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MSMT
MINISTRY OF EDUCATION,
YOUTH AND SPORTS



ATMOSPHERIC CHEMISTRY

Lecture No.: 5

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)

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Uveřejněné materiály jsou určeny studentům Vysoké školy chemicko-technologické v Praze jako studijní materiál. Některá textová i obrazová data v nich obsažená jsou převzata z veřejných zdrojů. V případě nedostatečných citací nebylo cílem autora/ů záměrně poškodit event. autora/y původního díla. S eventuálními výhradami se prosím obraťte na autora/y konkrétního výukového materiálu, aby bylo možné zjednat nápravu.

Scope of lecture 5

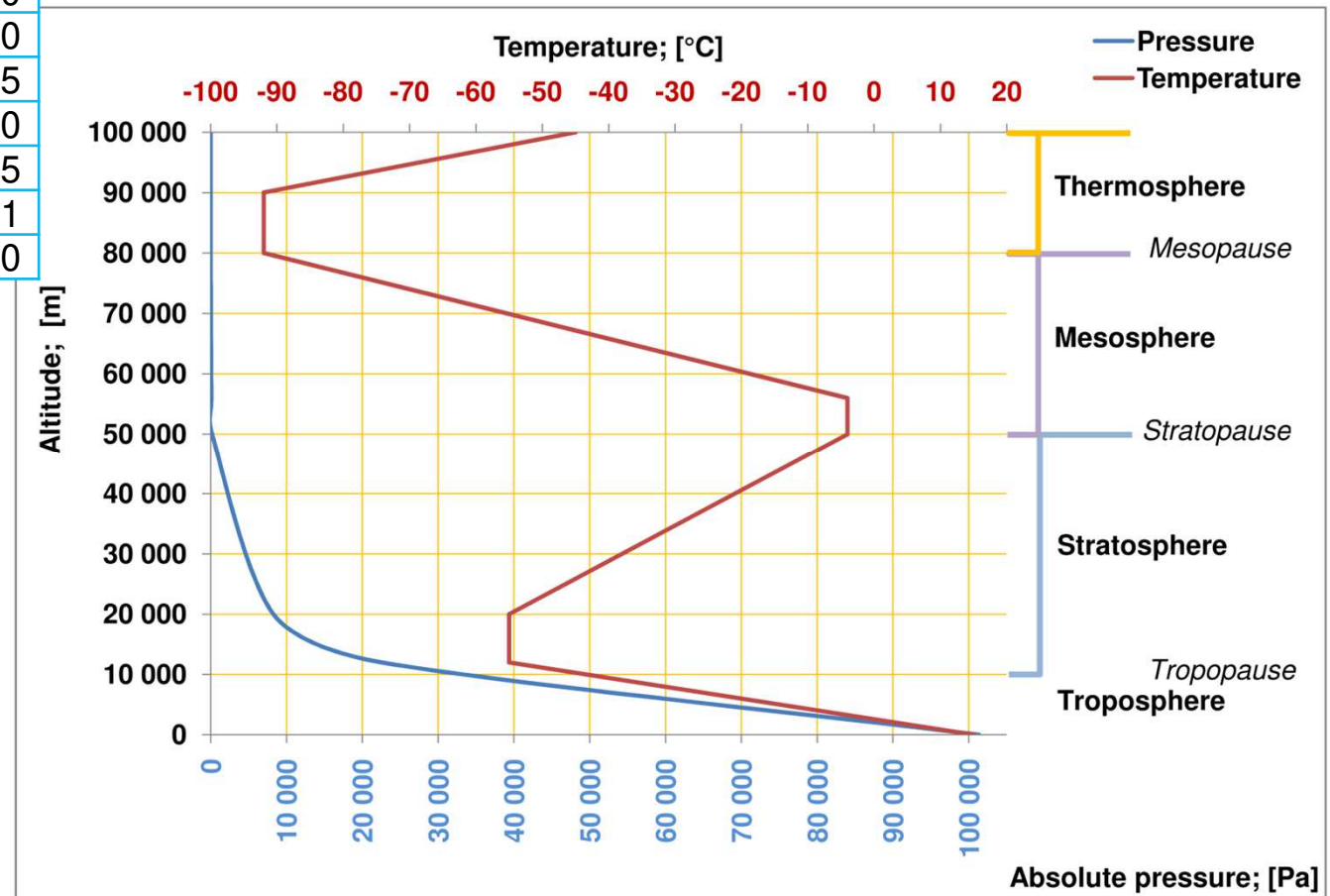
Basic reactions in the atmosphere, homogeneous and heterogeneous reactions

- Common characteristics of atmospheric reactions
- Problems of active and passive air sampling
- Distribution of reactants appearing in the air
- Distribution of reactions according to various criteria
- Monomolecular reactions
- Bimolecular reactions
- Termolecular reactions
- Photochemical reactions – ways of excitation and losing excessive energy
- Main acid base reactions in the atmosphere
- Characteristics of nuclear reactions and natural radioactive background

Common signs of reactions in air

- Low concentrations of reactants – low partial pressures and total pressure;

Altitude [km]	Temper. [°C]	Pressure [Pa]
0	15	101 325
12	-55	22 600
20	-55	8 300
50	-4	195
56	-4	90
80	-92	5
90	-92	1
100	-45	0



Common signs of reactions in air

- Main components leading atmospheric reactions:
 - acidic components
 - oxidizing components
- Laboratory simulations of stratospheric (and higher) reactions are problematic:
 - very low pressure; components are released from walls of sampling containers and cans (desorption) \Rightarrow undesired interference;
 - differences in reaction kinetics; at high altitudes low concentration of substances absorbing energy released during some reactions \Rightarrow slow reaction rate; in laboratories, the wall of apparatus absorbs energy higher by order of magnitude \Rightarrow much faster reactions
 - risk of involvement of the apparatus itself into the reaction:
catalytic effect of materials, which the apparatus is made of
adsorption of some compounds on the apparatus surface or reaction of the material with reactants (e.g. with radicals, etc.)

Possibilities of air sampling

- Distribution of sampling techniques

Active sampling = sample taken with additional energy using external force rather than diffusion; active element is pump (inlet or outlet) or vacuum (suction into evacuated sampling can)

→ sampling together with whole matrix (air)

→ sampling with isolation of selected components

Passive sampling = free diffusion flow of molecules of sampled substance from air to collection media till reaching equilibria concentrations of analytes in both environments;

→ only sampling with isolation of selected components

Possibilities of air sampling

- Active sampling with collecting whole matrix
 - Example of sampling into evacuated sampling canister (producer e.g. SUMMA®)
 - Material – stainless steel with electrochemically polished internal surface + in some cases equipped with silica layer
 - Sampling through special valve (mechanical or electromagnetic), assuring constant sampling time and gas flow.
 - Sampling stopped with residual vacuum 5 kPa due to changes in barometric pressure.
 - Alternative method is sampling into a special bag.



