Report

The atmosphere of our Earth, of planets of our solar system and of exoplanets

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2. Physics and Chemistry of the Atmosphere
2.1 Overview and Content

In this Chapter a survey about the physical and chemical properties of air and the global Atmosphere is given.

In Section 2.2 we discuss the most important molecules and atoms of the dry Atmosphere: molecular nitrogen ($N_2$), oxygen ($O_2$), ozone ($O_3$), atomic Argon (Ar) as well as very small amounts of trace gases, for example Carbon dioxide ($CO_2$).

The most important properties of the Troposphere are discussed in Section 2.3: General properties, water vapor, clouds, winds and barometric height formula.

Section 2.4 is dedicated to the Stratosphere: General properties, temperature profile as well as properties and function of ozone.

In Section 2.5 we are concerned with the Mesosphere: General characteristics, temperature profile and $CO_2$ – concentration.

In Section 2.6 the most important properties of the Thermosphere are discussed: $H_2$ - molecules and He – atoms – radiation temperature.

In Section 2.7 we discuss the outermost layer, the so-called Exosphere. In the Exosphere the concentration of the particles is negligibly small and the particles are almost completely ionized. The radiation temperature changes strongly between day and night.
## 2.2 Average Composition of the dry Atmosphere

### Average composition of dry Air in the Troposphere (s. A-2-1)

<table>
<thead>
<tr>
<th>Principle constituents</th>
<th>Volume (%)</th>
<th>Volume (ppm)</th>
<th>Masse (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen ( (N_2) )</td>
<td>78.084</td>
<td>780'840</td>
<td>75.518</td>
</tr>
<tr>
<td>Oxygen ( (O_2) )</td>
<td>20.942</td>
<td>209'420</td>
<td>23.135</td>
</tr>
<tr>
<td>Argon ( (Ar) )</td>
<td>0.934</td>
<td>9'340</td>
<td>1.287</td>
</tr>
<tr>
<td><strong>Sub - total</strong></td>
<td><strong>99.960 %</strong></td>
<td><strong>999'600 ppm</strong></td>
<td><strong>99.940 %</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trace gases</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide ( (CO_2) )</td>
<td>380.00*10^{-4}</td>
<td>380</td>
<td>580.000*10^{-4}</td>
</tr>
<tr>
<td>Neon ( (Ne) )</td>
<td>18.18*10^{-4}</td>
<td>18.18</td>
<td>12.670*10^{-4}</td>
</tr>
<tr>
<td>Helium ( (He) )</td>
<td>5.24*10^{-4}</td>
<td>5.24</td>
<td>0.720*10^{-4}</td>
</tr>
<tr>
<td>Methane ( (CH_4) )</td>
<td>1.76*10^{-4}</td>
<td>1.76</td>
<td>0.970*10^{-4}</td>
</tr>
<tr>
<td>Krypton ( (Kr) )</td>
<td>1.14*10^{-4}</td>
<td>1.14</td>
<td>3.300*10^{-4}</td>
</tr>
<tr>
<td>Xenon ( (Xe) )</td>
<td>0.09*10^{-4}</td>
<td>0.087</td>
<td>0.400*10^{-4}</td>
</tr>
<tr>
<td>Hydrogen ( (H_2) )</td>
<td>~ 0.50*10^{-4}</td>
<td>~ 0.5</td>
<td>~ 0.036*10^{-4}</td>
</tr>
<tr>
<td>Nitrous oxide ( (N_2O) )</td>
<td>0.31*10^{-4}</td>
<td>0.317</td>
<td>0.480*10^{-4}</td>
</tr>
<tr>
<td>Carbon monoxide ( (CO) )</td>
<td>~ 0.2*10^{-4}</td>
<td>~ 0.2</td>
<td>~ 0.100*10^{-4}</td>
</tr>
<tr>
<td><strong>Sub - total</strong></td>
<td>~ 0.040 %</td>
<td>~ 400 ppm</td>
<td>~ 0.060 %</td>
</tr>
</tbody>
</table>
Elemental gaseous nitrogen is present only in the form of diatomic molecules. (molecular nitrogen); its molecular formula is $\text{N}_2$. Molecular nitrogen is the principal constituent in air. Air contains 78 Volume % of nitrogen gas.

Molecular nitrogen is a colourless, odourless and tasteless gas.

The two N atoms of the $\text{N}_2$ molecule are bound by a stable triple bond (see Figure), and the molecule is very inert, i.e. it does hardly participate in chemical reactions. The associated high dissociation energy for the reaction $\text{N}_2 \rightarrow \text{N} + \text{N}$ is 942 kJ/mol (1 mol of nitrogen gas contains $6.023 \times 10^{23}$ $\text{N}_2$ molecules).

Elemental oxygen is a chemical compound containing two oxygen atoms, i.e. its molecular formula is $\text{O}_2$. The two O-atoms of $\text{O}_2$ are bound by a stable covalent double bond.

Molecular oxygen is a colourless and odourless gas. Air contains about 20.9% $\text{O}_2$ and about 78% $\text{N}_2$.

Nearly all living beings need oxygen for breathing.

In contrast to nitrogen, oxygen is a highly reactive gas. But because of the chemical inactivity of nitrogen, $\text{N}_2$ does usually not react with $\text{O}_2$ in the atmosphere; reactions are only possible in very special cases, for instance in the case of a lightning.
Concentration in Air: 0.9340 %; corresponds to 934 ml per 100 litres of Air.

Argon is the third most abundant element in Earth’s Atmosphere (s. p. 16). The reason for the high abundance of Ar is due to the fact, that Ar results by the decay of $^{40}$K, the abundance of which is 2.6% in the Earth’s crust. It then has been transported into the Atmosphere by volcanic activities.

