

High Energy Chemistry: **Principles, Implications and Applications**

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Outline

- Energy scale in chemistry
- Thermal chemistry and high energy chemistry
- Quantitative estimates: the energy yield
- Basic physical mechanisms and their implications for chemistry
- Spatial inhomogeneity of the primary events: the radiation-induced nanostructures and their evolution
- Mechanisms of secondary chemical reactions
- Applications of radiation chemistry: an overview
- Fabrication of nanostructures: inside the track and beyond of it
- Secondary nanostructures: nanogels and nanocomposites
- What is coming: an outlook

Physical methods to initiate chemical reactions

- **Heating (“thermal chemistry”)**
- **Action of electromagnetic radiation**
- - ionizing radiation (radiation chemistry)
- - UV/VIS radiation (*photochemistry*)
- - high-power IR radiation (*IR laserochemistry*)
- Electric discharge (*plasma chemistry*)
- Ultrasonic waves (*sonochemistry*)
- Intense mechanical treatment (*mechanochemistry*)

Energy scale in chemistry I: a characteristic scale

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad (\bar{\nu} = \frac{1}{\lambda}) \quad h = 6.63 \cdot 10^{-34} \text{ J}; c = 3 \cdot 10^8 \text{ m/s } (3 \cdot 10^{10} \text{ cm/s})$$

Molecular scale	Laboratory scale
$e = 1.6 \cdot 10^{-19} \text{ C}$	$F = eN_A \approx 96500 \text{ C/mol}$
$k_B = 1.38 \cdot 10^{-23} \text{ J/K}$	$R = k_B N_A = 8.31 \text{ J/(mol}\cdot\text{K)}$
1 eV	96.5 kJ/mol (23 kcal/mol)
«Thermal scale»: $E = k_B T$ ($E = RT$) at $T = 293 \text{ K}$	
~0.025 eV	~2.4 kJ/mol
Intarmolecular vibrations ($\bar{\nu} = 400 - 4000 \text{ cm}^{-1}$)	
0.05 – 0.5 eV	5 – 50 kJ/mol
Dissociation of chemical bonds (D_0)	
1 – 5 eV	100 – 500 kJ/mol
Molecular electronic excitation (EE)	
1 – 10 eV	100 – 1000 kJ/mol
Ionization of molecules (IE)	
~ 10 eV	~ 1000 kJ/mol

Maxwell-Boltzmann distribution. Relaxation.

Definition of sub-systems

$$n_f(x, y, z, v_x, v_y, v_z) = n_0 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(- \frac{E_{\Pi}(x, y, z) + E_K(v_x, v_y, v_z)}{kT} \right)$$

- **The condition of conservation: fast relaxation**
- **Adiabatic approximation** – splitting of molecular system to “fast” and “slow” sub-systems (a particular case: the Born –Oppenheimer approximation)

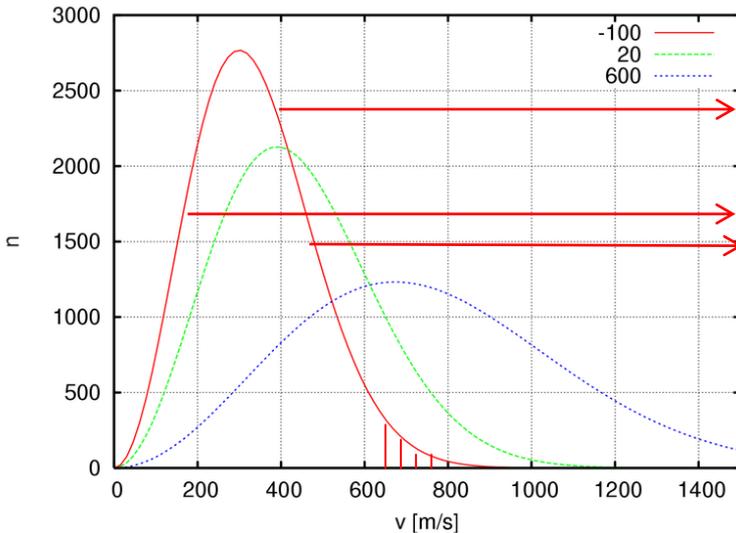
Principal molecular sub-systems:

- Fast (electronic) $\tau_{rel}^e \sim 10^{-15} \text{ c}$
- Slow (vibrational-rotational) $\tau_{rel}^v > 10^{-14} \text{ c}$

Other sub-systems:

- Phonon (intermolecular - in condensed media) $\tau_{rel}^p \sim 10^{-13} - 10^{-12} \text{ c}$
- Spin (electron and nuclear) $\tau_{rel}^s \sim 10^{-9} - 10^0 \text{ c}$
- Direct pumping of the fast sub-system may result in slow relaxation due to restricted energy exchange between the sub-systems (**a strongly non-equilibrium condition**)

Average temperature and “local temperature”. The sub-system temperature



Macroscopic system: substance
Microscopic system: atom, molecule, cluster...