Possibilities of air sampling

- Active sampling with isolation of selected components

(Source: <http://www.population-protection.eu>)

- Approaches using filtering of the air through active element, where analysed substances are selectively and quantitatively captured.
- Following processes serve for capture:
 - Absorption in solvents
 - Adsorption on solid sorbents
 - Filtration using dust filters
- Realisation of capture is provided e.g. By a sampling gas pump with an adjustable flow rate (usually range 0 – 5 l.min⁻¹).
- The pump is equipped with a correctly calibrated gas flow meter or gas meter displaying the volume passed.

Possibilities of air sampling

- Active sampling with isolation of selected components

(Source: <http://www.population-protection.eu>)

- Example: adsorption of organic compounds using sorbent in sampling tube.

- 3 groups of different sorbents available:

- Non polar sorbents type I. on the basis of active coal (Carbotrap, Carbosieve, Anasorb and so on) ⇒ sorption of aliphatic hydrocarbons including polycyclic types;
- Hydrophilic sorbents type II. with positive surface charge on the basis of silica gel ⇒ sorption of carboxylic acids and their derivatives.
- Partially hydrophilic polymer sorbents type III. with negative surface charge (Amberlite XAD2, Tenax and so on) ⇒ sorption of polar derivatives of hydrocarbons.

Possibilities of air sampling

- Example of utilisation of the sorption tube
 - Sorption tubes are supplied either welded and pre-activated (type I.), or they require additional activation, immediately before application (silica gel 150 °C with N₂ flow, polymeric Tenax 80 °C with He flow)
 - Before sampling both edges of tubes must be broken off, or the caps must be removed and the tube is connected to the pump inlet.

Tenax tubes before application



Hermetic capsule for saturated tubes



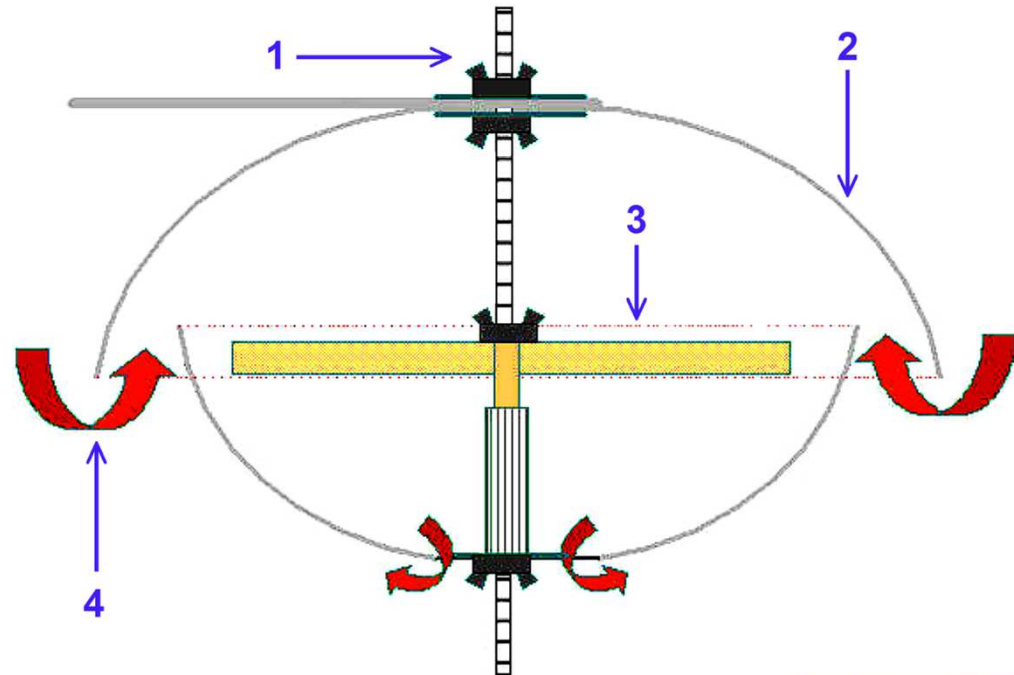
Possibilities of air sampling

- Passive sampling with isolation of selected components

(Source: <http://www.population-protection.eu>)

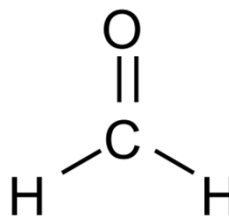
- Separation is based on differences of concentration of analytes in the air and in the sorbent. Sampling realised either during fixed time interval or till reaching equilibria concentrations.
- Sorbents: polyurethane foam, XAD resin, polyethylene semipermeable membrane with triolein filling etc.

- 1 – fixing screw
- 2 – stainless steel hemispheric cover
- 3 – sorbent
- 4 – free circulation of air



Distribution of reactants

- Primary energy for initialisation of reactions = solar radiation;
- Distribution of reactions according to presence of the above mentioned energy:
 - Day reactions; basic reactant = hydroxyl radical $\text{HO}\bullet$
 - Night reactions; basic reactant = nitrate radical $\text{NO}_3\bullet$
- Other gaseous reactants (distribution into groups may overlap):
 - Inorganic oxides; CO , CO_2 , NO , NO_2 , SO_2
 - Oxidants; O_3 , H_2O_2 , $\text{NO}_3\bullet$, $\text{HO}\bullet$, $\text{HO}_2\bullet$, $\text{ROO}\bullet$
 - Reducing substances; CO , SO_2 , H_2S , hydrocarbons
 - Organic compounds; in clean atmosphere only CH_4
 - close to the pollutants higher C_xH_y and derivatives
 - Photochemically active; NO_2 , $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (formaldehyde)



Distribution of reactants

- Other gaseous reactants (distribution into groups may overlap):

- Acids; H_2SO_4
- Bases; NH_3
- Salts; NH_4HSO_4
- Unstable components; $\text{HO}\bullet$, other radicals,
electrically excited NO_2^*

- Other components of atmosphere entering into reactions:

- Liquid particles = places, where reactions in solution take place
- Solid particles = surfaces for heterogeneous reactions (possibly surface-catalysed reactions)

Both types of particles also allow the descend of absorbed gases to lower atmospheric layers.

