SELECTED TOPICS

***Non-thermal activation*:**

- electrochemistry (*dynamic electrochemistry*),
- photochemistry*
- radiation chemistry*
- microwave chemistry*
- magnetochemistry*
- sonochemistry**
- mechanochemistry, tribochemistry

* We live in a constant ***radiative environment***, in a ***radiant sphere***: there are natural and artificial radiations, useful and dangerous ones among them.

Types of radiations:

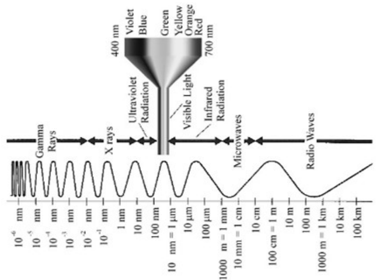
- ***electromagnetic waves*** **(Maxwell):**
  energy propagation in electromagnetic field – quantized, in the form of photons with $h\nu$ energy
- ***corpuscular radiation***: particles with non-zero rest mass, *e.g.* α, β, n, ion, … (fast) movement – this movement is not quantized

both types have a high (relativistic) speed

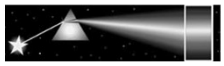
- [*mechanical waves: the medium is the carrier (e.g. water, sound-, shock wave, earthquake, ...)* these are not radiation, they are just "waves".
  - They can also cause chemical changes!

Characteristics of radiations:

- <u>***radiation intensity***</u>**:** the number of photons / particles (in time and space) in the beam (flux) (*examples: light sources, radioactivity, laser, etc.*)
- <u>***energy***</u> of a photon/particle
  - photon: $E = h\nu$ (*nu!*) [*c* speed of light]
  - particle: $E = ½ mv^2$ (*vee!*) [$v < c_{light}$]
- <u>***spectrum***</u>**:** particle number distribution according to energy *(wavelength, wave number)*
  - *lines*: discrete energy values (H, γ, etc.)
  - *bands:* "intertwining" lines (UV)
  - *continuous*: has "all kinds of" energy, but with a typical distribution (like black-body radiation)

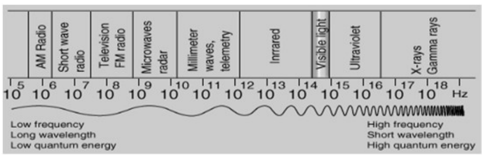


White light dispersion:
prism, grid, rainbow



Electromagnetic radiation ranges

kHz MHz GHz mm nm keV MeV



„FATE" of PHOTONS (and particles)

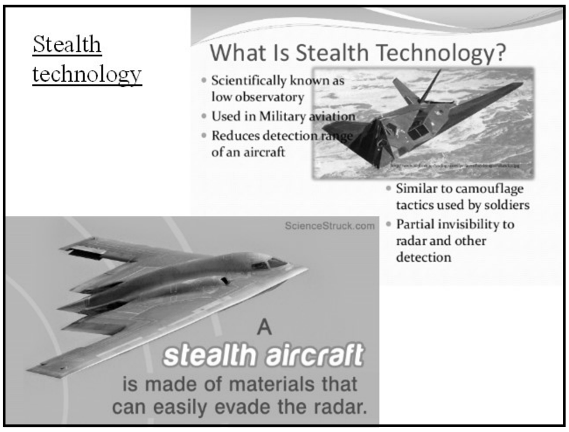
When arriving to a new medium, **the light** (photon beam and electromagnetic vibration) and – in part – also the beam of elemental particles is partially or completely

1. ***reflected*** (*diffraction*) (on a flat or parabolic mirror, slit, crystal lattice, *etc.*) [*e.g.* X-ray diffraction, electron diffraction];
2. ***passed over*** (*e.g.* it forms an image through a lens);
3. ***absorbed*** (as a result <u>*permanent chemical changes*</u> may be caused)

1. Reflection

- **physical (optical):** plane and parabolic mirror imaging
- **diffraction:** wave (not particle) property
  - ***- photon*** *(most cases we interpret it as a wave) – X-ray diffraction of crystals; on a slit*
  - ***- electron, neutron, α particle:*** *particle but behaves like a wave in this interaction (e-, n-diffraction, Rutherford's α-scattering experiment)*

Stealth technology



2. Pass over: the law of light absorption

The *A* light absorption (absorbance) is directly proportional to the concentration of the absorbing species (*c*), to the *optical path length l*, and a proportionality constant *ε* called *molar absorbance*.