Decay reaction: $^{40}$K$_{19}$ → $^{40}$Ar$_{18}$ + 1 positron; half-life time = 11.93 Gyr

($^{40}$Ar$_{18}$: mass number of Ar = 40, proton number $Z$ = 18; positron = antiparticle of the elektron); (1 Gyr = 1 Giga-year = $10^9$ years).
**Trace gases in the Air (s. p. 16)**

**Xenon (Xe)**
- colourless, odourless and inert noble gas;
- atomic number \( Z = 54 \); neutrons: \( N = 77 \); \( A = Z + N = 131 \);
- density \( \rho = 5.8982 \text{ kg/m}^3 \) at 273.15 K and 1 atm = 1013 hPa;
- Xenon is heavier than air;
- in Air: about 0.09 ppm

**H\(_2\)**
- two protons and 2 electrons
- covalent bond
- diatomic gas
- in Atmosphere: very small concentration (s. p. 16)

**N\(_2\)O**
- Nitrous oxide: colourless gas (laughing gas)
- laughing gas: respiration can cause euphory
- \( \text{N}_2\text{O} \) is a greenhouse gas (6% are anthropogenic)
- \( \text{N}_2\text{O} \) contributes to the depletion of the \( \text{O}_3 \) layer (s. p. 22)

**CO**
- CO: colourless, odourless and tasteless
- very poisonous → dangerous for breathing
- CO is combustible
- doubling of the CO- concentration since pre-industrial times
- increase of tropospheric CO
- contribution to global warming

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**Ozone: Formation and Properties**

Ozone (\( \text{O}_3 \)) is formed from the dioxide \( \text{O}_2 \) and a oxygen atom \( \text{O} \). The oxygen atom \( \text{O} \) is formed from \( \text{O}_3 \) by the action of ultraviolet light (UV) but also by atmospheric electrical discharges. \( \text{O}_3 \) is present in low concentrations throughout the Earth's atmosphere. In total, ozone makes up only 0.6 ppm of the atmosphere.

Ozone is a pale blue gas with a distinctively pungent smell. It is an allotrope of oxygen \( \text{O}_2 \). The term allotrope refers to one or more forms of an elementary substance. The allotropes of oxygen are \( \text{O} \), \( \text{O}_2 \) and \( \text{O}_3 \).

Ozone is not a very stable molecule: it decomposes in a short time into normal oxygen. This instability is due to its high reactivity and aggressivity with other compounds.
Some properties of the Ozone molecule

The molecular structure of the polar molecule is bent and the dipole moment is 0.5337 D. The O-O distance is 127.8 pm (= 1.278 Å = 0.1278 nm). The angle between the 3 oxygen atoms is 116.8°. [1 D = 1 Debye = 3.338*10^{-30} Cm (1 C = 1 Coulomb)]

The actual structure of the ozone molecule is the «average» of two resonance structures. This means that the bonding can be expressed as a resonance hybrid with a single bond on one side and a double bond on the other, producing an average bond order of 1.5 for each side.

Formation: \[ 3 \text{O}_2 \rightarrow 2 \text{O}_3 \; ; \; \Delta H = +286 \text{kJ} \]

In the atmosphere, O₃ is produced by the following three mechanisms:

a) Dissociation of O₂-molecules into O-atoms by solar UV-radiation. The O-atoms recombine with O₂-molecules to form O₃-molecules in the Stratosphere.
b) Low level ozone (i.e. close to Earth’s surface) is produced by reaction of nitrous oxides (i.e. NO₂) with O₂ under the influence of UV radiation.
c) From thunderstorms: The electric current existing between clouds and Earth’s surface from lightnings can produce O₃.
2.3 The Troposphere

2.3.1 General Properties

The Troposphere is the layer of our Atmosphere which is closest to the Earth (s. pp 9 and 11). It contains the air around us, from the ground up to the highest clouds.

The thickness of the Troposphere is about 10 km at the Poles, and about 18 km at the Aequator. The Troposphere contains about 90% of the total air. Since a large part of the weather takes place in this layer, the Troposphere is also called the weather layer. The reason it is warmer at the surface is simple: The air is warmed up by heat given off by the Earth.

The farther away from the surface the air moves, the less heat there is to be absorbed. The temperature of the atmosphere at \( h = 10 \) km is about \(-50^\circ\text{C}\). (In the Figure, the scale of \( h \) is non-linear).

From 10 to 20 km the temperature of the atmosphere is stable. This region is called the Tropopause. The Stratosphere extends from 20 to about 50 km. In this region, the air actually warms with height! Ozon is concentrated in this part of the Atmosphere and it absorbs ultraviolet (UV) light from the Sun. More light is absorbed at higher altitudes compared to the lower stratosphere, so the temperature increases again.
General Properties - 2

The Troposphere is warmed up only to a small extent by solar radiation. The large part of warming originates from the surface of the Earth. For this reason, the temperature of the air decreases by about 6.5 °C per km height. This decrease is known as the vertical atmospheric temperature gradient. In dry-adiabatic areas (cloud-free areas of the sky) it amounts to about 1 °C per 100 m, while in humid areas of the atmosphere (areas covered by clouds and fog) this decrease is about 0.6 °C per 100 m. In the Tropopause (s. pp 9 and 26), the temperature is about -75 °C at the Equator and about - 45 °C at the Poles.

An Inversion layer is a layer in which the atmospheric temperature is inverted, i.e. its change is deviated from the normal pattern. A very stable inversion is formed at the Tropopause and is explained by the fact, that for an altitude between 10 and 15 km the concentration of ozone starts to increase slowly. Ozone (O₃) is a very strong UV-absorber of the Sun light. This causes a temperature increase, opposite to the general trend of the temperature decrease with increasing altitude (s. Figure at p. 25).

The chemical composition of the dry Troposphere (N₂, O₂, Ar, ... s. p. 16) is essentially steady. But this is not the case for water vapour and clouds. The water content of the Troposphere depends usually very strongly on the location and altitude (s. Chapter 3).

Pressure and density of the atmosphere are largest at sea level and decrease strongly with increasing altitude (s. p. 54). In a first approximation the decrease of pressure with increasing altitude can be described by the barometric height formula (s. pp 27 – 29).

It should be noted that nearly the whole weather activity of our Planet takes place in the Troposphere.

Barometric height formula - 1

The barometric height formula describes the vertical distribution of the (gas-) particles in the Earth’s atmosphere, i.e. the relation between the air pressure p and altitude h. The result is a vertical pressure-gradient, but due to the weather dynamics present in the lower atmosphere, the function p(h) of the barometric height formula is only a first approximation of the actual more complicated situation.