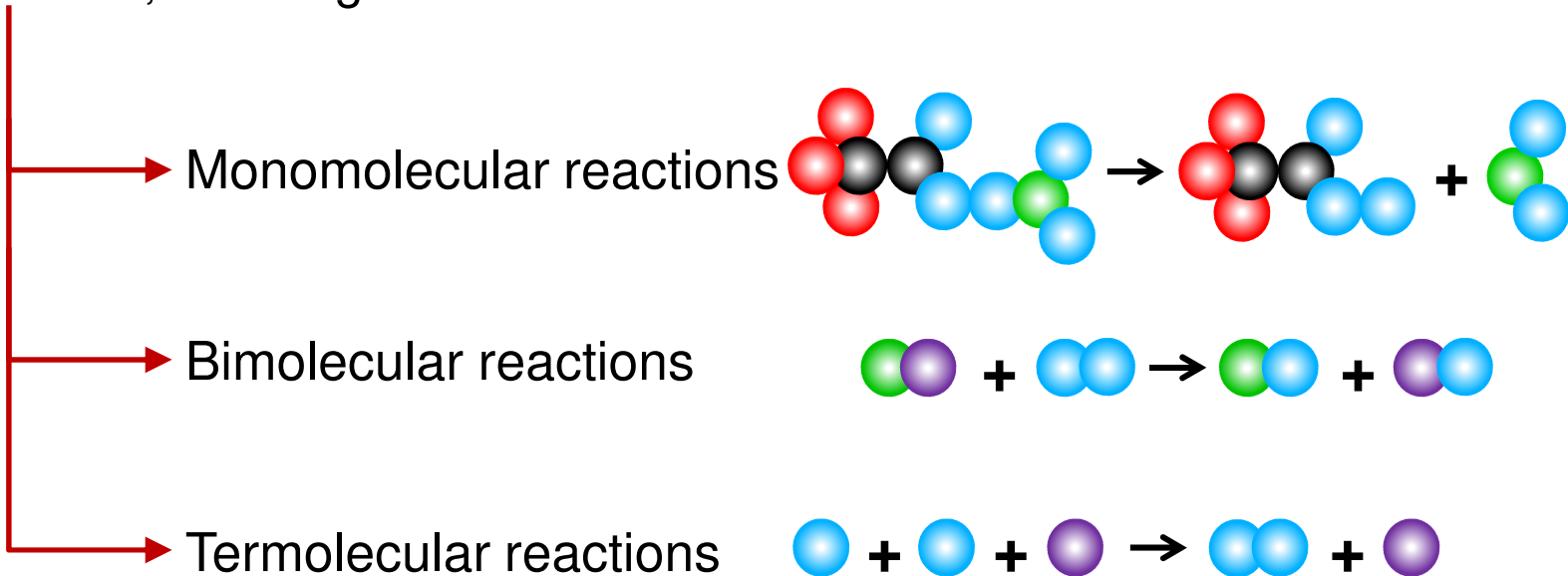
Distribution of atmospheric reactions

- The highest number of reactions: Troposphere
 - Sufficient partial pressures of components + sufficient temperature (penetration of radiation > 330 nm)
 - Contrariwise the amount of UV radiation with shorter wavelengths is filtered by ozonosphere;
- Basic distribution of reactions:
 - Homogeneous reactions
 - Run only in gaseous phase
 - Products of homogeneous reactions influence the course of heterogeneous reactions (e.g. oxidative influence of O_3 , H_2O_2)
 - Heterogeneous reactions
 - Interaction of microphysical processes with chemical reactions;
 - adsorption = process on the surface of solid particles
 - absorption = process in liquid phase (water droplets)

Distribution of atmospheric reactions

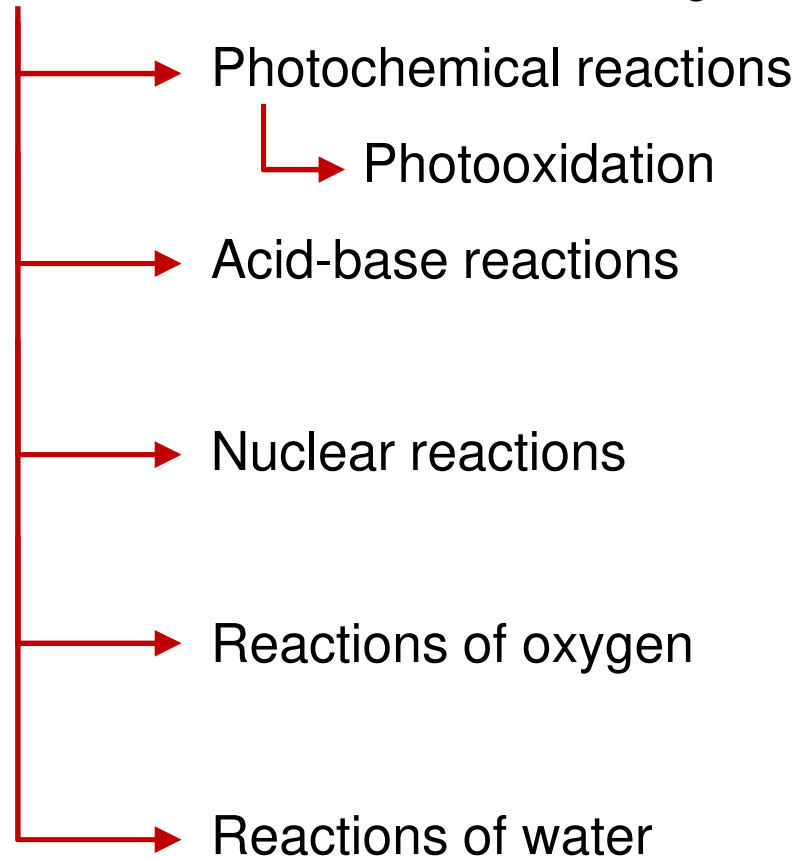
- Distribution of homogeneous reactions

- One possibility of distribution is according to the number of atoms or molecules, entering the reaction:



Distribution of atmospheric reactions

- Distribution of reactions according to chemical basis of process:



- One specific reaction can accomplish more categories.
 - e.g. At the same time, a reaction can be: homogeneous, bimolecular, acid-base and, etc.

Distribution of atmospheric reactions

■ Homogeneous monomolecular reactions

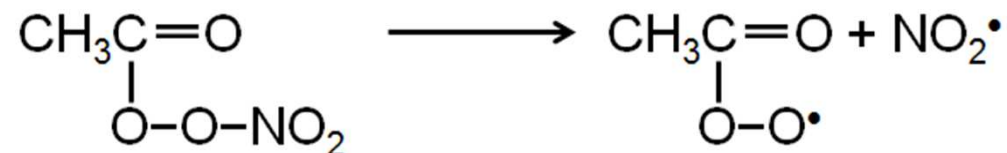
- Principle: cleavage of molecule into two or more products.
- Main mechanism - absorption of heat energy.
- Initial molecule must be, therefore, thermolabile and must have excess of energy, which is induced by the following ways:

Thermal excitation by elastic collision with third substance (it does not participate in the reaction)

Photoexcitation \Rightarrow photolytic reaction

- Examples of the most important reactions:

Decomposition of peroxyacetyl nitrate to nitrogen dioxide:



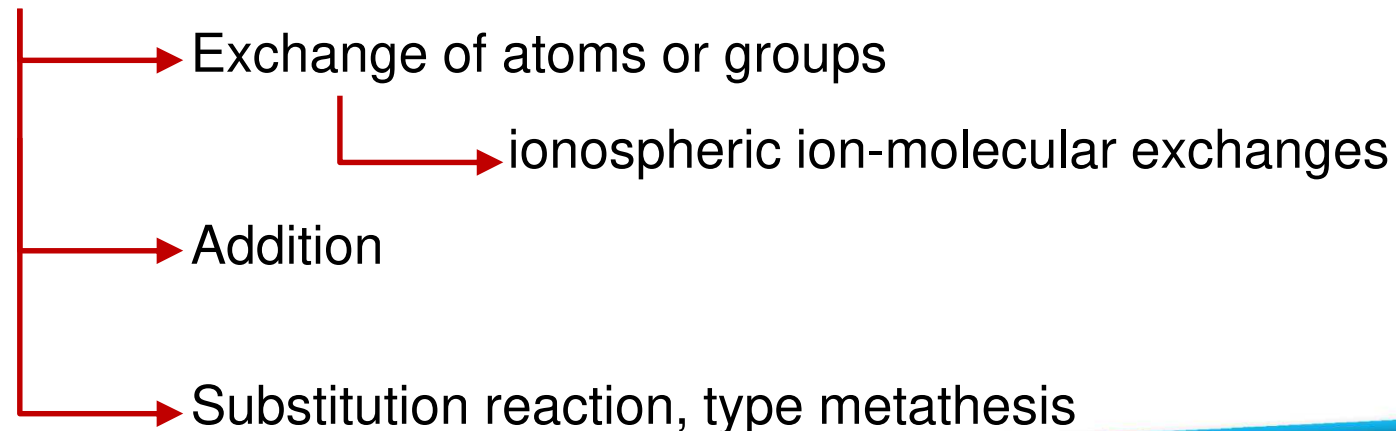
Stratospheric decomposition of chlorine dioxide:



Distribution of atmospheric reactions

■ Homogeneous bimolecular reactions

- Main principle: increasing of energy in the system of two molecules, which have collided together (so called kinetic collision theory of gases).
- Increase of energy occurs due to overcoming the repulsive force between the molecules, in case they have sufficient kinetic energy in the moment of collision.
- Reaction rate - directly proportional to initial concentrations of both reactants.
- 3 basic types of bimolecular atmospheric reactions:



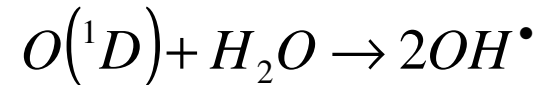
Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**

- Reaction on the principle of exchange of atoms or groups;

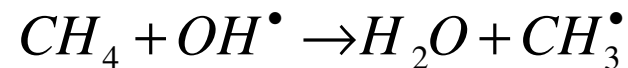
Following reactions in the atmosphere have this mechanism:

- Hydrogen – atom transfer

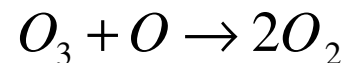


where $O(^1D)$ is Oxygen atom in excited singlet state

- Exchange Hydrogen– atom



- Exchange Oxygen– atom



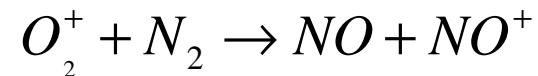
Distribution of atmospheric reactions

- **Homogeneous bimolecular reactions**

- Ion-molecular reactions

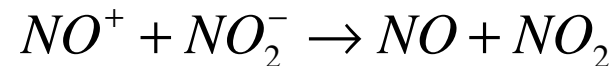
Reaction mechanism typical of ionosphere – abundance of ions in troposphere is lower by order of magnitude, so this reaction mechanism is not usual

- Charge transfer

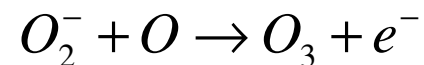


or $N_2^+ + O_2 \rightarrow N_2 + O_2^+$

- Ion – ion recombination



- Associative detachment



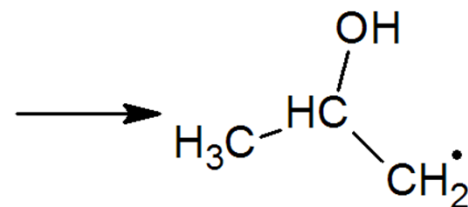
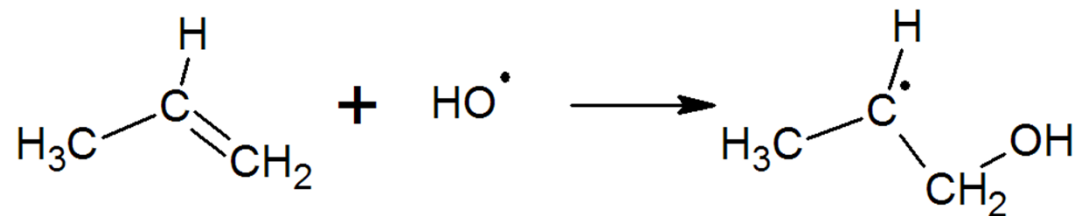
Distribution of atmospheric reactions

■ Homogeneous bimolecular reactions

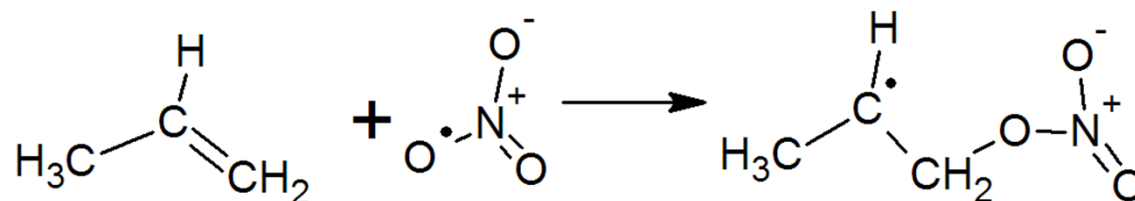
- Reactions on the basis of addition;

Either 2 molecules combine together, or (more often) a radical is adopted by a neutral molecule; Examples:

→ Reaction of hydroxyl radical with propylene:



→ Reaction of nitrate radical with propylene:

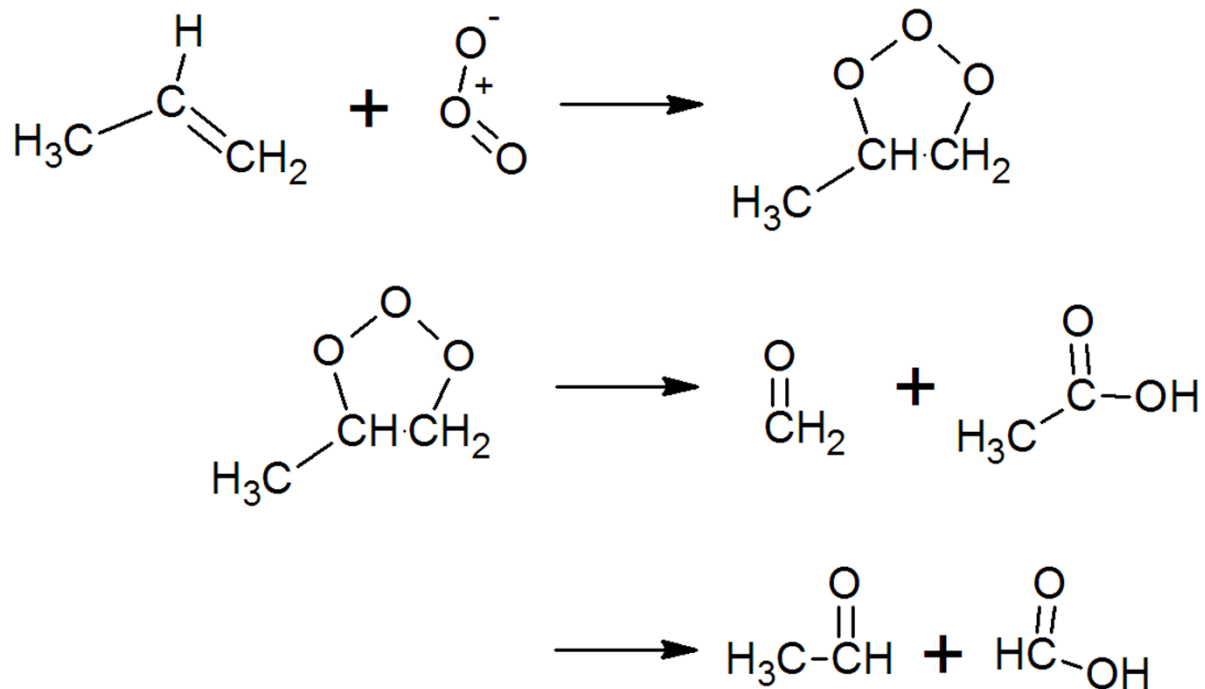


Distribution of atmospheric reactions

■ Homogeneous bimolecular reactions

- Reaction on the basis of substitution type metathesis

Less frequent type of atmospheric reaction with formation of transition state with more reaction centres and subsequent cleavage of the intermediate into products: Example – ozonolysis of propylene with primary addition of O_3 on double bond of olefine (so called ozonide)



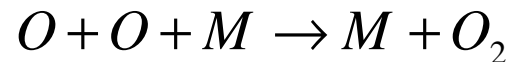
Note: in fact bimolecular addition, followed by monomolecular cleavage of an intermediate (adduct)

Distribution of atmospheric reactions

■ Homogeneous termolecular reactions

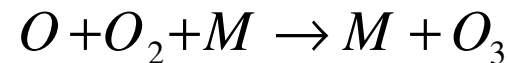
- Common principle: recombination of 2 molecules, atoms or radicals in presence of third particle, which conditions the reaction course by absorption of excessive energy.
- 2 particles, entering the reaction, usually contain excess of energy ⇒ second condition for reaction course. Examples:

Combination of atoms of O to form a molecule:

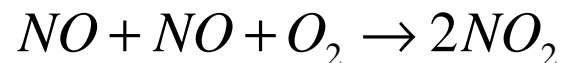


Importance of M: removal of energy from O_2 , otherwise the energy exceeding the limit causes homolytical molecule cleavage.

Generation of Ozone:



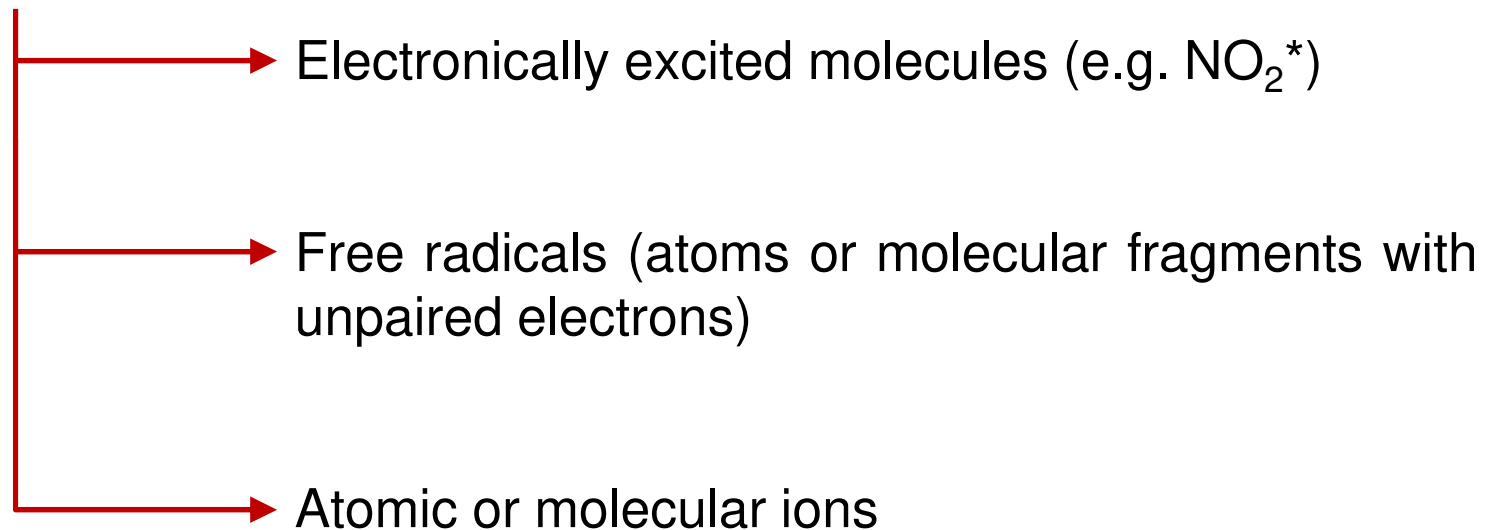
Oxidation of nitrogen oxide by oxygen (see chapter NO_x):



Reactions distribution by mechanism

■ Photochemical reactions

- Reactions of the highest importance for atmospheric chemistry;
- First step for realisation of a photochemical reaction = absorption of light quantum by a molecule;
- Absorption of energy induces excitation of the molecule;
- In the atmosphere, there are 3 types of unstable, very reactive particles:



Reactions distribution by mechanism

■ Photochemical reactions

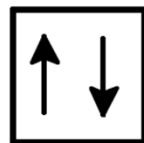
- Excitation allowable by absorption of UV + VIS irradiation (low E ⇒ lowest excited states):

Excited singlet state

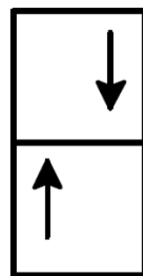
= one of the electron pairs from the highest occupied orbital shifts into a higher orbital and has an opposite spin than that of its counterpart