***Beer*'s law:**

$$\lg (I_0 / I) = A = \varepsilon c l$$

The value of *ε* depends on the chemical identity of the absorbing species and the wavelength of the light. → Absorption spectrum (UV-VIS, IR, MW, RW).

Spectroscopy can be used only when the absorbed light ***has no chemical effect*** **(no photochemistry!!!)**

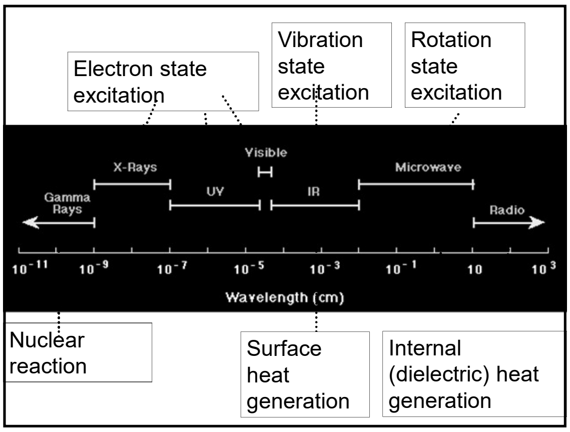
3. The *absorbed* photon (depending on its *E*) can

a) ***excite:***
- **rotation** (in a molecule),
- **vibration** (in a molecule),
- **electron state / electron structure** (in atom, molecule).

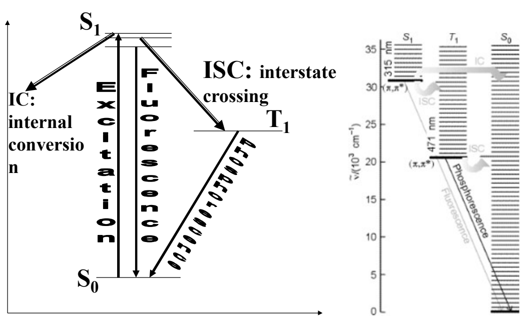
b) ***ionize***
- **physical change:** in a photocell, ESCA instrument
- **chemical change:** in a photo emulsion: $Br^- + h\nu \rightarrow Br + e^-$

c) ***break bond(s)***
- **homolytically,** two radicals (not ions) are formed: this is called **photolysis.** $Cl_2 + h\nu \rightarrow 2\ Cl^\cdot$

These are the **primary** processes**.** These are often followed by **secondary** processes (e.g. sensitization, photocatalysis, chain reactions, etc.)



a) The fate of the excited state: **Jablonski diagram**



$$h\nu_{exc} > h\nu_{fluor} > h\nu_{phosphor}$$

The fate of the excited state:
the wavelength of the emitted (fluorescent) light (photon) is longer than that of the exciting (UV) light.
***Stokes*' law (1852), *see* Jablonski diagram.**

Sir G. G. Stokes found this law when he studied the UV-induced fluorescence of the mineral fluoride. Exceptions to this law are known, but rarely mentioned.

b) Basic laws of photochemistry

1. ***Grotthus–Draper* law** (also called the principle of photochemical activation) states that only that light which is absorbed by a system can bring about a photochemical change.

T. Grotthus (1818) and W. Draper (1843)

2. *Bunsen–Roscoe* law, *reciprocity* law

The exposure duration required to elicit a given photobiological or photochemical response varies as the reciprocal of the incident irradiance:

$$H = I \times t \text{ (lux s)}$$

Bunsen, R., Roscoe, H. E: *Photochemische Untersuchungen*, Poggendorff's Annalen, 1855:96: 373-394

3. *Einstein* or *Stark–Einstein* law, *photochemical equivalence (photoequivalence)* law

Every photon that is absorbed will cause a (primary) chemical or physical reaction– which can be followed by many secondary processes.

