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Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

ATMOSPHERE CHEMISTRY

Lecture No.: 10

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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)
- Note: This subject „Atmospheric chemistry“ is loosely followed by the subject named „Technology of Air Protection“ (not direct follow-up)
  ⇒ confluence of content ca 10 %

Scope of lecture 10

Reactions of oxygen and water, formation of clouds and precipitations

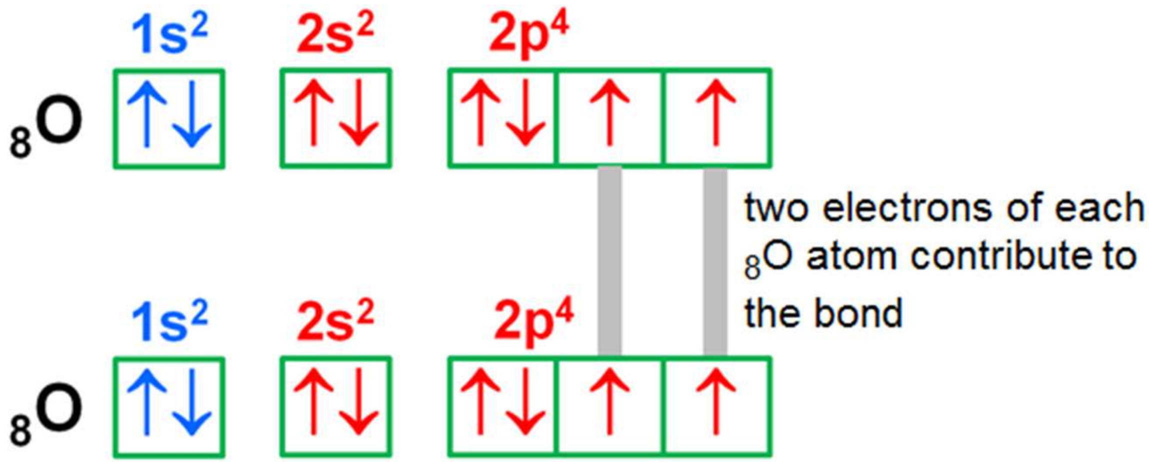
- Oxygen, its electron configuration in the base and excited state and possible ways of excitation
- Concentration of different forms of oxygen in atmosphere, generation of atomic oxygen and its ions
- Origin of water in the troposphere and stratosphere
- Importance of cloud cover for energetic balance of the planet
- Mechanism of rainfalls and their annual volumes
- Morphology of clouds

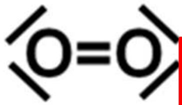
Reactions of oxygen in atmosphere

- **Configuration of oxygen**
  - Electron configuration: [He] $2s^2\ 2p^4$
  - Molecular oxygen:

Base state triplet (parallel spin) with two unpaired e^-

$^{3P}O_2$





delta g and sigma g+ have all e^- in pairs ↑↓

Excited states: singlet (antiparallel) $^{1D}\Delta g$ or $^{1D}\Sigma g^+$ without unpaired electrons
$^{1D}O_2$ highly reactive ⇒ significantly responsible for polymers photodegradation

Reactions of oxygen in atmosphere

- **Configuration of oxygen**
  - Molecular oxygen – excited singlet states $^{1D}\Delta g$ or $^{1D}\Sigma g^{+}$:

    Excitation via 4 processes
    - direct photochemical excitation
    - adopting energy from other excited particles
    - photolysis of ozone
    - high energy reactions generating oxygen

  - Atomic oxygen

Base state	triplet	^{3P}O
Excited state	singlet	^{1D}O

Reactions of oxygen in atmosphere

- **Occurence of oxygen**
  - The most frequent biogenic element on the Earth
  - Sum of free + bonded O_2 (hydrosphere + lithosphere + atmosphere) = 45.5 weight %;
  - Content in atmosphere = 20.95 vol. % $\cong$ 23 weight %;
  - Content in hydrosphere (in H_2O molecules + dissolved) = 85 wt. %
  - Note: Even on the Moon surface there is elevated concentration present (oxide minerals), namely 44.6 wt. %.
  - Free oxygen in fact by 100 % generated biochemically $\Rightarrow$ photosynthesis:

$$H_2O + CO_2 + h\nu \xrightarrow{chlorophyl,\, enzymes} O_2 + CH_2O\,(saccharides)$$

In total photosynthesis is strongly endothermal sequence of processes

Energy supplied by solar radiation $\sum_i \Delta H0_i = 469\ kJ.mol^{-1}$

Reactions of oxygen in atmosphere

- **Appearance of oxygen**
  - Free molecular O_2 on Earth is always gaseous

    ⇒ melting point = –218,8 °C

    ⇒ boiling point = –182,97 °C

  - Beware of mistake:

    In gaseous phase O_2 is fully transparent and colourless.