Excited triplet state

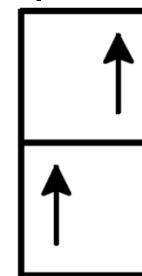
= e⁻ in the higher orbital and its counterpart in the initial orbital have identical spins



base singlet state



excited singlet state



excited triplet state

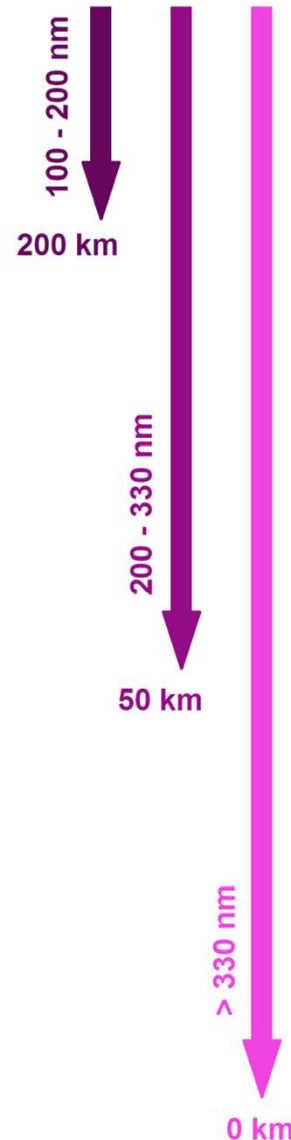
Reactions distribution by mechanism

■ Photochemical reactions

Radiation

throughput

– see 1st lecture



Termosféra; Thermosphere (80 - 700 km)

Mesosféra; Mesosphere (50 - 80 km)

Stratosféra; Stratosphere (12 - 50 km)

Troposféra; Troposphere

Reactions distribution by mechanism

- Photochemical reactions

- General range of wavelengths, involved in photochemical reactions: 280 – 750 nm; Radiation with shorter wavelengths does not penetrate into lower atmosphere;
- Infrared radiation does not have sufficient energy for particles excitation (absorption in IR part of spectrum only increases kinetic energy \Rightarrow elevation of atmospheric temperature);
- NO_2 is the most absorbing gas among photochemical reactants:
 - between 300 – 370 nm 90 % dissociation into $\text{NO} + \text{O}$
 - between 370 – 420 nm decrease from 90 % to 0 %
 - over 420 nm does not react
- Other significant participants in photochemical reactions are:
 O_3 , formaldehyde, higher aldehydes and ketones, nitrous acid;

Reactions distribution by mechanism

- Photochemical reactions

- The following substances **do not react** within wavelengths available in troposphere:



SO₂

NO

CO, CO₂

C_xH_y and derivatives (except carbonyl compounds)

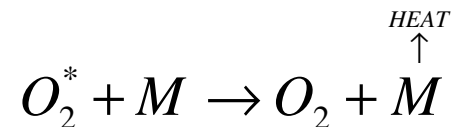
Reactions distribution by mechanism

■ Photochemical reactions

- After excitation, a particle has excessive energy, which is unloaded alternatively by the **7** following ways:

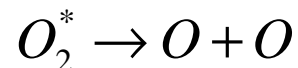
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→ **Energy transmission to another particle**, which gets higher translational energy and subsequently releases it as heat;



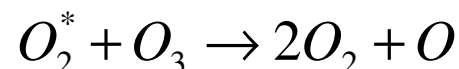
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→ **Dissociation of excited molecule**, example – formation of atomic oxygen in higher layers of atmosphere;



3

→ **Direct reaction with another substance**: creation of other molecules or one molecule and a cleaved atom, etc.



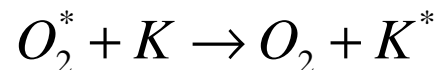
Reactions distribution by mechanism

■ Photochemical reactions

- After excitation, a particle has excessive energy, which is unloaded alternatively by the **7** following ways:

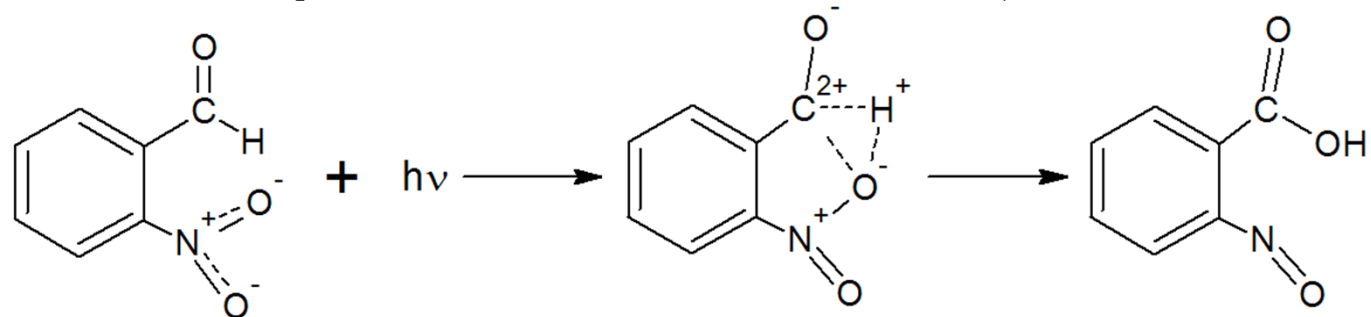
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→ **Deactivation by collision:** the excited particle gives energy to another particle, which is excited secondarily;



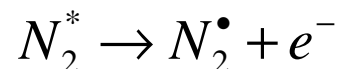
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→ **Spontaneous isomerisation,** energy is consumed to change the structure of a molecule: example transformation of o-nitrobenzaldehyde into o-nitrosobenzoic acid;



6

→ **Photoionization,** loss of electron

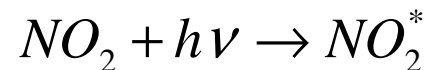


Reactions distribution by mechanism

■ Photochemical reactions

- After excitation, a particle has excessive energy, which is unloaded alternatively by the **7** following ways:

7 → **Luminescence** = loss of energy via radiation of electromagnetic quanta, e.g. reaction of nitrogen dioxide as the main reactant in photochemical smog;



2 variants of luminescence:

- Fluorescence (immediate radiation, so-called re-emission)
- Phosphorescence (radiation with time delay)

- Note: Phosphorescence occurs during forbidden transitions. Due to the uncertainty principle, electrons are able to pass within them. But it happens slowly.