Einstein, A.: Ann. d. Physik, 1912: 37(4): 832-838

Einstein: $E = h\nu$, $E = mc^2$
$m_{photon} = h\nu/c^2$ ***(relativistic mass)*]**

Quantum yield, quantum efficiency

***Quantum yield (quantum efficiency)* Φ:** we can refer to any effect caused by the absorbed photons, *e.g.* primary process, product formation, fluorescence, *etc.*

The ratio of *primary processes* for 1 absorbed photon is: *QE quantum efficiency*

The amount of product molecules formed is the *secondary processes* when only 1 photon was absorbed is called: *QY quantum yield*

$HI + h\nu \rightarrow H\cdot + I\cdot$ (primary)
$H\cdot + HI \rightarrow H_2 + I\cdot$
$I\cdot + I\cdot \rightarrow I_2 + M^*$

Due to the chain reaction mechanism, the value of the ***QY*** is high in this reaction. $H_2 + Cl_2$: $\Phi \sim 10^6$

HCl formation

Stoichiometry: $H_2 + Cl_2 \rightarrow 2\,HCl$

Kinetics:
- complicated chain reaction, caused many problems:
- dry, dark, room T: no reaction,
- $h\nu$ > 478 nm: explosion.
  I ……. irradiation intensity
- the presence of O_2 slows down the explosion, v will be measurable:

$$\frac{d[HCl]}{dt} = \frac{k \cdot I \cdot [H_2][Cl_2]}{m[Cl_2] + [O_2]\{[H_2] + [Cl_2]/10\}}$$

The simplified mechanism:

$Cl_2 + h\nu \rightarrow 2\,Cl\cdot$

$Cl\cdot + H_2 \rightarrow HCl + H\cdot$

$H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$

$Cl\cdot$ + wall → recombination

$H\cdot + O_2 \rightarrow HO_2\cdot$

$Cl\cdot + O_2 \rightarrow ClO_2\cdot$

$Cl\cdot + X \rightarrow ClX$

$d[HCl]/dt = k_2\,[Cl\cdot][H_2] + k_3\,[H\cdot][Cl_2]$

Steady state: $d[Cl\cdot]/dt = 0$, $d[H\cdot]/dt = 0$.

Very long chain length: ***QY*** ~ 10^6

Sensitization

Not the reactants are excited, but the ***"photo-catalyst":*** an energy transfer atom / molecule.

- **In the $H_2 + CO \rightarrow HCHO$ reaction:**

$Hg + h\nu \rightarrow Hg^*$ (excited Hg atom)

$Hg^* + H_2 \rightarrow H\cdot + H\cdot$

$H\cdot + CO \rightarrow HCO\cdot$

$HCO\cdot + H_2 \rightarrow HCHO + H\cdot$

$HCO\cdot + HCO\cdot \rightarrow HCHO + CO$

Chain reaction happens, so the quantum yield is high.

- **In *photography,*** spectral sensitizers (*e.g.* meso/cyanines) make the blue-sensitive AgBr crystals sensitive to yellow–green–red photons also.
- **In the (cold temperature) *fluorescent lamps*** Hg* atoms **sensitize**: they transfer the energy of the photon.
- **In *biology,*** there are many processes like this. For example, chlorophyll is a sensitizer (photo-catalyst) of photosynthesis.

SUNTEST UV dosimeter[1,2]

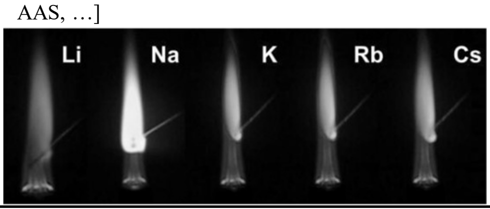
$Fe_2(C_2O_4)_3 + h\nu \rightarrow 2\,Fe^{2+} + 2\,C_2O_4^{2-} + 2\,CO_2$

$Fe^{2+} + Ag^+ \rightarrow Fe^{3+} + Ag$ (colloid)

Protective polymer coating: (PVA, PMMA)

Hot flames

- Light emission of thermally excited particles in exothermic chemical processes ($T > 500$ °C).
  - E.g. candle, torch, coat, Bunsen burner, $H_2 + Cl_2$ … (flame: standing explosion)
  - [+ color of flames (Na, K, Ba …), flame photometry, AAS, …]



Comparison of photochemistry and radiation chemistry

***Photochemistry*:**
studying and utilizing chemical changes due to electromagnetic irradiation.
Mainly UV-VIS photons*: Specific effects*

***Radiation chemistry*:**
studying, utilizing and preventing harmful chemical changes caused by high energy irradiation.
Mainly: *X, α, β, γ, n. Non-specific effects (destroy)*

Microwave chemistry: MW chemical (heat)effect

***Constant** radiations* – *„cannot be turned off”:*

- **Sun:** *UV-VIS + heat (some X, γ) – „life-giving Sun”*
- heat radiations *(Sun + artificial)*
- *„*background radiation*”: **cosmic and terrestrial radioactivity***
- **artificial** radio- (and micro)waves*: today there is a constant mild background*