    In liquid and solid state it is light blue, however (!) blue sky is not caused by oxygen but due to Raleigh dispersion of light.

≠

Reactions of oxygen in atmosphere

- **Occurrence of oxygen**
  - Content of O_2 in water – limited solubility

    At 0 °C 49 $cm^3.l^{-1}$

    At 20 °C 31 $cm^3.l^{-1}$

    Note: in some organic solvents the oxygen solubility is by ca. 10 times higher!

  - Natural oxygen = mixture of three isotopes (superscript = nucleon number):
    - ^{16}O (99,76 %)
    - ^{17}O (0,04 %)
    - ^{18}O (0,2 %).

Reactions of oxygen in atmosphere

- **Creation of atomic oxygen**
  - Stability of atomic O is generally low but increases in thermosphere (80 – 700 km);

    Reason: very low pressure ⇒ low number of collisions with a particle M, taking the excessive energy during synthesis O + O = O_2 and stabilising O_2 molecule:

    Thermosphere:

    $$O + O + M \longrightarrow O_2 + M$$

    Decrease of molecular O_2 with rising altitude occurs in so called heterosphere: 400 km above the sea level … only 10 %;

  - Formation of atomic oxygen:

    photolysis of O_2 by UV radiation in the range of 135 – 176 nm or 240 – 260 nm

    photolysis of ozone (O_3 less stable ⇒ easier cleavage)

    $$O_3 + h\nu \xrightarrow{\lambda < 308\,nm} O^* + O_2$$

Reactions of oxygen in atmosphere

- **Generation of atomic oxygen**
  - Besides O_3 photolysis excited O* is formed by high energy reactions, like:

$$3O \longrightarrow O^* + O_2$$

- **Properties and extinction of atomic oxygen and generation of ions**
  - Excited O* emits radiation within visible part of spectrum with maximum λ = 636, 630 and 558 nm
  - This visible radiation is permanently emitted by the atmosphere as so called airglow;
  - Atomic oxygen in ionosphere products cations O^+, contributing to formation of other cations:

$$O + h\nu \xrightarrow{UV} O^+ + e^-$$

$$O^+ + O_2 \longrightarrow O_2^+ + O$$

$$O^+ + N_2 \longrightarrow NO^+ + N$$

Appearance of water in atmosphere

- **Tropospheric and stratospheric water**
  - Water in troposphere – evapotranspiration from surface (hereinafter described within the chapter about cloud cover);
  - Water in stratosphere – vapour is blocked by tropopause ⇒ another origin of H_2O molecules: photochemical oxidation of methane (see the lecture about GHG – reactions of methane);
  - Water in stratosphere = source of hydroxyle radicals:

$$CH_4 + 2O_2 \xrightarrow{h\nu;\ several\ steps} CO_2 + 2H_2O$$

$$H_2O + h\nu \longrightarrow HO^{\bullet} + H$$

Atmospheric moisture

- Importance of cloud cover
  - Cloud cover = ratio of square covering of the visible sky by clouds
  - Important factor for energetic balance of the planet (due to albedo = reflection coefficient)

albedo of clouds	up to 75 %
albedo of continents	up to 30 %
albedo of oceans	up to 2 – 7 %

  - global value of cloud cover ca. 54 %
- Generation of cloud cover
  - evapotranspiration from the surface (continents + oceans)
  - maximum saturation of air by water 4 % vol.
  - vapor carried by ascending (convectional) flows with speed between 20 and 80 km/hour ⇒ decrease of pressure and temperature occurs.

Atmospheric moisture

- Generation of cloud cover
  - Due to temperature drop below dew point condensation or desublimation may occur alternatively (desublimation takes place if $T < 0°C$);
  - Liquid aerosol or aerosol consisting of ice crystals is generated;
  - Height of condensation level depends on season and region; average value is ca. 1 km;
  - Height of desublimation level in summer season 5 – 6 km, in winter season 1 – 2 km;
- Characterisation of cloud cover
  - cloud cover = all types of clouds without respect to their shape, height and so on;
  - cloud = visible conglomeration of particles of liquid water or ice (+ anthropogenic or natural pollutants in aerosol);
  - diameter of condensed or desublimated particles ca. 0.01 mm.

Mechanism of rainfalls

- **Rainfalls are generated solely by tropospheric water**
  - Evapotranspiration → generation of clouds → long range transport → precipitations;
  - Formation of raindrops: mechanism of coalescence = clustering

    Primary condensation on condensation cores (dust particles, ice or salt crystals); primary droplets are very small and kept hovering by vertical flows.