Temperature (average) – a measure of average kinetic energies of molecules in a *macroscopic system* (defined only at $t \gg \tau_{rel}$)

$$T^* = E^* / k_B$$

Local temperature (in high energy chemistry) – a measure of energy locally transferred to a *microsystem* at $t < \tau_{rel}$

The sub-system temperature – a measure of energy locally transferred to a *sub-system X* at $t < \tau_{rel}^X$

“Thermal chemistry” and high energy chemistry

- “Thermal chemistry”:
- energy is transferred to a macroscopic system, the reactive molecules are selected from a statistic ensemble (*a “bottom – up” energetic scheme*)

- Quasi-equilibrium regime
- Maxwell-Boltzmann distribution is conserved

$$T_{rel} \ll \tau_{chem}$$

- Arrhenius kinetics:
 $k = A \cdot \exp(-E_A/RT)$
- “Thermal selection” of reaction channels: minimum E_A
- High temperatures are often required

- High energy chemistry
- energy is targeted to specific molecules (very large microscopic portions) and than distribute through the ensemble (*a “top – down” energetic scheme*):



$$T^* = E^* / k_B \gg T$$

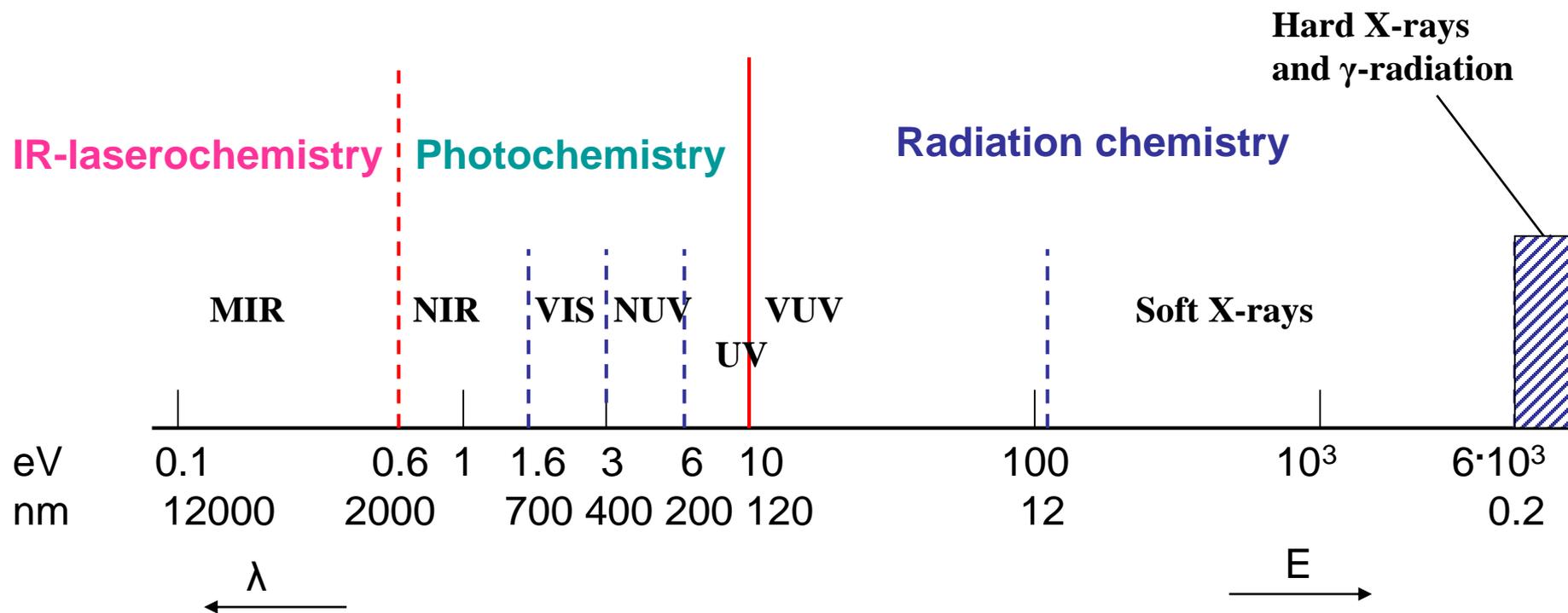
(“hot” spots in a cold medium)