The air pressure at sea level is 1 bar = 10⁵ Pascal = 10⁵ Pa = 10⁵ hPa; 1 hPa = 100 Pa. In the simplest approximation it can be assumed, that the air pressure at sea level and 0 °C decreases by Δp = -1 hPa per Δh = 8 m height: Δp / Δh = -1 hPa/ 8 m = -12.5 Pa / m. This pressure corresponds to about 1‰ of the pressure p(0) = 10³ hPa at sea level.

In the isothermal barometric height formula, the temperature T is assumed to be constant, independent on altitude h (isothermal atmosphere). Let h₀ and h > h₀ be two altitudes above sea level and p(h₀) and p(h) the corresponding pressures. In this case, the barometric height formula reads:

\[ p(h) = p(h₀) \cdot \exp(-Δh / h₀) \]  \hspace{1cm} \text{where the height difference is} \hspace{1cm} (1)

\[ Δh = h - h₀ \]  \hspace{1cm} \text{(at sea level h₀ = 0). h₀ is the so-called scale height: h₀ = R·T / M·g} \hspace{1cm} (2)

R is the universal gas constant (R = 8.314 J/(mol·K)) and M = 28.9644·10⁻³ kg/mol is the molar mass of air. For 300 K (27 °C), h₀ = 8779 m, for T= 288 K (~ 15 °C), h₀ = 8437 m and for T = 273 K (0 °C), h₀ = 7989 m. For the Troposphere, h < 12 and hence \( g(h) \approx g(0) \).

The density \( ρ \) is obtained from the ideal gas law \( pV = RT \) and \( ρ = M/V \) and one obtains

\[ p(h) = ρ(h₀) \cdot \exp(-Δh / h₀) \]  \hspace{1cm} (3)

26

2 – 8
Barometric height formula - 2

Atmosphere with linear temperature dependence

For the derivation of the formulae 1 tp 3 it has been assumed that the temperature \( T \) is independent on altitude \( h \). However, the Figures at p. 1-A-3-1 and p. 25 show, that in the Troposphere the temperature decreases with increasing altitude. [For the time being we disregarded inversions, i.e. possible temperature increases with increasing altitudes]. In a first approximation we assume a linear dependence for \( T(h) \), namely

\[
T(h) = T(h_0) - a^*(h - h_0) \quad (4)
\]

where \( a^* \) is a positive constant. By substituting eq. (4) into the basic barometric equation, namely \( dp/p = -[Mg/R^*T(h)] \), integration over the height \( h \) gives the following result (s. Ref. R.2.3.18):

\[
p(h) = p(h_0) \times \left[1 - \left(a^*h/T(h_0)\right)^{(Mg/R^*a)} \right] \quad \text{where} \quad \Delta h = h - h_0 \quad (5)
\]

For the density \( p(h) \) it follows:

\[
p(h) = p(h_0) \times \left[1 - \left(a^*\Delta h/T(h_0)\right)^{(Mg/R^*a)} \right] \quad (6)
\]

Note that in eq. (6) the exponent is reduced by 1. It is easy to show that a combination of eqs. (4), (5) and (6) gives the following relation between densities and pressures:

\[
p(h) = p(h_0) \times \left[\left(T(h_0)/T(h)\right)^*\left(p(h)/p(h_0)\right)\right] \quad (7)
\]

---

Barometric height formula - 3

Measurements of the temperature profile in the Troposphere show, that the assumption of a linear temperature decrease is in general a good approximation, even if in some cases distinct deviations are observed, for instance if inversion layers are present (*).

The principle reason for the temperature decrease with increasing altitude is the warming of the lower air layers as a consequence of the heating of the Earth’s surface, while the upper air layers are radiating heat into space. In the average over all weather conditions, the temperature gradient is 0.65 K per 100 m, and from eq. (4) the temperature decrease is equal to \( a = \Delta T/\Delta h = 0.65 \text{ K/100 m} = 0.0065 \text{ K/m} \). [Remember that these numbers are valid for the Troposphere only]. In the Stratosphere, the temperature decreases distinctly slower. In most cases, it even increases again with increasing height. This is due to the absorption of UV-radiation by the ozone layer (s. pp 9, 1-A-3-1, 37 - 42).

For a temperature gradient of \( a = 0.0065 \text{ K/m} \), the value of the exponent \( M^*T/R^*a \) in eq. (5), p. 28 is 5.255, i.e. one obtains

\[
p(h) = p(h_0) \times \left[1 - 0.0065^*\Delta h / T(h_0)\right]^{5.255} \quad (8)
\]

If the reference height is \( h_0 = 0 \) (sea level) and if we assume an average atmospheric state at sea level as defined by the Internationale Standard-Atmosphere (temperature = 15 °C, air pressure = 1013.25 hPa, \( a = 0.0065 \text{ K/m} \)), one obtains the International barometric height formula for the Troposphere (up to a height of 11 km):

\[
p(h) = 1013.25^* \times \left[1 - 0.0065^*\Delta h / 288.15\right]^{5.255} \text{ hPa} \quad (9)
\]

(*) An atmospheric inversion is an inversion of the normal temperature profile with increasing altitude, i.e. in the Troposphere the temperature is increasing instead of decreasing.

(**) For the actual application the accuracy of formula (9) is, however, limited, since a mean atmosphere has been assumed.
The specific heat capacity of a compound at constant pressure is given by

$$C_p = \frac{\Delta Q}{m \Delta T} \quad (10)$$

$\Delta Q$ is the thermal energy transferred to an object with mass $m$, $C_p$ is the specific heat at constant pressure and $\Delta T$ is the resulting increase in temperature. Lifting an air packet of weight $G = mg$ by a height $\Delta h$ requires the potential energy $\Delta Q = m \ G = m \ g \ \Delta h$ and we obtain

$$C_p = g \left( \frac{\Delta h}{\Delta T} \right) = g / a \quad (11)$$

According to p. 29, the mean temperature gradient is $a = \Delta T / \Delta h = 0.0065$ K/m or $\Delta h / \Delta T = 153.8$ m/K. Substitution in eq. (11) and using $g = 9.81$ m/s$^2$ we obtain the mean value of $C_p$ for all weather conditions (mean over dry and humid air), namely

$$C_p = 1509 \text{ (m}^2/\text{s}^2\text{K}) = 1509 \text{ (Ws/kg K)} \quad (12)$$

This value lies between the specific heat for dry air with $C_p = 1005$ (Ws/kg K) and the specific heat of water vapor with $C_p = 2034$ (Ws/kg K).