    Coalescence occurs by joining droplets in liquid phase (so called warm rain) or by growth of ice crystal from overcooled water (-10 to -30 °C, so called cool rain) followed by melting during fall ⇒ Bergeron's process;

    Falling velocity is directly proportional to droplet diameter: after reaching the equilibrium between air resistance and friction against gravity the velocity becomes constant;
  - Final raindrop diameter 0,1 – 5 mm, seldom up to 8 mm and exceptionally (especially in tropics) up to 10 mm.

Rainfall volumes

- Annual rainfalls
  - Extremely low volumes: Aswan (Egypt) 0,5 $mm.year^{-1}$
  - Extremely high volumes: Kauai (Hawai) 12 090 $mm.year^{-1}$
  - Czech Rep., normalized values 1981-2010: 686 $mm.year^{-1}$
- Basic tools – manual or automated rain gauges
  - recording rain gauge called ombrograph (older type with writing on paper)
  - recording tipping bucket

    rain gauge with datalogger and

    online connection

Morphology of clouds

- Clouds are divided into 10 basic types according to their shape (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
  - Specific altitude range – height level – is typical for each of the types.
  - Low, middle and high level clouds can be recognised.
  - Borders between the levels are not defined precisely, there are differences during calendar year due to seasons. See examples:

  Winter: cirrus-like clouds (normally in high level) descend below 5 km

  Summer: altocumulus (normally in middle level) rises up to 6 km

- List of basic types of clouds:

1. Altocumulus	**6. Cumulus**
2. Altostratus	**7. Cumulonimbus**
3. Cirrus	**8. Nimbostratus**
4. Cirrocumulus	**9. Stratus**
5. Cirrostratus	**10. Stratocumulus**

Morphology of clouds

- Height distribution of cloud cover (Source: http://altamontanha.com)

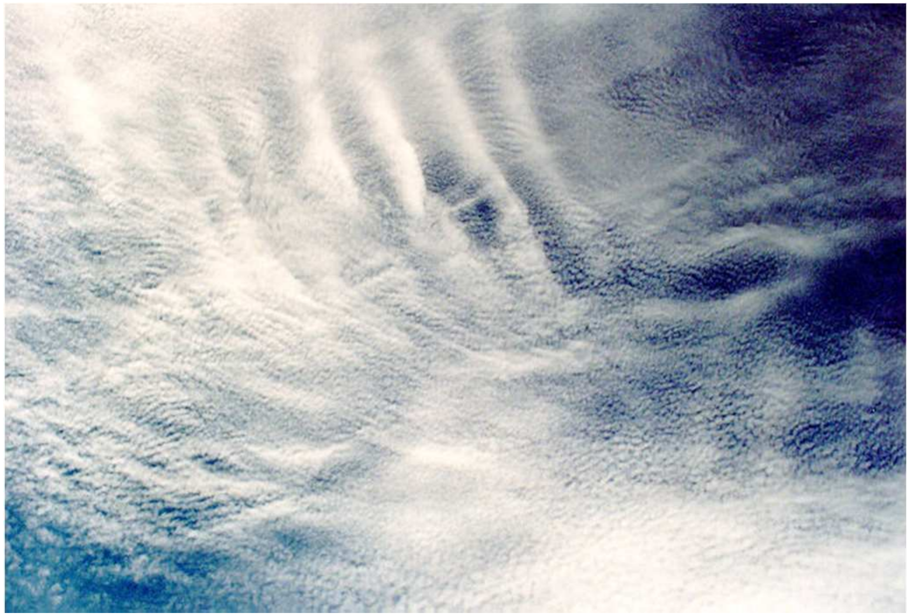
Warning: This is schematic drawing only.
In real state the clouds are not present
in more levels at once!

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrus (Ci) = so called „mares' tails"
  - Localisation: high level; 7 – 10 km
  - Description: separated clouds, having a form of white fine fibers, white stripes and so on. Ci has often fiber-like appearance and silk gloss. Ci is composed of ice particles ⇒ it does not form any rainfalls, but it can be a symptom of incoming front or high pressure ridge.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrocumulus (Cc)
  - Localisation: high level; 7 – 10 km
  - Description: smaller or larger groupings of white clouds, sometimes having ribbon structure. Its appearance is possible as separated clouds as well as regular ordered conglomerates.



Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cirrostratus (Cs)
  - Localisation: high level; 7 – 10 km
  - Description: translucent whitish haze, with fiber appearance and covering partly or completely the sky. In some cases it is formed by increasing number of cirrus clouds till the moment, when they join together to form the uniform layer.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Altocumulus (Ac)
  - Localisation: middle level; max. ca. 5 km
  - Description: grouping of white or grey cloud, consisting mainly of water droplets; unlike the cirrus-like clouds Ac drops its own shadow. Ac may exist also as entire cloud cover, but with visible division into particular clouds.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Altostratus (As)
  - Localisation: middle level; ca. 5 km, sometimes high 8 km
  - Description: greyish layer with smooth, uniform appearance, sometimes with fiber or ribbon structure. In the thinnest parts it can be slightly permeable for sunshine. Rainfalls produced by As in some cases reach the surface.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Nimbostratus (Ns)
  - Localisation: middle level, extended into low and high levels
  - Description: grey or dark grey uniform cloud cover. Rainfalls caused by Ns usually reach the surface (soil) and are long lasting and intensive. Under the low basement of NS, there is sometimes low cloudy haze present.

Morphology of clouds

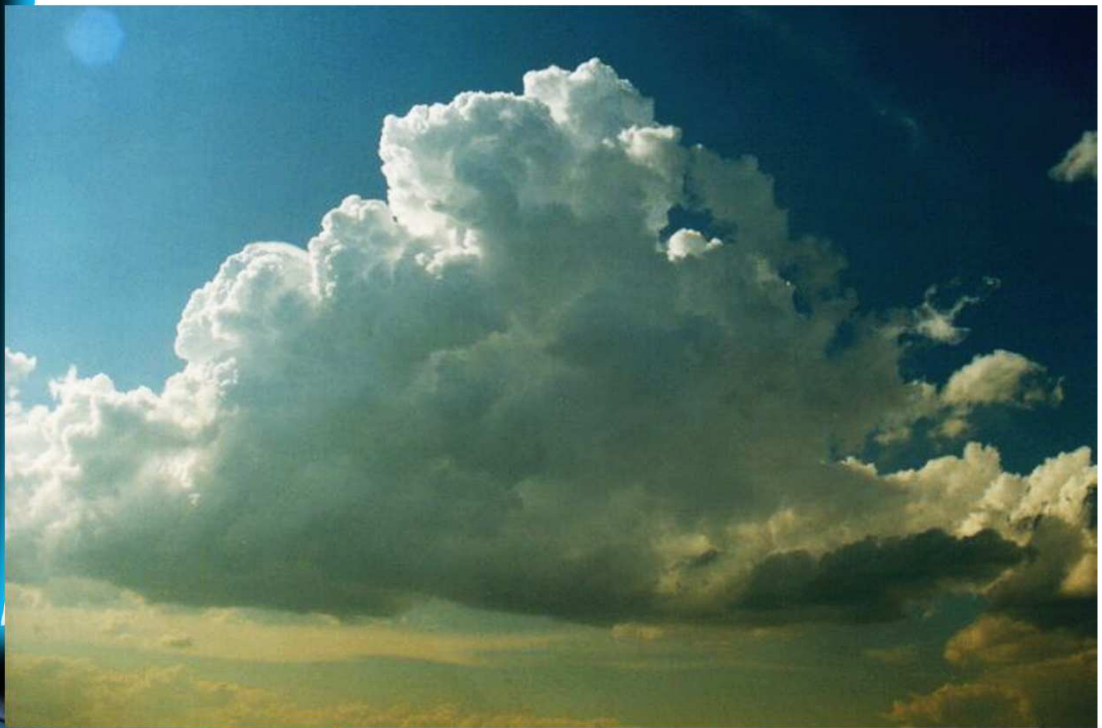
- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Stratocumulus (Sc)
  - Localisation: low and middle level 1,5 – 3 km
  - Description: grey and whitish conglomerates of clouds, which are formed by parts looking like spherical stones or fluffs. Sc has no fiber-like appearance. It may cause rainfalls with low intensity.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Stratus (St)
  - Localisation: low or middle layer 0,3 – 2 km
  - Description: grey, continuous cloudy layer with uniform and low basement; It often covers top of the hills. St is partially transparent for sunshine. St is quite often formed only as a local cloud and it may cause low intensity rain showers.

Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cumulus (Cu)
  - Localisation: low or middle level 0,5 – 3 km
  - Description: Solitary bright white or greyish cloud with „mound“ shape and sharp edges. It undergoes time disintegration with several stages of the process (Cu humilis, Cu mediocris, in case of sufficient humidity it forms Cu congestus). Cu is composed of water aerosol, with ice crystals in the middle level; It can be a source of short rain showers.



Morphology of clouds

- Characteristics of cloud types (Source: http://www.ok1jfh.net/oblaka/oblaka.htm#Ac)
- Cumulonimbus (Cb)
  - Localisation: basement 0,2 km, top 7 – 9 km
  - Description: huge, opaque, storm cloud, with cone shape, from the basement to the top it sometimes forms flat discoid or „anvil“ shape; the basement is very dark colored.