- Strongly non-equilibrium regime
- Maxwell-Boltzmann distribution **is not conserved**

$$T_{rel} \sim \tau_{chem}$$

- **Non-Arrhenius** kinetics (limit: k_{eff} does not correlate with T)
- *Specific selection rules*
- Chemical reactions may occur at very low T (example: photodissociation of molecules in a solid Ar matrix at $T < 10$ K) since $E^* > D_0$

Energy scale in chemistry II: chemistry and radiation



Energy threshold for radiation chemistry: $E > IE$

In practice, the radiations with much higher energy ($E = 10 \text{ keV} - 10 \text{ MeV}$, up to 100 MeV for heavy ions) are mainly used

Efficiency factor: the radiation-chemical yield

- **Absorbed dose :** $D = dE/dm$ (1 Gy = 1 J/kg = $6.25 \cdot 10^{18}$ eV/kg)
- **Absorbed dose rate:** $I = dD/dt$ (Gy/s)
- **Radiation-chemical yield:**

$$G = dN/dE = dC_m/dD$$

- G is a characteristic of **energy efficiency of using radiation for chemical transformations**

- **Initial (“true”) radiation-chemical yield**

$$G^0(X) = \left[\frac{dC_m(X)}{dD} \right]_{D=0}$$

- **Effective radiation chemical yield**

$$G_{eff}(X) = \frac{C_m(X)}{D} \quad G_{eff} = f(D)$$

- G is usually expressed in molecules/100 eV:

$$1 \text{ molecule/100 eV} \approx 1.04 \cdot 10^{-7} \text{ mole/J}$$

- $G \sim 10$ (maximum value for non-chain processes) corresponds to an efficiency factor of 40 – 50%

- G is also a measure of radiation damage efficiency (radiation sensitivity)

$$G_{eff}(-M) = \frac{\Delta C_m(M)}{D} \quad [\Delta C_m = C_m^0 - C_m(D)]$$

Physical grounds of radiation chemistry

- Basic energy losses of a high-energy particle (photon, ion, electron) are due to *ionization and electronic excitation of the medium molecules*
- Independent on the radiation type and initial energy, the energy is mainly transferred by secondary electrons with relatively low energy ($E < 100 \text{ eV}$) → *“keVs” and “MeVs” have no meaning from the chemical viewpoint*
- In contrast to photochemistry, *primary energy absorption is non-selective* (all the bound electrons are “similar”)

Interaction of charged particles with matter

Basic mechanism: inelastic collisions with electrons (**ionization losses** – ionization and electronic excitation of the medium molecules)

N. Bohr (non-relativistic calculation):

$$-(dE/dx)_{ion} = \frac{4\pi z^2 e^4 N_e}{m_o V^2} \ln \frac{2m_o V^2}{I}$$

m_o – rest mass of electron,
 e – electron charge

Ionizing particle characteristics: V – velocity, z – charge number

Medium characteristics: $N_e = N_A \rho (Z/A)$

N_A – Avogadro number, Z – atomic number, A – atomic mass ($Z/A \approx 0.5 \rightarrow N_e \sim \rho$)
 I – “mean excitation potential”

- **$dE/dx \sim 1/V^2 \sim M/E$ (M – ionizing particle mass)**

H. Bethe, J. Ashkin (with relativistic corrections): $\beta = V/c$ (c – скорость света)

$$-(dE/dx)_{ion} = \frac{4\pi z^2 e^4 N_e}{m_o V^2} \ln \left[\frac{2m_o V^2}{I(1-\beta^2)} - \beta^2 \right]$$

Non-relativistic electron case ($E < 0.5$ MeV):

$$-(dE/dx)_{ion} = \frac{2\pi e^4 N_e}{m_o V^2} \ln \left[\frac{m_o V^2}{2I} \sqrt{\frac{e}{2}} \right]$$

Interaction of high-energy photons with matter

1. Photoelectric absorption: removal of a bound electron

$$E_e = h\nu - E_b$$

At $h\nu = 10 - 500$ keV:

Mass absorption coefficient $\tau/\rho \sim Z^3/(h\nu)^3$ (except for H and very heavy elements)
(*basic mechanism at $h\nu < 30$ keV, up to 150 keV for heavy atoms*)

2. Compton effect: non-coherent scattering at a “weakly bound” electron

$$E_e = h\nu - h\nu'$$

Mass absorption coefficient σ/ρ is **virtually independent of Z**
(*basic mechanism at $h\nu = 150$ keV – 5 MeV*)

3. Formation of electron-positron pairs

$$E_e + E_p = h\nu - 2m_0c^2.$$

Threshold energy: $h\nu \geq 2m_0c^2$ (1.02 MeV)

Mass absorption coefficient $\kappa/\rho \sim Z^2/A \sim Z$

(*basic mechanism at $h\nu > 10$ MeV, not used in radiation chemistry and technologies*)

$$\mu/\rho = \tau/\rho + \sigma/\rho + \kappa/\rho$$

In any case, the energy is mainly transferred by secondary electrons via inelastic loss mechanism

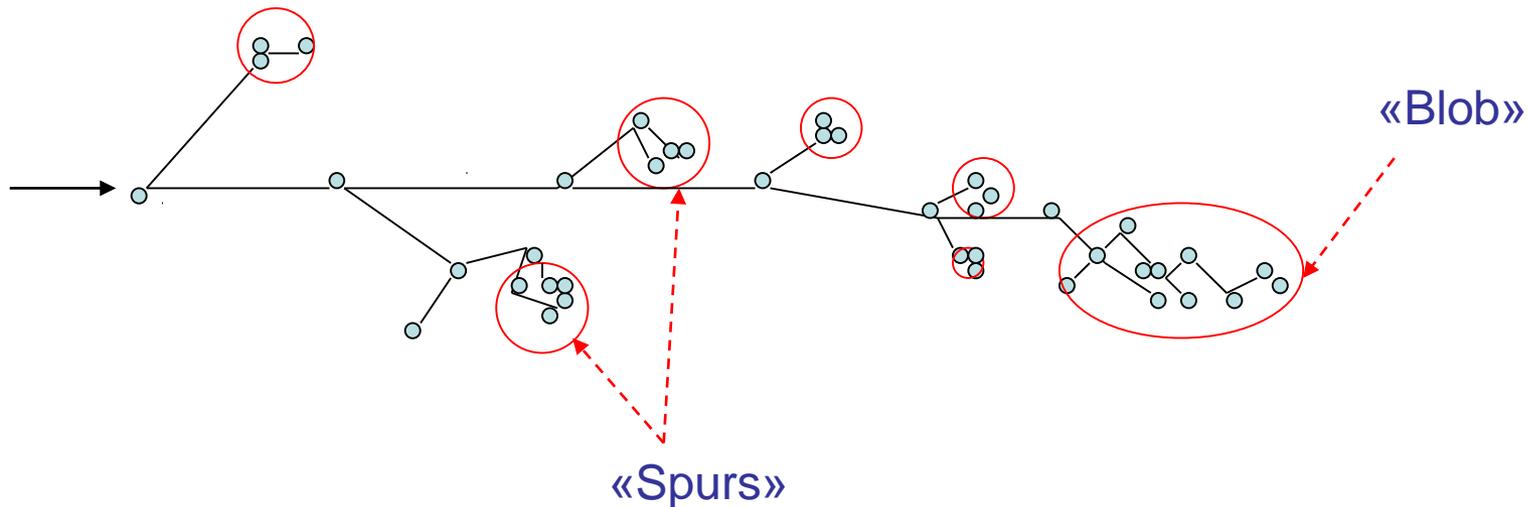
Generalization: linear energy transfer

- Linear energy transfer (LET) – energy *locally* transferred to medium per the unit of ionizing particle “track” length (for photon radiation ionizing particle means secondary electron)

$$\text{LET} = dE/dl \text{ (eV/nm} \equiv \text{keV/}\mu\text{m)}$$

- Electrons (1 MeV), γ -quanta (1.25 MeV): **LET \approx 0.2 eV/nm**
electrons (10 keV): **LET = 2.3 eV/nm**
- Protons (1 MeV): **LET \approx 27 eV/nm**
(10 MeV): **LET \approx 4.7 эВ/нм**
- Heavy multicharge ions: **LET $>$ 1000 eV/nm**