Occasional – *in time/space changing – artificial radiations:*

- ***individual*** radio- and microvawe *exposure (e.g. TV, computer screen, radio phones, etc.)*
- ***ind.*** X-ray- *and* γ-radiations *(for medical purposes)*
- *the same ones in* workplace
- disasters: *atomic blasting, accidents*

Measuring and detecting radiations:

- A wide variety of methods and tools are known, approx. a range of 16-18 orders of magnitudes must be covered.
- Human „detectors”:
  - for VIS light: *eyes*
  - for UV (with „delay”): *skin*
  - for heat (IR and microwave): *skin*
  - for ionizing radiations *all living organisms physiologically (destroy)* relatively quickly, the *genome* (inheritably) much slower!

NON-IONIZING RADIATIONS

The Sun: Earth's main energy source.

5785 K black-body radiation:

- IR radiation heats up
- the visible components illuminate
- components of UV irradiation
  - UV-A: relatively innocent
  - UV-B partially reaches the Earth: sunburn + cancer
  - UV-C is absorbed by the atmosphere (O_3!): that is why the ozone layer (and the ozone hole) is important
- the *X* and *γ* components are of low intensity

Artificial hot and cold light sources.

IONIZING RADIATIONS
RADIO ECOLOGY

***a)* Natural sources of radiation:**

- ***cosmic radiation*** (not much reaches the surface) indirectly also: e.g. ^{14}C formation
- ***terrestrial radiation*:** primarily natural radioactive isotopes: ^{3}H, ^{14}C, ^{40}K, ^{226}Ra, ^{222}Rn, ^{220}Rn, ^{210}Pb, ^{210}Po

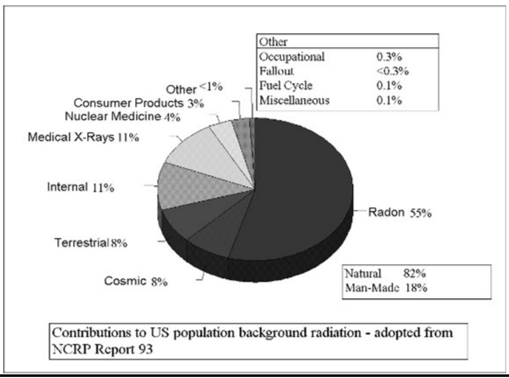
***b)* Artificial radiation sources:**

mainly artificial radioactive isotopes, and X-radiation

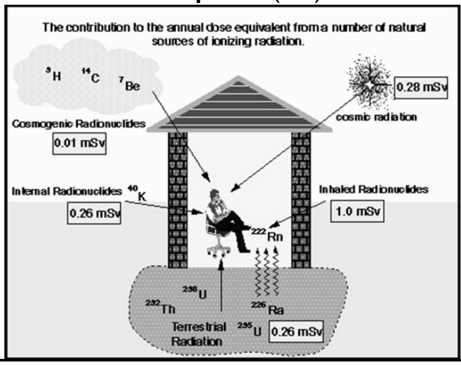
Characterization of ionizing radiation and their effects:

- ***Radioactivity*:** 1 becquerel (Bq) = 1 decay/min
- ***Absorbed ionizing radiation dose*:** 1 gray is defined as the absorption of one joule of radiation energy per kilogram of matter. 1 Gy = 1 J/kg
- ***Measure of the health effect of low levels of ionizing radiation on biological systems*:** 1 sievert (Sv) = 1 J/kg
- The energy range of the radiation: keV – MeV

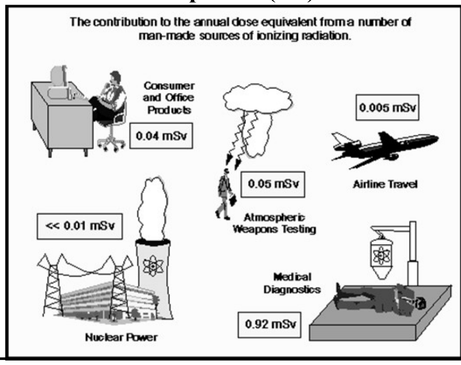
Sources of annual human radiation exposure („5/5”)