[Remark: The specific heat of dry air varies only slightly between $-100$ °C and $+40$ °C: $C_p = 1009$ (Ws/kg K) at $-100$°C and $C_p = 1005$ (Ws/kg K) at $+40$°C.]
The Tropopause is the small transition region (marked with small red points in the Figure) between the Troposphere and the Stratosphere. According to WMO (World Meteorological Organization) its thickness is very small, between some hundred meters and 2 – 3 km, and its vertical temperature gradient is - 0.2 K/100 m. The Figure show that the height of the Troposphere depends on the geographical place, mainly from the latitude. The height of the Troposphere is about 16 km above Australia and about 12 – 16 km in mean seasons. Its height decrease with increasing latitude and at the North- and South Poles it is about 9 km. The ozone layer starts just above the Troposphere and extends into the Stratosphere.
2.4 The Stratosphere

General Properties

The Stratosphere is the second layer of the Earth’s atmosphere. The interlayer region between the Troposphere and the Stratosphere is known as the Tropopause (s. p. 32). As shown at p. 32, the Tropopause is located in a height of about 9 km at the geographical Poles and between 12 and 16 km at the equator. At still higher altitudes the Stratosphere is followed by the Mesosphere (s. pp 7, 9 and 35). The interlayer between the Stratosphere and the Mesosphere is the so-called Stratopause in a height of about 50 km (p. 35).

In the Stratosphere, the mean temperature increases again, but in the lower region of the Stratosphere, up to an altitude of about 20 km, this temperature increase is vanishingly small.

The increase of temperature in the Stratosphere with increasing height is opposit to the behaviour of the Troposphere and the Mesosphere (s. Figure p. 35). The reason for this inverse temperature behaviour is mainly due to the presence of ozone in the Stratosphere. Ozone absorbs UV-radiation of the Sun, whereby the electromagnetic radiation is transformed into heat. The warming by this heat is strongest in the region of the ozone layer where the temperature increases from –60 °C to nearly 0 °C (s. p. 35 and Appendix 1-A-3-1).

As a consequence of the low temperature in the Tropopause, atmospheric water vapor condenses almost completely. For this reason the atmospheric air is very dry. Clouds are therefore formed in the Stratosphere only in the case of extremely cold conditions. (p. 36).
The Stratosphere (15 – 50 km) is the layer following the Troposphere. Its temperature profile is layered (or stratified), and its temperature increases with increasing altitude, reaching about 0 °C near 50 km. This is contrary to the temperature profile in the Troposphere. The boundary layer between the Troposphere and the Stratosphere is the Tropopause (p. 32), while the boundary layer between the Stratosphere and the Mesosphere is the Stratopause (The boundary between the Mesosphere and the Thermosphere is the Mesopause).

The increase of temperature with increasing altitude in the Stratosphere originates essentially from the ozone layer, which absorbs the short wavelength UV contribution of the solar radiation (s. p. 37).

Polar Stratospheric Clouds (PSC’s)

In the Stratosphere, the water vapour concentration of air is very small, and therefore, conventional water clouds can not be formed. Polar Stratospheric Clouds (PSC’s) consist of Nitric acid (HNO₃) and/or of a mixture of Sulfuric acid (H₂SO₄) and Nitric acid, where both modifications are coated by a layer of water ice. They can also consist on pure water ice. For this reason, the following types are distinguished:

Type Ia: Crystals of Nitric acid Trihydrate with a layer of water ice
Type Ib: Sulfuric acid and Nitric acid with a layer of water ice
Type II: Consisting of pure water ice

At the surface of the crystals, chemical reactions can take place, which are important for the ozone depletion in the Stratosphere and the formation of the hole in the ozone layer.

These stratospheric clouds, also called mother of pearl clouds or nacreous clouds, are formed in the Stratosphere in altitudes above 20 km, most often in the region between 22 and 29 km. During winter this appears always in the polar regions, beyond 80° northern or 80° southern latitudes.
The Ozone layer is a part of the Stratosphere, in which under the influence of the energy-rich ultraviolet (UV)-radiation of the sun, oxygen in the form of O$_2$ is converted into ozone (O$_3$). The ozone layer begins at an altitude of 10 to 17 km and extends to an altitude of about 50 km. (Concerning the structure and layers of the ozone molecule s. pp 22 and 23.

Ozone O$_3$ is formed from molecular O$_2$. The comparatively high concentration of ozone [2–8 ml/m$^3$ or 2–8 ppm] absorbs UV-radiation, in particular UV-B, and part of this ozone is partially decomposed by this radiation into O$_2$. A chemical equilibrium is formed, the so-called *ozone – oxygen cycle*, in which the amount of ozone remains essentially constant. In equilibrium, the formation and decomposition of ozone are balancing each other:

**O$_3$ formation:** $3 \text{O}_2 \rightarrow 2 \text{O}_3$ by radiation of UV-B and UV-C

**O$_3$ decomposition:** $2 \text{O}_3 \rightarrow 3 \text{O}_2$ by radiation of UV-B and UV-A

Wavelengths of the UV-radiation:

- UV-A: 400 – 315 nm
- UV-B: 315 – 280 nm
- UV-C: 280 – 100 nm

$(1 \text{ nm} = 10^{-9} \text{ m})$

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Ozone Profils in Troposphere and Stratosphere

- Contains 90% of atmospheric ozone
- Beneficial role: Acts as primary UV radiation shield
- Current issues:
  - Long-term global downward trends
  - Springtime Antarctic ozone hole each year

- Contains 10% of atmospheric ozone
- Harmful impact: Toxic effects on humans and vegetation
- Current issues:
  - Episodes of high surface ozone in urban and rural areas

Ozone Amount (milli-Pa)

1 milli-Pa = 10$^{-3}$ Pa = 10$^{-8}$ bar
Largest Antarctic Ozone hole

 Observation of the largest Antarctic Ozone hole which has been observed in September 2006.