Spatial distribution of primary events at low LET: Spurs and blobs

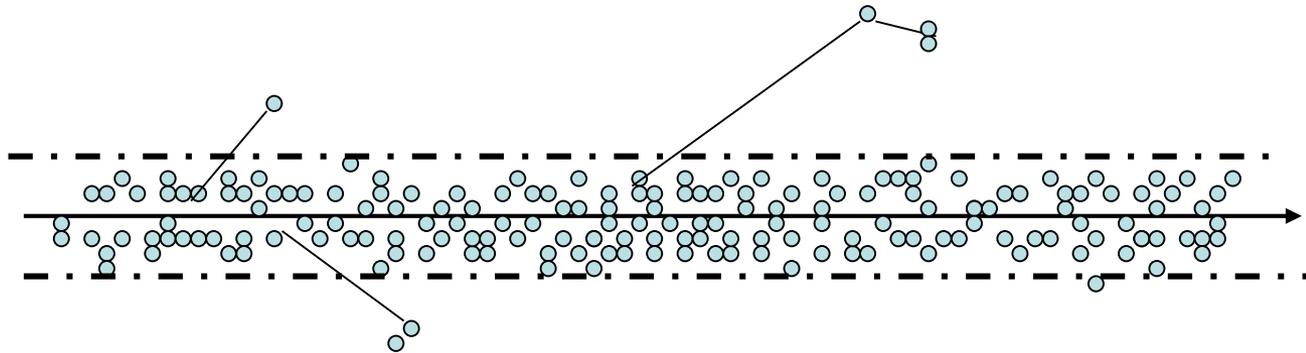


«Spurs» ($r = 1 - 5$ nm, $d(s-s) \sim 100$ nm, $N = 2 - 5$ ion pairs)
«Blobs» ($r = 5 - 20$ nm, $N = 5 - 50$)

The track of fast electron ($E \sim 1$ MeV) (LET $\sim 0,2$ эВ/нм)
the final part is shown

Spatial distribution of primary events at high LET: a dense track

Heavy particle track (**LET > 20 eV/nm**)



A dense cylindrical track (“column of spurs”) is formed along the particle path
The track diameter increases with increasing LET

In any case, $C_{loc} \gg C_{av}$ at the initial stage.

Radiation-induced nanostructures: summary

- **Ionizing radiations create (“induce”) nanostructures** of various shape and size in *any* initially homogeneous and isotropic condensed medium, independent of its chemical composition
- **The nanostructure type is determined by parameters of ionizing radiation** (in first approximation, the **LET** value)
- **The lifetime and implications** of primary nanostructures are determined by the **medium characteristics**

The timescale of radiation-induced processes: between physics and chemistry

1. “Physical stage”: ionization and excitation (fast processes)

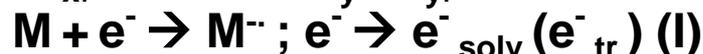


Ionizing radiation does not break directly any chemical bonds (only the electronic sub-system is involved)!

Limit: involvement of vibrational sub-system \rightarrow “start of chemistry”

$$\tau \sim 10^{-14} \text{ s (10 fs)}$$

2. “Physico-chemical stage” (inhomogeneous): reactions of primary species in unrelaxed system under the conditions of inhomogeneous spatial distribution



Limit: diffusion-induced decay of the track nanostructures

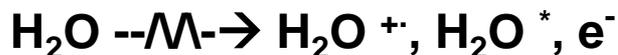
Liquids $\rightarrow \tau = 10^{-13} - 10^{-7} \text{ s (I, II)}$

Solids and polymers $\rightarrow \tau = 10^{-13} - 10^{-7} \text{ s (I)}$; up to 10^8 s (II)

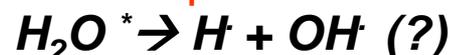
3. “Chemical” (homogeneous) stage: secondary reactions in the bulk – non-specific for radiation chemistry:



Chemistry: mechanism of water radiolysis



"Superfast" reactions (sub-picosecond time range)



"Initial" radiation-chemical yields ($\sim 10^{-12}$ s):

$$G(\text{e}_{\text{aq}}^-) \sim 4.8; G(\text{OH}\cdot) \sim 5.6; G(\text{H}\cdot) \sim 0.6$$

Reactions in "spurs" ($\tau \sim 10^{-12} - 10^{-7}$ s) :



Radiation-chemical yields after completion of the "spur" reactions ($\sim 10^{-7}$ s) :

$$G(\text{e}_{\text{aq}}^-) = 2.8; G(\text{OH}\cdot) = 2.9; G(\text{H}_2\text{O}_2) = 0.75; G(\text{H}\cdot) = 0.6; G(\text{H}_2) = 0.45$$