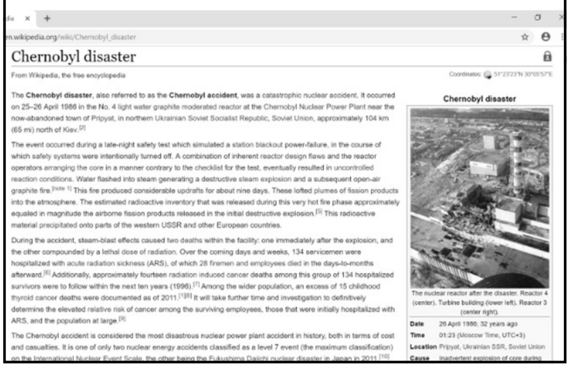
Natural sources of annual human radiation exposure (4/5)



Artificial sources of annual human radiation exposure (1/5)



Chernobyl disaster


en.wikipedia.org/wiki/Chernobyl_disaster

Chernobyl disaster

From Wikipedia, the free encyclopedia

Coordinates: 51°23′23″N 30°05′57″E

The **Chernobyl disaster**, also referred to as the **Chernobyl accident**, was a catastrophic nuclear accident. It occurred on 25–26 April 1986 in the No. 4 light water graphite moderated reactor at the Chernobyl Nuclear Power Plant near the now-abandoned town of Pripyat, in northern Ukrainian Soviet Socialist Republic, Soviet Union, approximately 104 km (65 mi) north of Kiev.[2]

The event occurred during a late-night safety test which simulated a station blackout power-failure, in the course of which safety systems were intentionally turned off. A combination of inherent reactor design flaws and the reactor operators arranging the core in a manner contrary to the checklist for the test, eventually resulted in uncontrolled reaction conditions. Water flashed into steam generating a destructive steam explosion and a subsequent open-air graphite fire.[note 1] This fire produced considerable updrafts for about nine days. These lofted plumes of fission products into the atmosphere. The estimated radioactive inventory that was released during this very hot fire phase approximately equaled in magnitude the airborne fission products released in the initial destructive explosion.[5] This radioactive material precipitated onto parts of the western USSR and other European countries.

During the accident, steam-blast effects caused two deaths within the facility: one immediately after the explosion, and the other compounded by a lethal dose of radiation. Over the coming days and weeks, 134 servicemen were hospitalized with acute radiation sickness (ARS), of which 28 firemen and employees died in the days-to-months afterward.[6] Additionally, approximately fourteen radiation induced cancer deaths among this group of 134 hospitalized survivors were to follow within the next ten years (1996).[7] Among the wider population, an excess of 15 childhood thyroid cancer deaths were documented as of 2011.[1][8] It will take further time and investigation to definitively determine the elevated relative risk of cancer among the surviving employees, those that were initially hospitalized with ARS, and the population at large.[9]

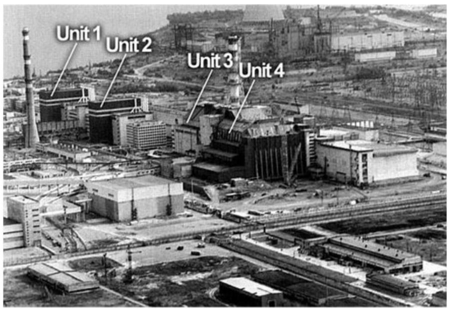
The Chernobyl accident is considered the most disastrous nuclear power plant accident in history, both in terms of cost and casualties. It is one of only two nuclear energy accidents classified as a level 7 event (the maximum classification) on the International Nuclear Event Scale, the other being the Fukushima Daiichi nuclear disaster in Japan in 2011.[10]

Chernobyl disaster

The nuclear reactor after the disaster. Reactor 4 (center). Turbine building (lower left). Reactor 3 (center right).

Date	26 April 1986; 32 years ago
Time	01:23 (Moscow Time, UTC+3)
Location	Pripyat, Ukrainian SSR, Soviet Union
Cause	Inadvertent explosion of core during

The Chernobyl Nuclear Power Plant today



Reactor 4 exploded in Chernobyl

Microwave Chemistry

Microwaves: 1 GHz – 300 GHz range

Physics: laser, radar, bluetooth, gsm *etc.*

Microwave „oven”: 2.45 GHz = 12 cm. (The polar water molecule does, but the air does not absorb it.) (Not an oven, only for cooking/heater. For baking, you need a separate grill)

Microwave chemistry (reactors): more than thermal effect, energy transfer through dipolar polarization
→ selective excitation of certain bonds,
→ thereby initiating certain reactions
→ and providing their (activation) energy.

