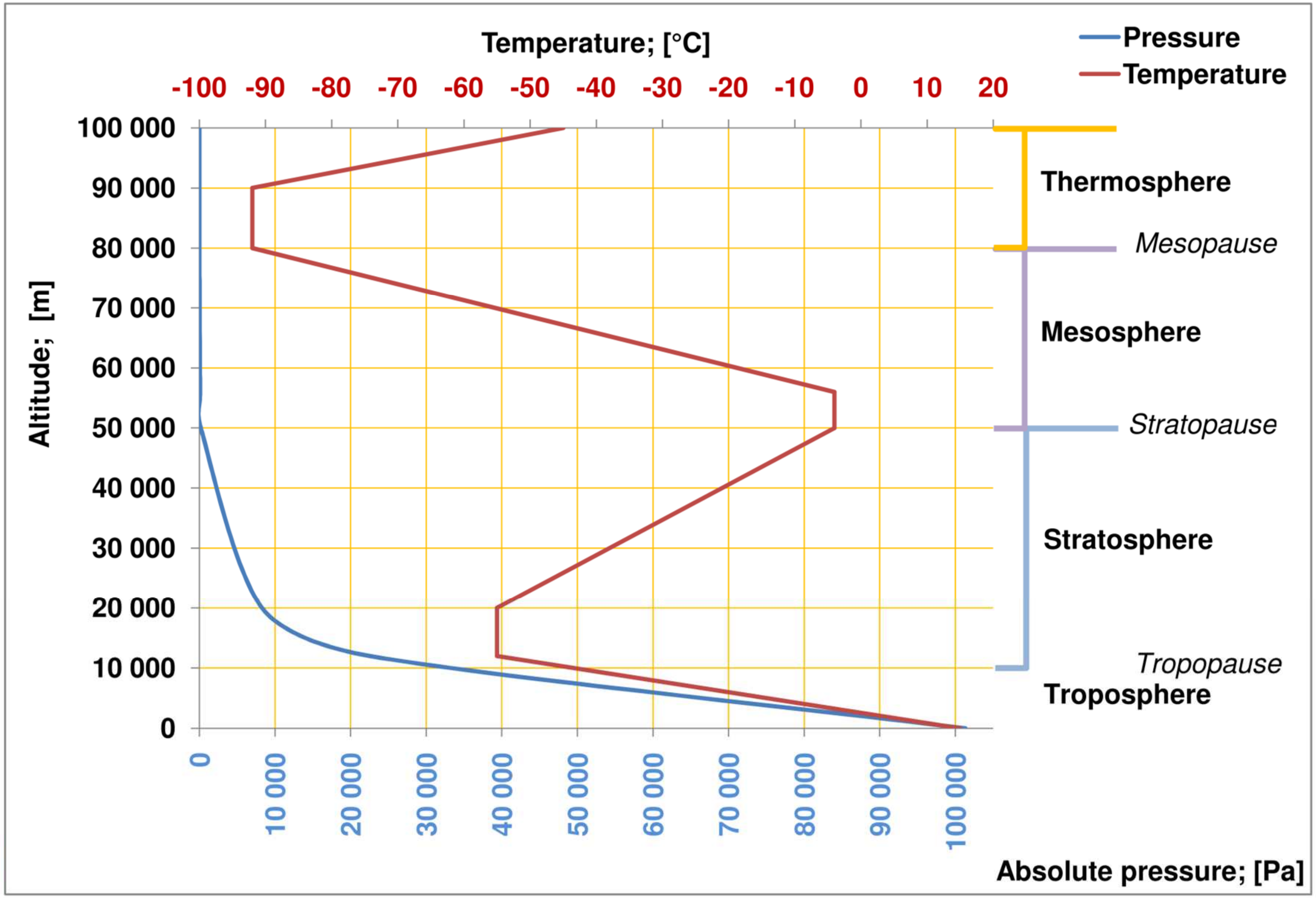
Alternative equation for air pressure with wider applicability range

$$p = p_s \cdot e^{\left[\frac{g \cdot M \cdot (h - h_s)}{R \cdot T_s}\right]}$$

Where:				
	p	… pressure in the given altitude		[Pa]
	p_s	… pressure on the sea level		[Pa]
	g	… gravity acceleration	9.80665	$m.s^{-2}$
	M	… average molar weight of air	0.0289644	$kg.mol^{-1}$
	R	… molar gas constant	8.31432	$N.m.mol^{-1}.K^{-1}$
	T_s	… average temperature on the sea level		[K]
	h	… altitude (height above sea level)		[m]
	h_s	… reference height	0	m

Relation altitude - parameters

- Using the equation $p = p_s \cdot e^{\left[\frac{g \cdot M \cdot (h - h_s)}{R \cdot T_s}\right]}$ the following graph is obtained:



Relation altitude - parameters

- Example: Mount Everest
  - height = 8,848 m (above the sea level)
  - average air pressure = 33.7 kPa (33 % of the standard pressure)

Basic chemical composition

- Chemical composition of dry atmosphere (volume percentage):

N_2	78.08 %;	O_2	20.95 %;	Ar	0.93 %
CO_2	0.04 %;	Ne	18.18×10^{-4} %;	He	5.25×10^{-4} %
CH_4	2×10^{-4} %;	Kr	1.14×10^{-4} %;	N_2O	0.5×10^{-4} %;
H_2	0.5×10^{-4} %;	Xe	0.087×10-4 %;	O_3	$0\text{-}0.07\times10^{-4}$ %
SO_2	$0\text{-}1\times10^{-4}$ %;	NO_2	$0\text{-}0.02\times10^{-4}$ %		

H_2O overall content represents 0.25 % of the total weight of the atmosphere.

Characterisation of layers

- Troposphere
  - average scale of 12 km
  - thickness depends on latitude and on the season of the year
  - thickness near poles is 8 – 9 km, over the equator up to 17 km
  - represents 85 % of the overall weight of atmosphere
  - has 2 sub -layers:

    Planetary Boundary Layer (PBL)
    Open Troposphere (OT)
  - PBL thickness is ca. 1 km; it is significantly turbulent due to contact with the relief ⇒ mixing of gases + pollutants + aerosols
  - OT temperature decreases with the altitude (negative temperature gradient) down to -55 °C in moderate latitudes; gas composition homogeneous, mixing independent on the relief (determined by pressure gradients and Coriolis force); OT accumulates majority of water (layer where rains are generated).

Characterisation of layers

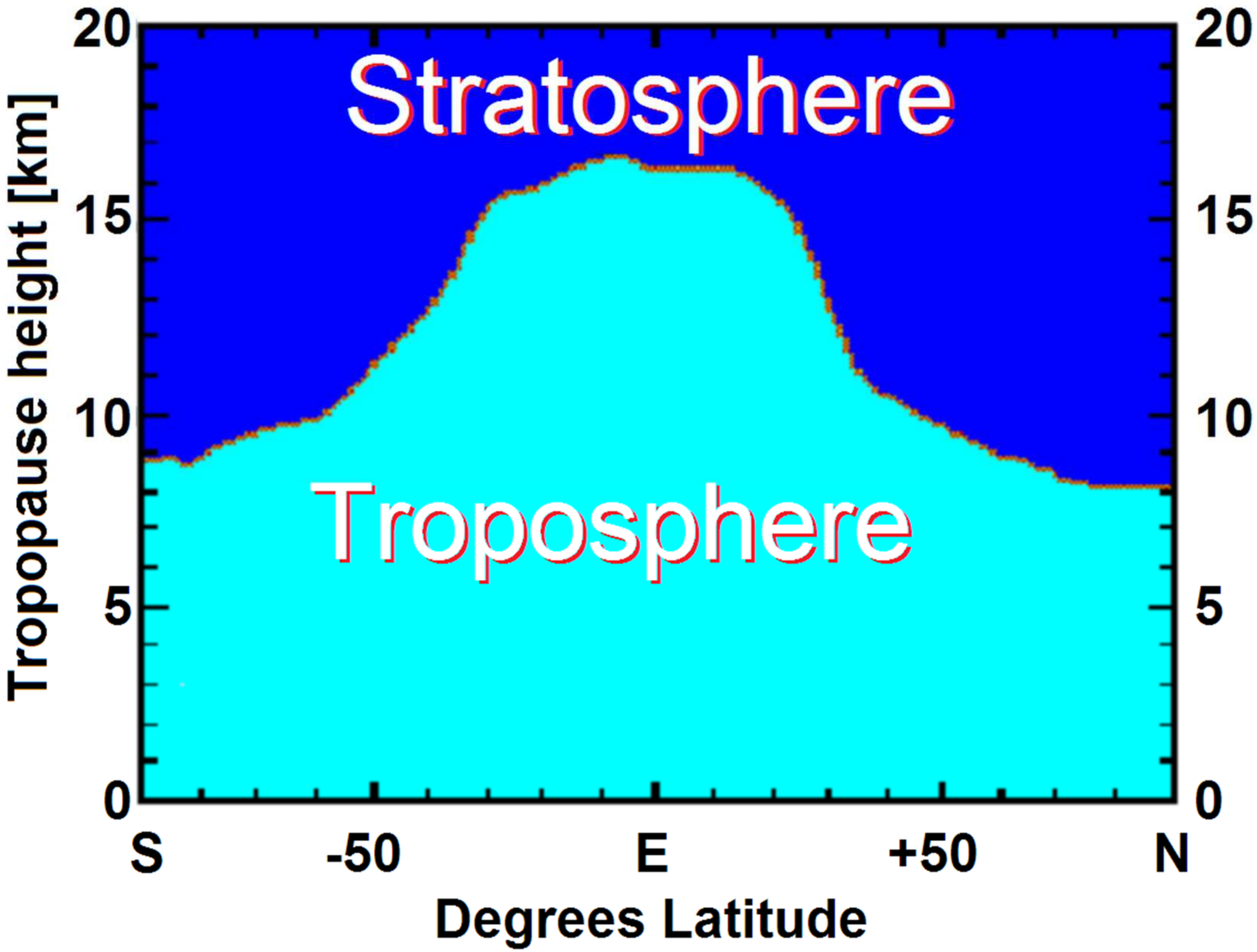
- Tropopause
  - Cold, thin layer between troposphere and stratosphere;
  - Temperature ca. -55 °C, altitude ca. 12 km;
  - Significant barrier blocking raising of water vapours to higher atmospheric layers;
  - In case of the absence of tropopause, water would ascend to the layer with high-energetic irradiation, subsequent photodissociation and leakage of Hydrogen to outer space:

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2$$

  - it happened in the geological history of the planet; Earth lost irreversibly the majority of Hydrogen and Helium by this chemical mechanism.

Characterisation of layers

- Variable thickness of troposphere according to latitude (E = Equator)



Characterisation of layers

- Stratosphere
  - Layer above tropopause, limited by the area, where temperature ceases to decrease according to altitude, and area where temperature starts to decrease again;
  - Temperature -55 up to – 4°C, altitude 12 – 50 km;
  - Ozonosphere is a part of stratosphere (15 – 35 km);
  - Content of Ozone in the ozonosphere is 10 ppm ⇒ absorption of UV irradiation causes simultaneous emission of heat (therefore positive temperature gradient in stratosphere);
- Mesosphere
  - Layer with typical rapid decrease of temperature with altitude;
  - The reason is absence of molecules capable of absorbing the radiation from the Sun;
  - Temperature between -4 and -90 °C, altitude 50 – 80 km.

Characterisation of layers

- Thermosphere
  - Layer above mesosphere, which has a remarkable positive temperature gradient;
  - Thickness of the layer is bigger than the count of all the layers situated underneath; Thermosphere occupies altitudes between 80 and 700 km; temperature rises from -90 up to +1200 °C;
  - In this layer, the atmosphere has very low density (pressure drops from ca. 7 kPa practically to zero);
  - Temperature in its upper part (500 – 700 km) reaches 1200 °C due to the absorption of radiation with wavelength < 200 nm;
  - Note: The above mentioned high temperatures are not measurable using conventional methods, due to extremely low particle concentrations – the only available method is the measurement of mean kinetic energy of molecules.

Characterisation of layers

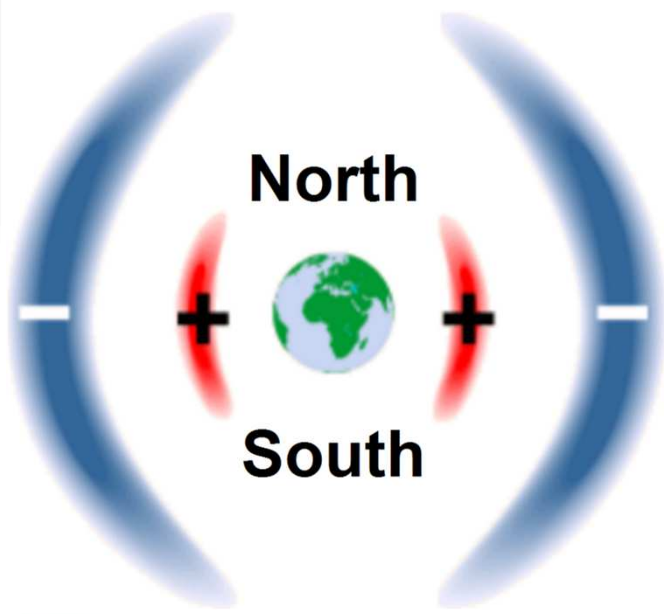
- Exosphere
  - Transition zone, whose residues can be measured by sensitive analysers up to the distance of 10 000 km from the Earth's surface;
  - Temperature changes are not significant;
  - Atoms, molecules and ions are irreversibly released into the interplanetary space;
  - Exosphere has very low density; containing almost only light gases H_2 and He;
  - Note. Decrease of concentrations of heavier gases is gradual, it means their concentrations change with the distance from Earth $\Rightarrow$ alternative denomination of the whole exosphere and thermosphere above ca. 85 km is heterosphere.