Additional bulk reactions ($\tau > 10^{-7}$ s):



Radiation chemistry of macromolecules: structural changes and their implications

H-links (crosslinking)

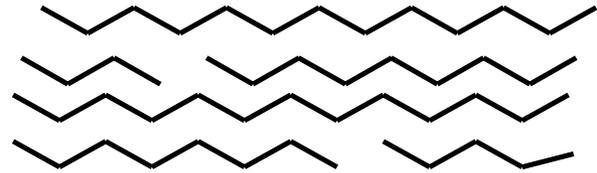


Decreasing solubility
Increasing mechanical strength
Increasing thermal stability
Formation of three-dimensional network



Y-links (grafting)

Formation of hybrid structures
Increasing hydrophilic properties
Increasing biocompatibility



Chain scission

Increasing solubility and processability
Decreasing mechanical strength

Applications of radiation chemistry: an overview

Radiation-chemical technologies (clean, controllable and efficient)

- Radiation treatment of waste water and fuel gases
- **Radiation modification of polymers**
- **Fabrication of nanostructures and nanomaterials**

Related radiation processing:

- Sterilization
- Conservation of cultural heritage, etc.

Prediction and minimization of radiation damage

- Nuclear technologies
- Space technologies

General principles: efficiency and selectivity

- $M \xrightarrow{-W} P_1, P_2, \dots, P_n$
- (P_1 – target product, P_i – other products)

Efficiency : **high $G(P_1)$ values**

Selectivity: **$G(P_1) \gg G(P_i)$ ($i \neq 1$)** (also may have spatial meaning for polymers - localization)

$G = 1 - 10$ molec./100 eV ($10^{-7} - 10^{-6}$ mole/J) – for non-chain reactions

$G > 10$ (often $\gg 10$ molec./ 100 eV) – *only for chain reactions* initiated by radiation

The proportion of “modified” molecules (converted to a product) at $G = 5$ и $D = 100$

Low-molecular compounds ($M \sim 100$) ~ 0.5%

Polymers ($M \sim 10^5$) ~ 50%

Resume: the most promising technologies are based on the modification of polymers or chain processes

Radiation modification of polymers: commercial- scale processes

Cross-linking and polymerization/cross-linking based technologies

- **Radiation modification of cable insulation** (mandatory for demanding applications in the USA)
- **Radiation curing and rubber vulcanization** (>90% of tires in Japan are made with radiation processing)
- **Production of thermostable pipes** (more than 80 mln m/ per year in Germany)
- **Production of thermo-shrinkable materials** (worldwide)
- **Production of foam plastics**
- **Hydrogels for medical applications (wound dressing, etc.)**