Reactions distribution by mechanism

- **Luminiscence variants according to excitation mechanism**

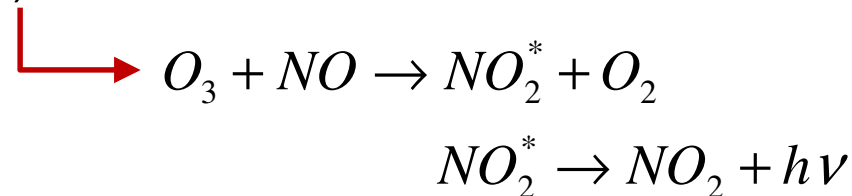
- Pholuminiscence

- important in the atmosphere

- Electroluminiscence

- Cathodoluminiscence (see old CRT screens)

- Chemiluminiscence – promoted by a chemical reaction (see the NO_x analysers)



- Thermoluminiscence

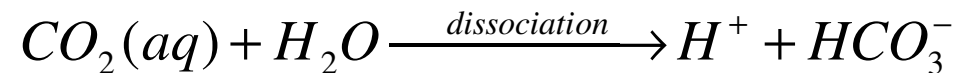
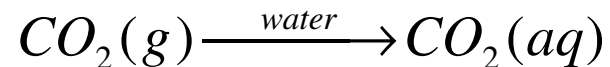
- Radioluminiscence

- Triboluminiscence – promoted by pressure acting e.g. on a crystal

Reactions distribution by mechanism

■ Acid base reactions

- Reactions involve acidic compounds: CO_2 , SO_2 , NO_x , and basic compounds: $\text{Ca}(\text{OH})_2$, CaCO_3 , NH_3
- On average, the atmosphere is slightly acidic due to dissolving CO_2 in water aerosol and its subsequent partial dissociation:



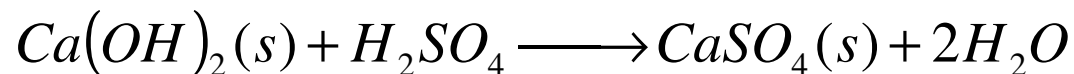
SO_2 and NO_x , react in a similar way, however they yield stronger acids \Rightarrow acidic deposition \Rightarrow eutrophication of water, damaging vegetation.

Note. Above mentioned effects are discussed in more detail in lectures aimed at sulphur and nitrogen oxides.

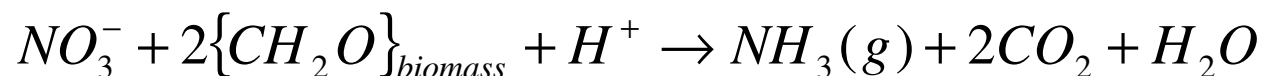
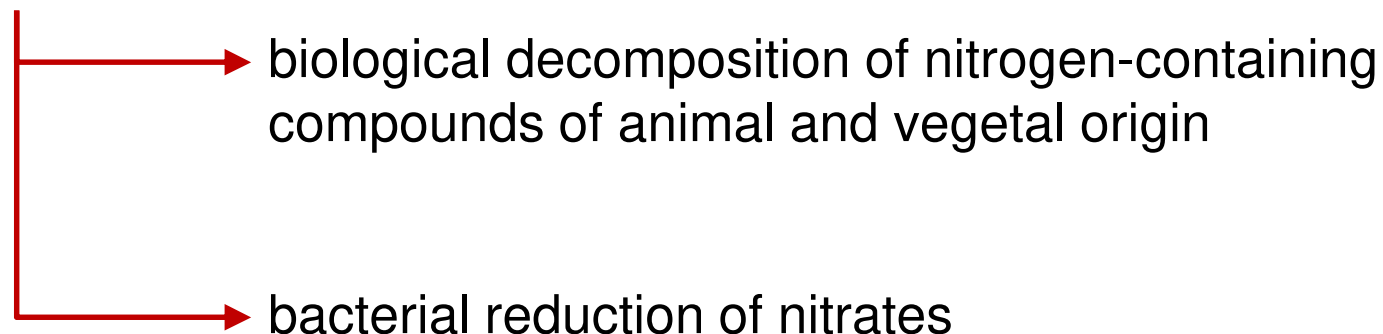
Reactions distribution by mechanism

■ Acid base reactions

- Concentration of basic compounds in air is lower due to its low pH;
- Ca(OH)_2 and CaCO_3 emitted into atmosphere in a form of dusty particles from mining activities and limestone treatment of building materials. Subsequent reaction with atmospheric acids, present in water aerosol:



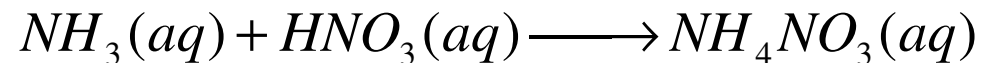
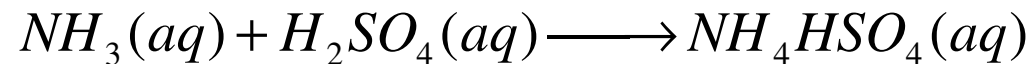
- Among bases, ammonia is the most important; NH_3 emitted via biological mechanisms:



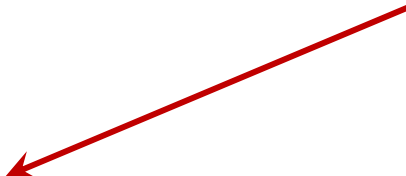
Reactions distribution by mechanism

■ Acid base reactions

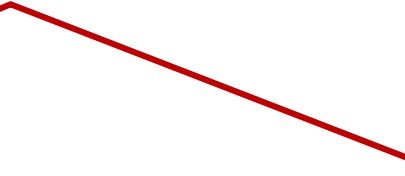
- Generated ammonia is dissolved in a water aerosol and further reacts with atmospheric acids:



- The mentioned processes have both positive and negative impacts:



neutralisation of acidic
corrosive components
(against acid rains)



generation of corrosive
ammonia salts
in a form of aerosol

Reactions distribution by mechanism

■ Nuclear reactions

- Atoms of heavy radioactive elements usually emit α particles (helions) or β particles (electrons).
- Cores of radioactive elements transform into cores of other elements via decay chains. From the viewpoint of atmospheric chemistry Uranium decay chain is the most important;
- Properties of U: bright silver metal, on air grey oxides form on the surface, $\rho_U = 19.01 \text{ g.cm}^{-3}$ at $25 \text{ }^\circ\text{C}$, ($\rho_{Au} = 9.3 \text{ g.cm}^{-3}$, $\rho_{Pt} = 21.45 \text{ g.cm}^{-3}$), melting p. $1132.3 \pm 0.8 \text{ }^\circ\text{C}$, occurrence in minerals:

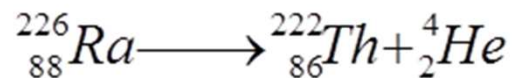
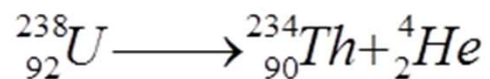


Autunite > 48 % U and Uraninite 88,15 % U (Source: [.wikimedia.org/wiki/File:Uraninite-39029.jpg](https://commons.wikimedia.org/wiki/File:Uraninite-39029.jpg))