 The sizes of these Ozone holes can be as large as three times the area of USA.

 The area of the Ozone hole is about $3.0 \times 10^6$ km$^2$.

 The area of USA is about $9.8 \times 10^6$ km$^2$.

 The Ozone hole has been discovered the first time in 1979 (s. pp 39 and 40) and is observed mainly over the colder part of the Antarctic. This discovery was based on the destructive chemical processes which are active most efficiently at cold conditions. The antarctic continent is colder than the arctic continent. During the following years, the size of the Ozone hole increased rapidly. The Ozone layer is present only during a period of three months per year. But it is just at the time of sun rise when plants and animals become active, that the sun also produces a dose of dangerous UV- radiation.

Ozon – killers and consequences for the Ozone hole

 Some particular gases, such as chlorofluorocarbons (CCFC’s) and nitrous oxides ($N_2O$), also called laughing gas, are able to increase a decomposition of ozone, thereby producing an increase of the $O_3$ concentration. As a consequence, this is responsible for the formation of the Ozone hole during the long polar nights.

 If the end of the polar night is approached, the Sun starts to radiate light through the Ozone holes to the Earth. As a consequence, the intensity of the UV- radiation increases at the surface of the Earth. This can cause a distinct increase of skin cancer as well as a severe increase of eye diseases. Furthermore, the UV-radiation can disturb the immune system. In addition it can affect the Photosynthesis in the Chlorophyll of plants leading to severe harvest shortfalls.
2.5 The Mesosphere

Mesosphere between Stratosphere and Thermosphere

Pressure about $10^{-3}$ atm

Pressure about $10^{-6}$ atm
Characteristics of the Mesosphere

The Mesosphere is the layer of the Earth's atmosphere that is directly above the Stratopause and directly below the Mesopause. (s. p. 35). The exact upper and lower boundary of the mesosphere vary with latitude and with season, but the lower boundary of the Mesosphere is usually located at heights of about 50 kilometers above the Earth's surface and the upper boundary is usually at heights near 80 kilometers.

Because of the extremely diluted air in the Mesosphere as well as due to the fact that ozone is practically absent and the absorption of the energy-rich UV-radiation takes place in the Stratosphere, the temperature decreases from about 0°C at the Stratopause to about –90°C at a height of about 80 kilometers (s. pp 35, 44, 47). The decrease of temperature is only about 3 °C/km, i.e. substantially smaller than in the Troposphere. The temperature then remains essentially constant and it is only in the Thermosphere, where it strongly increases again to nominal values as high as to 2000 °C.

The chemical composition of the Mesosphere consists mainly on some gases which according to their masses are layered (light gases above denser gases). If Meteors are approaching the Earth, they burn-out upon entering the Mesosphere.

The carbon dioxide (CO₂) present in the Mesosphere contributes significantly to the cold temperature. By collisions of CO₂ molecules, heat is absorbed. Part of this energy is transformed into photons; this is a process known as radiation emission of light. In this way, heat is transferred from the Mesosphere into the Thermosphere,
2.6 The Thermosphere

The Thermosphere is the layer of the Earth’s atmosphere directly above the Mesosphere and directly below the Exosphere. The Thermosphere is an atmospheric layer which starts at about 80 km and extends up to about 500 km. In this range of altitude, the concentration of molecules is so small that it nearly resembles the free space of vacuum. The temperature is therefore not an equilibrium temperature: there are essentially no molecular collisions. The high temperature is only a consequence of the very high velocity of the molecules and is referred to as radiation temperature. Because the protecting activity of the atmosphere is not present, one is exposed to the full radiation spectrum of the Sun and the Universe. The Ionosphere extends from about 70 km to more than about 1000 km.

- **Thermopause**: $h \approx 15 \text{ km}$; $\theta \approx -82 ^\circ \text{C}$
- **Mesopause**: $h \approx 10 \text{ km}$
- **Stratopause**: $h \approx 50 \text{ km}$; $\theta = 0 ^\circ \text{C}$
- **Tropopause**: $h \approx 50 \text{ km}; \theta = 0 ^\circ \text{C}$
- **Ionosphere**: $70 < h < 1000 \text{ km}$
- **Maximal electron density at 300 km**: $h \approx 82 \text{ km}$; $\theta \approx -110 ^\circ \text{C}$

For $h (h)$ compare also with diagram of p. 35.
Temperature $T$ and mean molar mass $<M>$ of air as a function of altitude $h$

<table>
<thead>
<tr>
<th>Temperature $T$</th>
<th>Molar mass $M$</th>
<th>$&lt;M(h)&gt;$</th>
<th>Radiation Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The reasons for the decrease of the mean molecular mass $<M>$ with increasing altitude $h$ in the Thermosphere is explained at p. 49.

Properties of the Thermosphere

Despite its name the «heat» of the Thermosphere can not be felt. This is due to the fact that the air density is extremely small compared to the density close to the surface of the Earth (s. pp 35, 54). The high temperature (300 to 1500 °C) implies only the rapid motion of the gas particles. Their mean free paths are of the order of several kilometers. This implies that interactions by collisions or energy exchange do not exist.

The International Space Station (ISS) has a stable orbit within the middle of the Thermosphere, between 320 and 380 kilometers.

The temperature of the Thermosphere first increases strongly with height and can rise up to 1700 °C. However, a person would not feel warm because of the Thermosphere’s extremely low gas density (s. p. 52).

The solar X-ray radiation and the extreme UV-radiation decompose the gas molecules into ions and electrons. For this reason, the Ionosphere is part of the Thermosphere.