Magnetochemistry

Methods to determine the **structure** of a molecule: magnetic moment measurements (metal complexes), NMR, ESR – no chemical reaction.

Magnetic activation: The energy of the largest magnetic fields is not enough to induce and "drive" chemical processes.

But: the spin state of particles with unpaired electrons (radicals) is influenced by these fields, and may have an effect on their reactions (NO, O_2, organic radicals, etc.), e.g. acceleration, influencing the ratio of pathways.

Sonochemistry

Production of ultrasound: with electrically vibrated quartz crystal

The ultrasound (longitudinal vibration, frequency greater than 20 000 Hz) effect: In condensed phase systems, bubbles of high pressure and temperature are formed locally. This is the **cavity** phenomenon.

Cavities can accelerate (chemical) processes (the 500 MHz generator is widespread in laboratories.)

Sonochemical procedures

- Artificial ripening of wine
- Dispersion of fat droplets in milk
- De-fogging at airports
- Healing with US waves
- US reflection for orientation (not only bats)
- US material testing, defect detection
- *etc.*

Mechanochemistry, tribochemistry

- Mechanical treatment on surfaces generates an "activation" or excess energy, which increases the rate of chemical reactions taking place there (catalysis).
- Theoretically unclear, complicated processes.
- Reproducible results and developed methods are known.
- High impact is achieved by milling in ball mills (*e.g.* cement solidifies faster, metal tool surfaces are more resistant, *etc.*)

Atmospheric chemistry

N_2: inert, important „dilution" gas – problem free
O_2: vital gas, at the same time O_3 source
Ar: it has no environmental or physiological function
CO_2: major environmental chemical compound
- source of plant carbohydrate synthesis
- animal / human life activity product
- an important participant of the C circle
- the reason of ***greenhouse effect*** and ***global warming*** (+ CH_4, freons, N_2O)
- the increase in CO_2 emission is critical

H_2O: cycle, physical and chemical role

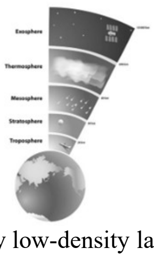
Changing components (trace gases):

compound	volume%	residence time
H_2O	0.004 – 4	~ 10 day
O_3	$(0 – 5)\times10^{-6}$	~ 2 year
CO_2	3×10^{-2}	4 – 20 year
CO	$(1 – 20)\times10^{-6}$	~ 0.3 year
N_2O	$(2 – 6)\times10^{-6}$	~ 4 year
NO_2	$(0 – 3)\times10^{-7}$	~ 3 day
NH_3	$(0 – 2)\times10^{-6}$	~ 7 day
SO_2	$(0 – 20)\times10^{-7}$	~ 5 day
H_2S	$(2 – 20)\times10^{-7}$	~ 40 day

The structure of the atmosphere:

thickness at the equator ~ 42000 km
it lasts until $E_{T,\mathrm{kin}} \sim E_{\mathrm{grav}}$
decreasing pressure: **barometric formula**

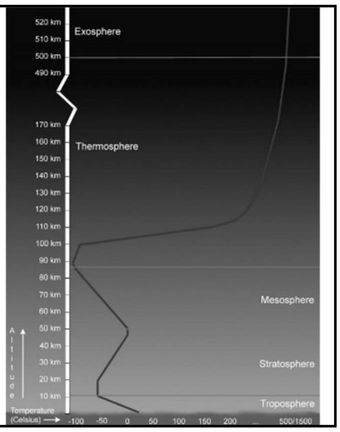
$$p = p_0 e^{-\frac{mgh}{kT}}$$

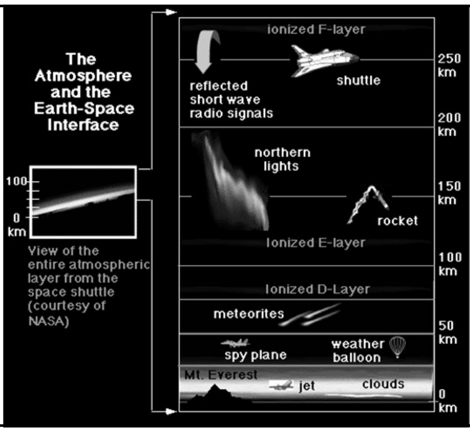


➢ ***homosphere***: ~85 km
- ***troposphere***
- ***stratosphere***
- ***mesosphere***
- ***thermosphere***