Reactions distribution by mechanism

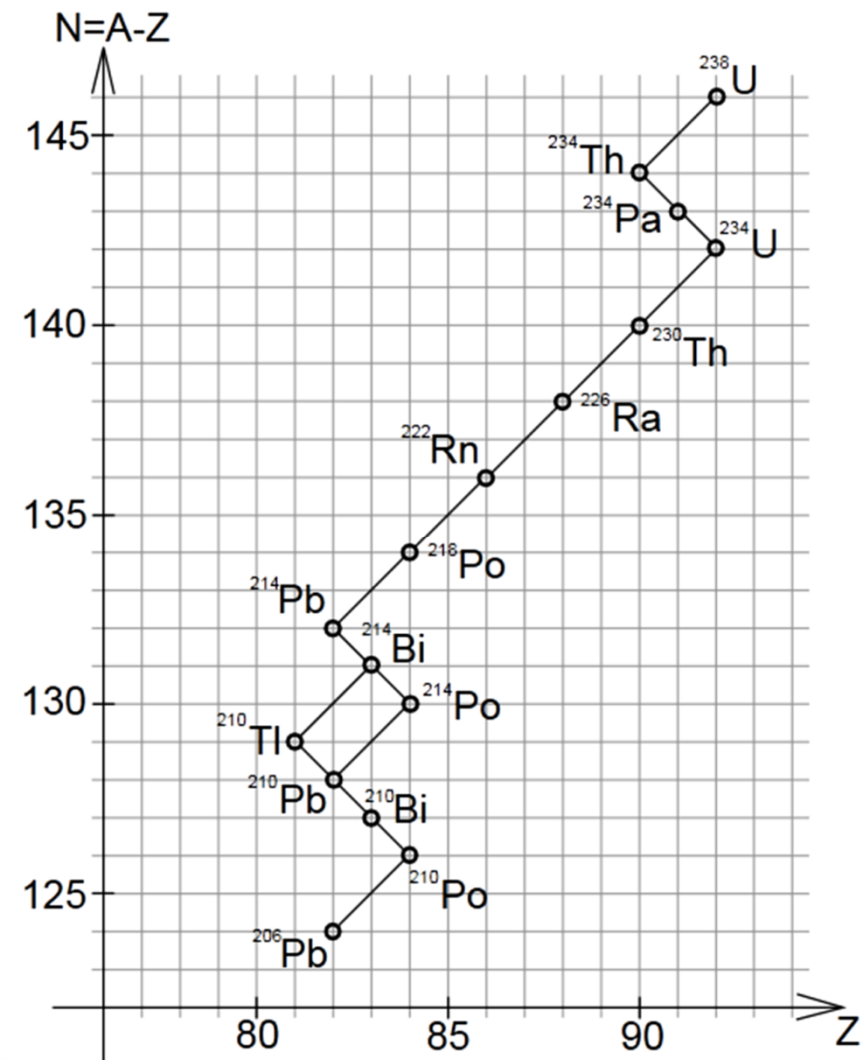
■ Nuclear reactions

- Uranium 238 exists in the Earth's crust in rocks (ca. 50 % of initial weight have already decayed since the planet formation)
- In the decay chain, decay into Rn is the most important for air:
1st α-decay into Th, 5th α-decay into Ra, 6th α-decay into Radon



Isotope	Decay halftime
${}^{238}\text{U}$	4.468 billion years
${}^{234}\text{Th}$	24.1 days
${}^{226}\text{Ra}$	1600 years
${}^{222}\text{Rn}$	3.824 days

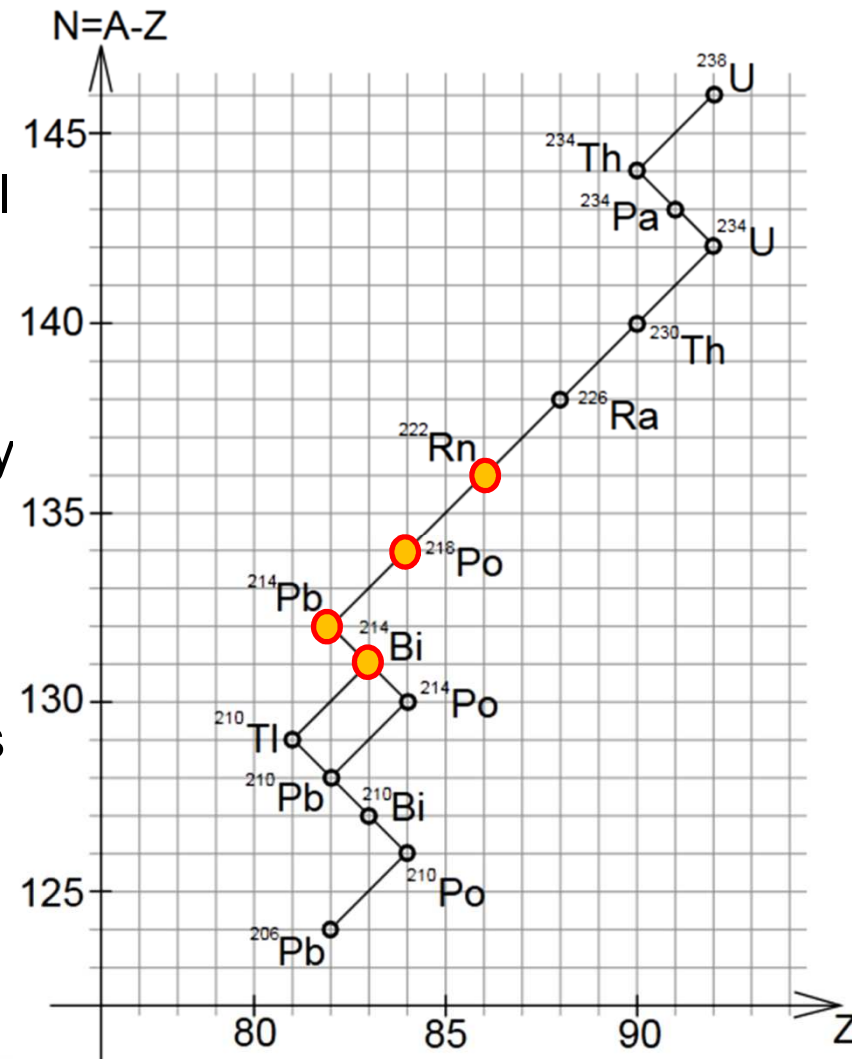
(A = nucleon, N = neutron, Z = atomic, proton number)



Reactions distribution by mechanism

■ Nuclear reactions

- Radon permeates through soil, rocks, bore holes and mines and escapes to the air.
- Background concentration of Rn is responsible for 50 % of natural atmospheric radioactivity
- Rn is not toxic by itself.
- Only products of its further decay are dangerous.
- Isotopes Po, Pb, Bi are easily adsorbed onto dusty particles, whose fraction $< PM_3$ penetrates into pulmonary alveoli and causes lung cancer.



Reactions distribution by mechanism

- Pathways of Rn leakage into houses (Source: www.rangerradonservicesinc.com)