With increasing altitude, the average mass of the individual gas particles decreases with increasing height. There are three reasons for this fact: (1) residual molecules in the upper part of the Thermosphere are easily decomposed by cosmic radiation into there constituent particles. (2) because of the small pressure, the recombination rate of these constituents to molecules is very small. (3) At a given temperature, light particles have a larger velocity and are less attracted to the Earth by gravitational forces. These three effects cause an increasing enrichment of light molecules ($\text{H}_2$) and atomic He with increasing altitude which explains the decrease of the molar mass with increasing height $h$ (s. green curve at p. 48).
The Thermopause is the atmospheric boundary of Earth’s energy system, located at the top of the Thermosphere (s. pp 9 and 47).

Below this, the atmosphere is defined to be active on the insulation received, due to the presence of heavier gases such as monoatomic oxygen. Beyond (above) this, the exosphere describes the thinnest remainder of atmospheric particles, mostly Hydrogen molecules and Helium atoms, having very large mean free paths.

The exact altitude varies by the energy inputs of location, time of day, solar flux, season, etc. and can be between 500 – 1000 km high at a given place and time. The thickness of the Thermopause is not well defined.

Although these layers at very high altitudes are all named layers of the atmosphere, the pressure is so negligible that the chiefly-used definition of outer space are actually below this altitude. Orbiting satellites do not experience significant atmospheric heating by collisions with particles, but their orbits do decay over time, depending on orbit altitude. Space missions such as the International Space Station (ISS), space shuttle, and Soyuz operate under this layer.
2.7 The Exosphere

The Exosphere is the outermost layer of Earth’s atmosphere. It represents the continuous transition from Earth’s atmosphere to interplanetary space. According to the definition of NASA it is already part of it.

The Exosphere is a part of the so-called Heterosphere, the part of the atmosphere higher than about 120 km in which the gases of different weights start to demix. Above a height of about 1’000 km only the lightest gas, namely Hydrogen (H₂) is present. This region is also known as geocorona.

The Thermosphere is followed by the Exosphere (s. p. 47). Depending on various Literature sources, it starts in a height between 400 km and 1000 km. The outer limit of the Exosphere is approximately 10’000 km. This upper boundary is, however, not well defined since the density of the gas decreases continuously and theoretically never reaches exactly zero.

All particles in the Exosphere are almost completely ionized. The Exosphere is the sole atmospheric layer in which due to their high velocities, gas molecules can escape the gravitational forces. Note that due to their extremely low density, retarding frictions can be neglected.

The high temperature of more than 1’000 °C, which is seemingly present in the Exosphere, refers only to the high velocities of the particles (see dashed line of the temperature curve T(h) at p. 48). Due to the vanishingly small number density of the particles, the temperature is not due to collisions of particles, but is rather due to the heat radiation of the Sun. During day time, the temperature is therefore very high, but during night it is very low.
In the Exosphere, the temperature is not due to interactions, i.e. due to collisions between particles, since because of the extreme small concentration of the particles, collisions are extremely seldom.

In the Exosphere, the temperature is rather determined by the heat radiation of the Sun. This heat radiation depends extremely strongly of whether a part of the Exosphere is exposed to the Sun (during day) or whether it is screened from the radiation field of the Sun (during night). During day time, the radiation can generate temperatures well above 1'000 °C. During night, however, the temperature is well below 0°C.

The Exosphere is almost a vacuum.

This picture shows the Hubble Space Telescope, which circles around the Earth in the Exosphere.

Those parts of the Telescope, which are exposed to the Sun, are extremely hot. On the other hand, the parts which are not exposed to the Sun are very cold.

Pressures p and Densities ρ as a Function of Altitude h

From ideal gas law:

\[ \rho = \frac{p}{R_s \cdot T} \]

\( R_s = \frac{R}{M} = 287.058 \, \text{J/kg}^{*}\text{K} \)

\( = \text{specific gas constant for dry air at } T = 273 \, \text{K} \)

s. also pp 27 - 30
Gravitational acceleration $g$ as a function of Altitude $h$

\[ g_E = g(h=0) = 9.81 \text{ m/s}^2 = \text{Gravitational acceleration at Sea level} \]

Gravitational force $F(r) = G M_E m / r^2 = m \cdot g(r) \rightarrow g(r) = G M_E / r^2$; $r = r_E + h$;

with $f = 1 + h/r_E$ it follows: $g(h) = g_E / f^2$; $G = 6.674 \times 10^{-11} \text{ m}^3/\text{kg s}^2 = \text{Gravitational constant}$;

$M_E = 5.972 \times 10^{24} \text{ kg} = \text{Mass of Earth}$; $r_E = 6371 \text{ km} = \text{mean Earth radius}$.
Appendix - Chapter 2

Page 16 contains a Table of the volume- and mass contributions of the various gases of air contained in the Troposphere. Here, we establish the relation between volumes and masses.

Let $M$ be the total mass and $V$ the total Volume while $M(k)$ and $V(k)$ are the mass and volume of gas $k$. Furthermore, let $\rho(k)$ be the density of gas $k$ at normal conditions. From $\rho(k) = M(k) / V(k)$, the mass ratio $\eta(k)$ of the gas $k$ is given by:

$$\eta(k) = \frac{M(k)}{M} = \frac{\rho(k) \frac{V(k)}{V}}{\sum \rho(k) \frac{V(k)}{V}}$$

Example for $N_2$, $O_2$, and $Ar$: (s. p. 16); in a first approximation we calculate $\eta(N_2)$, $\eta(O_2)$ and $\eta(Ar)$ only from $V(N_2)/V$, $V(O_2)/V$ und $V(Ar)/V$, i.e. we neglect all trace gases listed in p. 16. For normal conditions $\rho(N_2) = 1.2503 \text{ kg/m}^3$; $\rho(O_2) = 1.429 \text{ kg/m}^3$ and $\rho(Ar) = 1.7813 \text{ kg/m}^3$. By using the volume ratios listed in p. 16: $V(N_2)/V = 78.084$, $V(O_2)/V = 20.942$ and $V(Ar)/V = 0.934$, we obtain for the corresponding mass ratios:

$$\eta(N_2) = 75.5517 \% ; \ \eta(O_2) = 23.159 \% ; \ \text{and} \ \eta(Ar) = 1.287 \% .$$

These values are slightly larger than those listed in p. 16. This is due to the neglect of the trace gases listed in p. 16. If we would have included these trace gases (in particular $CO_2$), in the sum over $k$, we would have obtained the exact values for $\eta(k)$ listed in p. 16.
The most simple form of the barometric height formula is:

\[ p(h) = p_0 \exp(- h / h_s) \]

(\( p_0 = 1013.25 \text{ hPa} \), s. pp 27, 30).