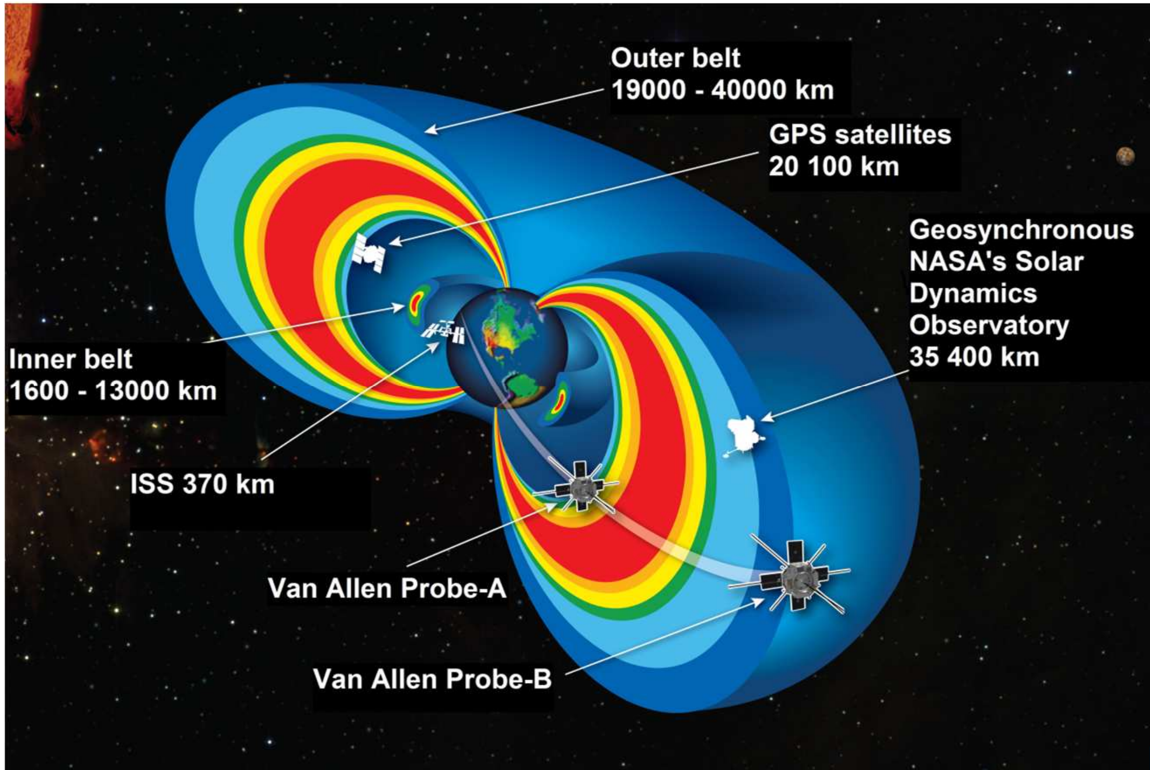
Characterisation of layers

- Ionosphere
  - Layer discovered in 1901 and defined on the basis of electrical criteria instead of altitude dependence of pressure etc.;
  - It occupies the whole mesosphere, whole thermosphere and lower part of exosphere;
  - Generation of ions induced by electromagnetic radiation in the range of UV wavelengths;
  - On the night side of the planet, a slow recombination of cations occurs with free electrons (disappearing of ions faster in lower layers, where a higher concentration of particles is achieved) ⇒ therefore, it causes night shift of the lower border of ionosphere to higher altitudes;
  - Big practical importance of ionosphere for communication = reflection of electromagnetic waves back to the surface ⇒ transmission of radio waves.

Characterisation of layers

- Influence of magnetic field – capture of charged particles, so called solar wind
  - Van Allen belts of ionized particles (discovered in 1958);
  - Inner belt with positive and outer belt with negative charge (range 400 - 50 000 km);
  - Alert! High energy p^+ a e^- in the belts dangerous for astronauts.





Atmosphere as irradiation filter

- Radiation with wavelength > 330 nm (i.e. part of UV, visible and IR)
  - breakthrough to the surface
- Radiation with wavelength 200 – 330 nm (i.e. part of UV)
  - breakthrough 50 km above the surface
- Radiation with wavelength 100 – 200 nm (i.e. part of UV)
  - breakthrough 200 km above the surface
- Note: so-called cosmic radiation in fact consists of particles (99 % cores of elements, 1 % electrons, regarding cores: 90 % isolated protons, 9 % alpha particles and 1 % heavier cores) ⇒ interaction with magnetic field.