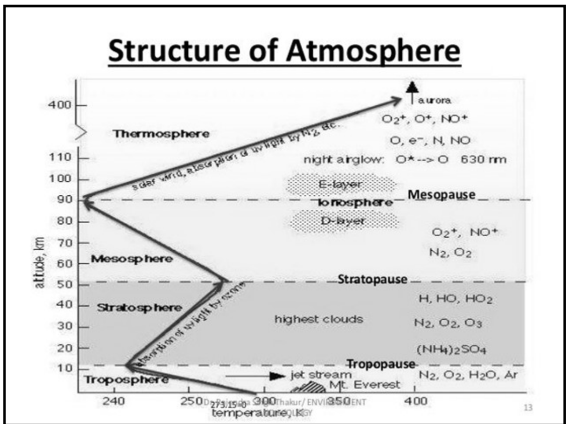
➢ ***heterosphere***: a thick but very low-density layer above the homosphere (radiations afferct it a lot).

The structure of the atmosphere

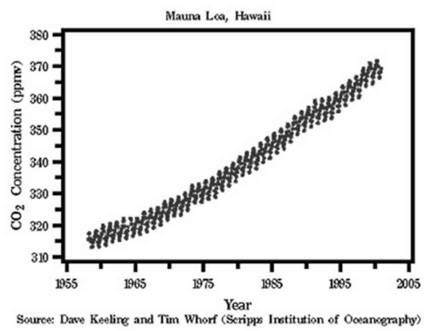




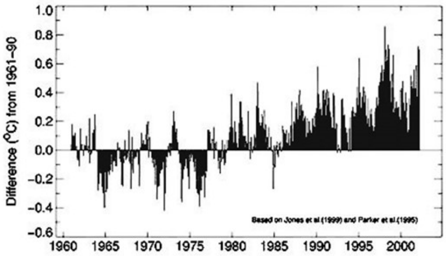
- ***troposphere*** – (then *tropopause*)
  - T decreases upward: 6.5 ºC/km
  - thickness at the equator:~18, at the poles: ~8 km
  - it gets its warmth from the ground
  - it mixes mainly through horizontal air movements and thus its composition is homogenized
- ***stratosphere*** – (then *stratopause*)
  - T increases upward: until ~0 ºC
  - ~50 km thick
- ***mesosphere*** – (then *mesopause*)
  - T decreases upward again until ~ –80 ºC
- ***thermosphere***
  - T increases upward; this is also called *ionosphere*



The increase in CO_2 concentration



Average temperatures on ground–monthly differences (1961–2002)



The 1995 Nobel Prize winners:
Paul **Crutzen** Mario **Molina** Sherwood **Rowland**

for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone



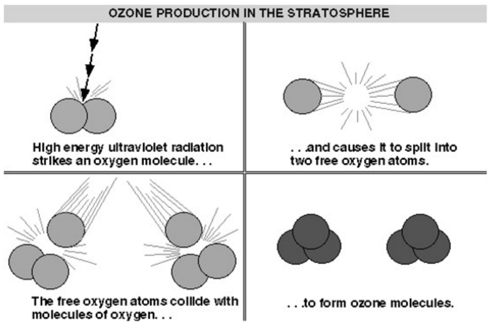
O_3: its importance has recently been recognized
- "ozone-rich" air mistake: surface ozone is physiologically harmful!
- ozone in the stratosphere is important because it absorbs UV C radiation (200–320 nm)!

synthesis: $O_2 + h\nu \rightarrow O + O$
$O_2 + O + M \rightarrow O_3 + M$ (3rd body)

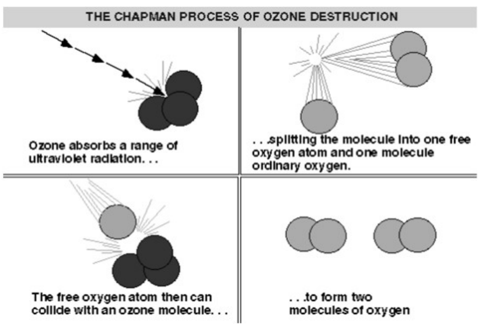
decomposition: $O_3 + h\nu \rightarrow O_2 + O$
$O_3 + O \rightarrow 2\ O_2$

ozone layer: at 1 atm, it would be 3 mm thin
ozone hole problem: NO_x and CFCl catalyze ozone decomposition, so at south pole (?) there is a concentration decrease.