We imagine that the total atmosphere under the curve \( K \) is compressed to a pressure of 1 atm = 1013 hPa. Let us then determine the height \( H \) of the resulting rectangle. If \( A \) is the surface under the curve \( K \), then we have:

\[ A = \int_0^h p(h) \, dh = p_0 \int_0^h \exp(- h / h_s) \, dh = p_0 h_s = p_0 H, \]

The height \( H = h_s \) is the so-called scale height \( h_s = (RT / (Mg)) \) (s. p. 27)

For a temperature \( T = 288 \text{ K} = 15 \text{ °C} \) we find

\[ h_s = 8.4 \text{ km} \]

(s. red-dashed rectangle with area \( A \))

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**Definition of Dobson Unit (DU)**

The Dobson Unit (DU) is a unit of measurement of the columnar density of a trace gas in the Earth's atmosphere. It is widely used as a measure of total-column ozone, which is dominated by ozone in the stratospheric ozone layer. One DU refers to a layer of 10 \( \mu \text{m} = 0.01 \text{ mm} \) thick under Standard Temperature and Pressure conditions (STP: \( T = 273 \text{ K}, p = 1 \text{ atm} \)).

300 DU of ozone brought down to the Earth at 0°C would occupy a layer of 3 mm thickness.

**Numerical example: Number of \( \text{O}_2 \) molecules contained in 1 DU**

**Ideal gas law:** \( p \cdot V = n \cdot R \cdot T \); \( p = \) pressure, \( V = \) volume; \( R = \) ideal gas constant, \( T = \) temperature, \( n = \) number of moles. We calculate \( n \) and the number of ozone molecules in 1 DU. With \( p = 1 \text{ atm} = 1.013 \text{ bar} \), \( R = 8.314 \text{ J/(mole} \cdot \text{K}) \), \( T = 273 \text{ K} \) and \( V = 1 \text{ m}^2 \cdot 10 \mu\text{m} = 1 \text{ m}^3 \cdot 10^{-5} \text{ m}^3 = 10^{-5} \text{ m}^3 \) one obtains: \( n = p \cdot V / (R \cdot T) = 0.4462 \cdot 10^{-3} \text{ mole} \). Since the Avogadro number \( N_A = 6.0224 \cdot 10^{23} / \text{mole} \) is the number of molecules in 1 mole, 1 DU contains \( N_{DU} = n \cdot N_A = 0.4462 \cdot 10^{-3} \text{ mole} \cdot 6.0224 \cdot 10^{23} / \text{(mole)} = 2.69 \cdot 10^{20} \text{ ozone molecules per m}^2 \).

The Ozone concentration in the Stratosphere is not constant; a normal range is 300 to 500 DU. But due to anthropogenic activities, the ozone concentration decreased considerably (s. pp 39 – 42).
2.2 Composition of dry Air in the Troposphere

R.2.2.3 p. 16: Luft - Zusammensetzung der Luft (Volumen- und Massanteile) - de.wikipedia.org/wiki/Luft
R.2.2.6 p. 18: Oxygen - www.en.wikipedia.org/wiki/Oxygen
R.2.2.10 p. 19: Radiogenic nuclide - http://en.wikipedia.org/wiki/Radiogenic - Radioaktiver Zerfall von $^{40}$K in $^{40}$Ar
R.2.2.11 pp 20 – 21: The structures of the molecules and atoms of the trace gases of dry air have been found in different sources, including Google
R.2.2.13 p. 23: [PDF] The concept of Resonance (in German: Mesomerie) (Example: Ozone) www.wou.edu/lsphyssci/.../Ch08-s12-part2.pdf
R.2.2.14 pp 22 - 23: Ozone
  a) http://de.wikipedia.org/wiki/Ozon - Ozon (Deutsch)
  b) http://www.udo-leuschner.de/basiswissen/SB126-01.html
  c) Mesomerie – http://de.wikipedia.org/wiki/Mesomerie
     Ozon (Deutsch, Figur links: p. 22; Figur rechts aus:)
### 2.3 The Troposphere

| R.2.3.1 | p. 25: Graphic: Temperature variation in the Troposphere, Tropopause and low Stratosphere. Troposphere – Images. (Graph from Elmar Uhrekr) - «Untere Atmosphäre (Basis / Vertikaler Aufbau») (Figure Text translated from German to English by P. Brüesch) [http://www.windows2universe.org/kids_space/temp_profile.htm](http://www.windows2universe.org/kids_space/temp_profile.htm) |
| R.2.3.5 | p. 30: Graph: International barometric height formula a) [http://www.ast-huerth.de/APT_WebSite/GB/barometrische-hoehenformel.html](http://www.ast-huerth.de/APT_WebSite/GB/barometrische-hoehenformel.html) (written in English) b) The two curves for p(h) (Isothermal barometric height profile and international barometric height profile) have been calculated by P. Brüesch on the basis of Reference R.2.3.4 c) - green curve: Barometric height profile for T(0) = 15 °C. (p. 27, eq. (1)) - red curve: Barometric height profile for T(h) linear in h according to: \(|T(h) = T(h_0) - a(h - h_0); T(h_0) = 288.15 K\) (15 °C) and \(a = 0.0065\) K/m (s. pp 28 and 29). c) Die internationale Höhenformel - [http://wetter.andreae-gymnasium.de/interaaktives/Drueb/toothenformel.html](http://wetter.andreae-gymnasium.de/interaaktives/Drueb/toothenformel.html) Graph von p(h) für h < 11'000 m - Eingabe von h \(\rightarrow\) p(h)

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### 2.4 The Stratosphere

| R.2.4.2 | p. 35: Temperature Profile in the Stratosphere Visionlearning / Earth Science / The Composition of the Earth’s Atmosphere - by Anne Egger, PhD [www.visionlearning.com/en/library/Earth-Science/6The-Composition-of-Earth-s-Atmosphere](http://www.visionlearning.com/en/library/Earth-Science/6The-Composition-of-Earth-s-Atmosphere) (contains Graph showing the temperature variation with altitude in Earth’s Atmosphere) [Figure of T(h) itself only accessible under «Bilder»]
R.2.4.3  p. 36: Polar Stratospheric Clouds – PSC’s
Left-hand Figure: Polar stratospheric cloud of type I (PSC I)
Right-hand Figure: Polar stratospheric clouds of type II (PSC II)
b) Polare Stratosphärenwolken - http://de.wikipedia.org/wiki/Polare_Stratosph%C3%A4renwolken

R.2.4.4  p. 37: The Ozone Layer in the Stratosphere
b) Ozone Layer / Climate Education Modules for K-12 - http://www.cc.climatemodules.edu/k12/ozonelayer
c) Ozonschicht - http://www.ping.de/schule/pg_herne/p-wetter/Luft/ozone1.html

R.2.4.5  p. 38: Ozone Proils in Troposphere and Stratosphere
a) from Google unter «Atmospheric Ozone» (Bilder)

c) http://www.atoptics.co.uk/highsky/hmeso.htm

R.2.4.6  p. 39: Ozone concentration (in DU): 1979-2011
a) Environmental Change on Earth
http://en.teachastronomy.com/astpedia/article/EnvironmentalChange-on_Earth-
b) The Ozone Hole - EPA. Bring Primatene Back – Use Some Common Sense


e) 1 Dobson Unit DU corresponds to 2.6867 * 10^20 O3 - molecules pro m^2 or 4.4615 * 10^-4 mole (O3)/m^2
Note: For the definition of the Dobson Unit, (DU), the total amount of gaseous O3 in the sky present over a
a selected unit area F is compressed to Normal Conditions (STP). The result is a height h and the volume of the
compressed Ozone is F*h. In other words, the height h is the hypothetical thickness of the Ozone
layer at STP (p = 1 atm = 1,013 bar = 1,013*10^5 Pa at T = 273 K (0°C), h(100 DU) = 1 mm.

R.2.4.7  p. 40: Average area of ozone hole in the Antarcits as a function of time
The Ozone Hole - http://www.e-education.psu.edu/egee/102/node/1972

R.2.4.8  p. 41: Largest Antarctic Ozone hole


R.2.4.9  p. 42: Ozone – killer and consequences for the Ozone hole
b) The hole in the ozone layer – a solved problem?
http://wwwUluslararasıplan.org/en/hole-ozone-layer-solved-proble,
c) The ozone layer - [PDF] www.fisica.ufmg.br/~dickan/transfers/…/Taylor8...

R.2.4.10 p. 42: Ozone killer und Konsequenzen für das Ozonloch
a) Fluorchlorkohlenwasserstoffe - http://de.wikipedia.org/wiki/Fluorchlorkohlenwasserstoffe
b) Fluorkohlenwasserstoffe FCKW und das Ozonloch
http://www.atmosphere.mpq.de/emd/2_ozonloch- Ozonloch FCKW Lmi.html

de) Ozonloch (PSC I)
http://en.wikipedia.org/wiki/Ozone

2.5 The Mesosphere

R.2.5.1  p. 44: Mesosphere between Stratosphere and Thermosphere
see «Images: Mesosphere» - Mesosphere : windows2.org
For temperatures at the lower and upper layer of the Mesosphere: s. p. 35
http://www.atoptics.co.uk/highsky/hmeso.htm

R.2.5.2  p. 45: Characteristics of the Mesosphere
Mesosphere - http://en.wikipedia.org/wiki/Mesosphere

R.2.5.3  p. 45: Charakteristica der Mesosphäre
a) http://www.uni-protokolle.de/Lexikon/Mesosph%C3%A4re.html
b) http://de.wikipedia.org/wiki/Mesosph%C3%A4re - Zum Text über CO2 in Mesosphäre

2 - 29
2.6 The Thermosphere

R.2.6.1 pp 46 – 50: Thermosphere


R.2.6.3. p. 48 Average pressure and molar mass as a function of altitude
http://de.wikipedia.org/wiki/Thermosph%C3%A4re

R.2.6.4 pp 47 – 49: Thermosphere
a) Thermosphere - http://www.iwf.oeaw.ac.at/de/forschung/erdloerper/atmosphere/therm
b) Thermosphäre - http://universal_lexikon.deacademic.com/192060/Thermosph%C3%A4re
c) Thermosphäre - http://www.uni-protokolle.de/LexikonThermosph%E4re.html

R.2.6.5 p. 50: The Thermopause

2.7 The Exosphere


R.2.7.2 p. 53: Exosphere-2: Hubble – Space - Telescoppe
http://www.windows2universe.org/earth/Atmosphere/exosphere_temperature

2.8 Varia

R.2.8.1 p. 54: Average pressure and density as a function of height Logarithmic representation for large altitudes- Graph - Reference R.2.3.4, p. 1 ; Graph adapted by P. Brüesch

R.2.8.2 p. 55: Earth’s gravitational acceleration g(h) - (Calculation and Figure from P. Brüesch)

Appendix

2-A-2-1 Appendix: Relation between volume and masses in air - (calculated by P. Brüesch)
s. als : Allgemeine Chemie: http://www.atm.ch.cam.ac.uk/tour/tour_de/dobson.html

2-A-3-1 Scale height: Effective height of atmosphere after compression to 1 atm
a) Scale height: http://de.wikipedia.org/wiki/Skalenhöhe%C3%B6he - Figure and Text from P. Brüesch
b) Scale height: http://en.wikipedia.org/wiki/Scale_height

2-A-4-1 The Dobson Unit
a) Dobson Unit: http://wikipedia.org/wiki/Dobson_unit
b) The Ozone Hole - http://www.theozonehole.com/dobsonunit.htm
d) Definition der Dobson-Einheit - http://www.atm.ch.cam.ac.uk/tour/tour_de/dobson.html