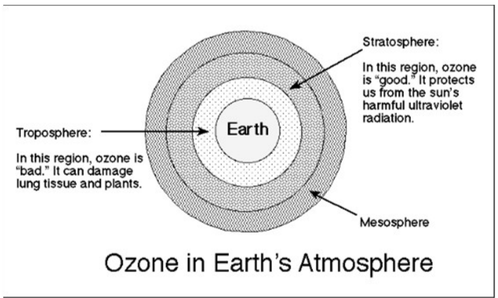
Formation of ozone is the stratosphere



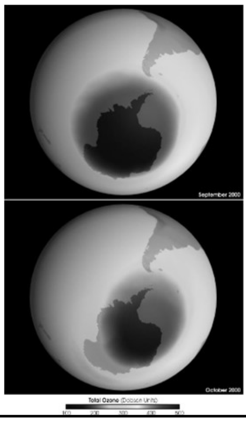
Decomposition of ozone



Two functions of ozone in the atmosphere



The ozone hole

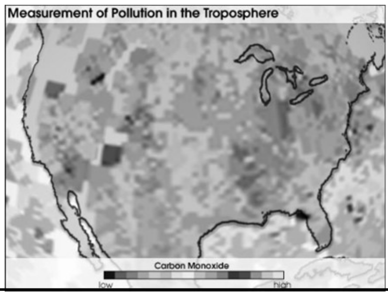


POLLUTANTS IN THE ATMOSPHERE

Sources of pollutants: natural and artificial
Pollutants: compounds containing C, S, N, halogen
six Kyoto „*greenhouse gases*" :
[CO_2, CH_4, NO_x, HFcarbons, perFcarbons, SF_6]
Colloidal pollutants: dust, fog, smoke, smog

- Measuring pollutants
- Self-cleaning of air
- Protection of clean air (prevention)
- Impact of pollution on living creatures

CO: - changing component; reactive
- natural source: volcanos
- artificial: cars, combustion
- highly toxic



SO_x: SO_2, SO_3, [H_2S, COS, CS_2, $(CH_3)_2S$]
- natural sources: volcanos, biosphere decay
- artificial: power plants, cars, chemical industry
- [4 compounds] are oxidized to SO_2
- **$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4 \rightarrow$ acid rain (fog)**

„Atmospheric chemistry":

a) $SO_2 + h\nu \rightarrow SO_2^*$
$SO_2^* + O_2 \rightarrow SO_4^{\cdot}$
$SO_4^{\cdot} + O_2 \rightarrow SO_3 + O_3$

b) $SO_2 + O \rightarrow SO_3$

c) heterogeneous: fog, smoke, surface of drops

Impact: plants, soils, structural metals, marble

NO_x: toxic, NO, NO_2 and NO_3 are dangerous
also: N_2O, N_2O_3, N_2O_5, NH_3, NH_4^+, NO_3^- …
- natural: living and dead beings, lightning, …
- artificial: power plants, cars, jets, industry, …
- NO: blood, irreversible binding to hemoglobin
- NO_2: acidic, harms the lungs

„*Atmospheric chemistry*":

forward: $NO + O_3 \rightarrow NO_2 + O_2$
$NO + H_2O \rightarrow NO_2 + HO$

reverse: $NO_2 + h\nu \rightarrow NO + O$ – equilibrium!

overall: $NO_2 + OH \rightarrow HNO_3$
$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

[NO_x:]
- certain plants (moss, lichen) are especially sensitive: indicator species
- acidity is harmful for many technical structures
- emission of NO_x can be reduced by modern methods (catalysts in cars, industrial absorption and adsorption methods, etc.)

ACID RAIN: pH of pure rain ~5.5 (CO_2)
effect of NO_x and SO_x: ~4.5, down to 2.25 (China)!

Impact: soils, plants, fish, structural metals, erosion of sculptures and buildings

Halogenated hydrocarbons (CFCl)

- formerly gases in refrigerators, sprays
- no direct harmful effect, stability
- decay upon UV irradiation in the stratosphere:
  the Cl, F formed are ozone-depleting catalysts
  (NO and NO_2 are also catalysts)

$$O_3 + h\nu \xrightarrow{Cl, F} O_2 + O$$

$$O_3 + O \longrightarrow 2O_2$$

$$NO_2 + O_2 \longrightarrow NO_3 + O_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Emission of *CFCls* has significantly dropped worldwide during the past two decades.

The CO_2 cycle