Grafting based technologies

- Hydrophilic and biocompatible materials
- Battery separator membranes

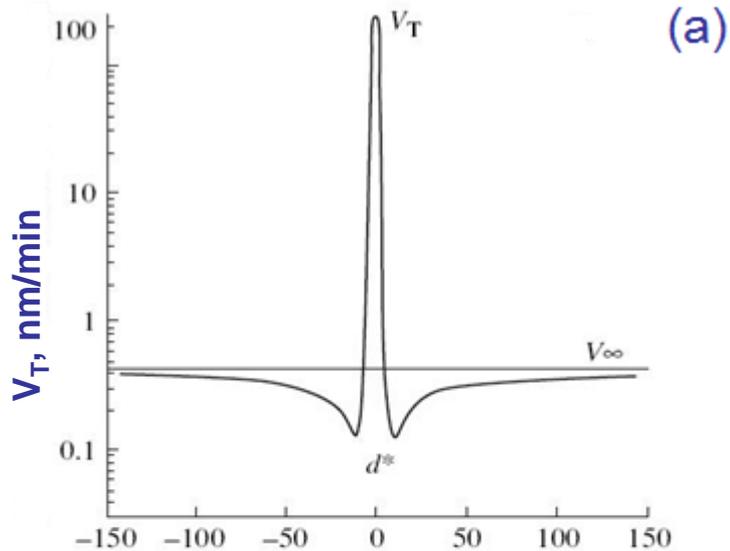
Scission-based technologies

- PTFE recycling

Fabrication of nanostructures and nanomaterials

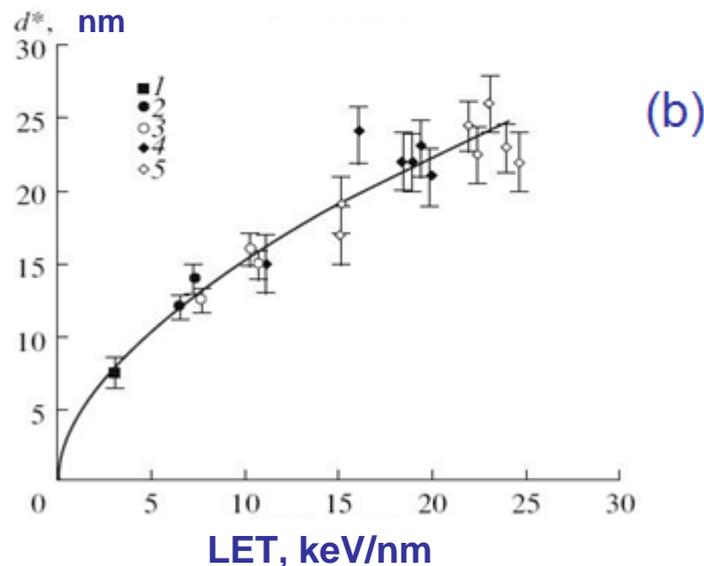
- Primary radiation nanotechnologies: development of the radiation-induced nanostructures (“track” technologies)
- Secondary radiation nanotechnologies: assembling of nanostructures from atoms, radicals and ions (“building blocks” created by radiation)

Development of track nanostructures in polymers



- (a) Local rate of chemical etching as a function of distance from the track axis in a PETP film (a)
- (b) LET effect on the characteristic track diameter (the boundary corresponds to minimum solubility)

- $d^* \sim (\text{LET})^{0.5}$

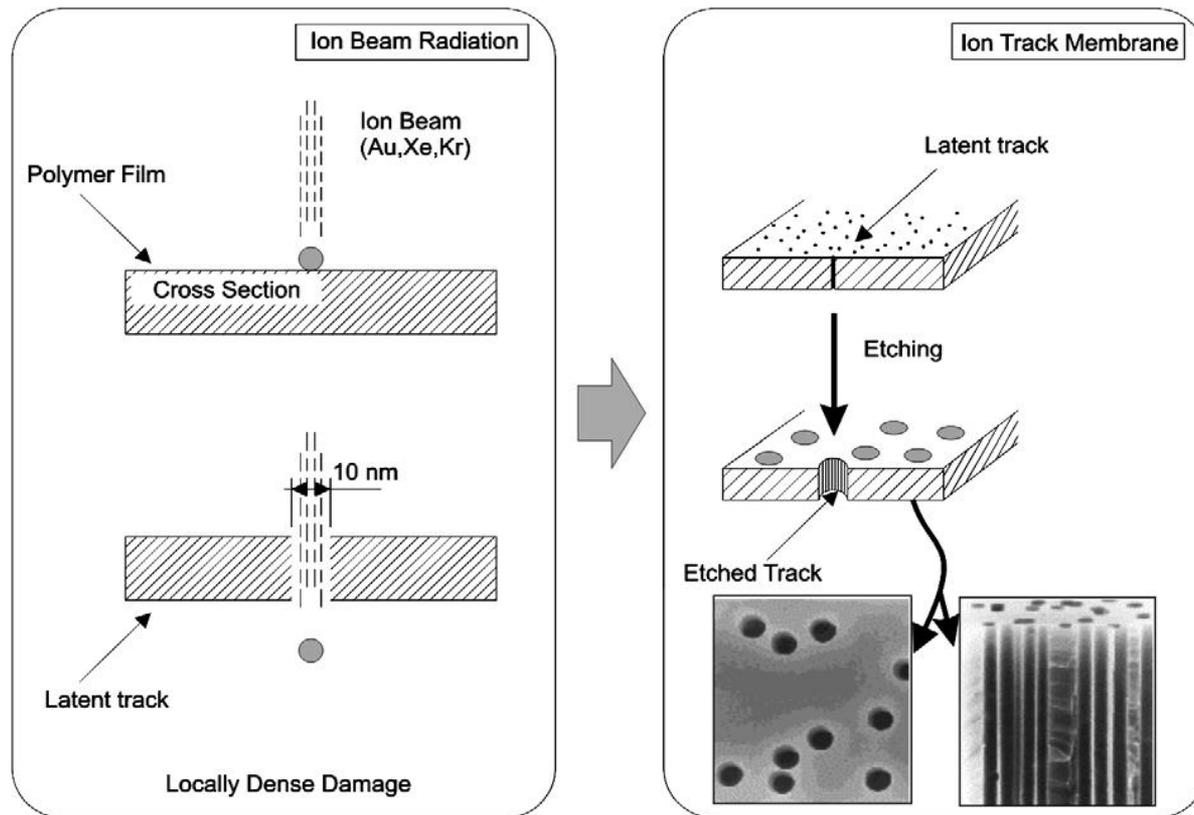


Taken from:

P.Yu. Apel et al., *Nucl. Instr. Meth. Phys. Res. B.*, 1998, **146**, 468;

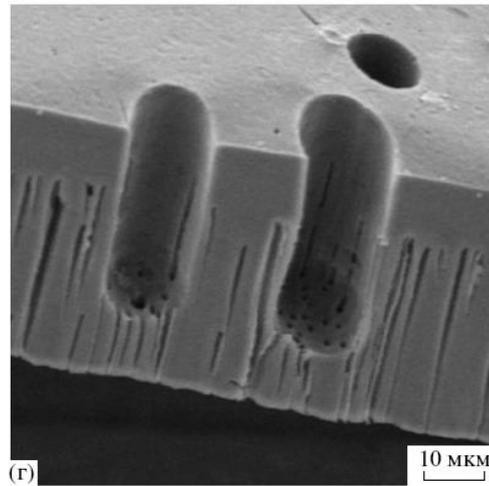
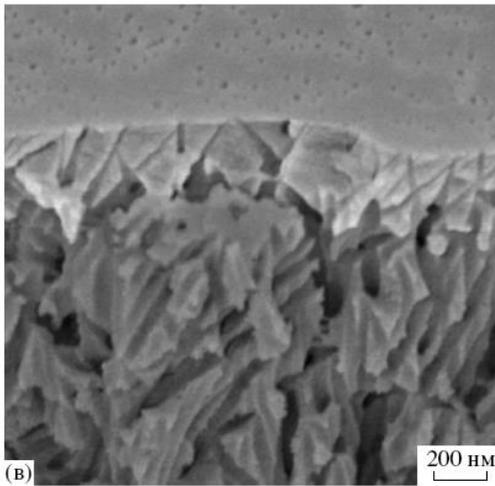
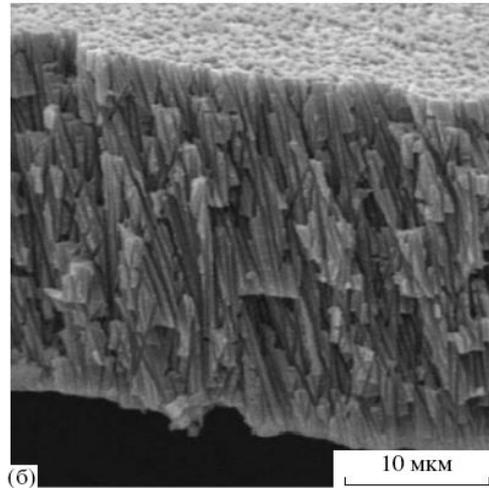
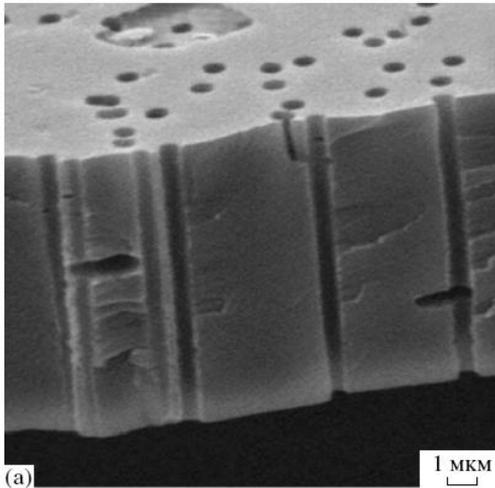
P.Yu. Apel et al., *Radiat. Meas.*, 1999, **31**, 51

Production of track membranes: basic scheme



- from A.G. Chmielewski et al., *Nucl. Instr. Meth. Phys. Res. B*, 2007, **265**, 339).

Track membranes: variety of structures



The pore diameter: 10 nm – 10 μ .

Control tools:

- physical (adjusting the LET value and beam intensity)
- chemical (adjusting etching regime, preliminary UV treatment)

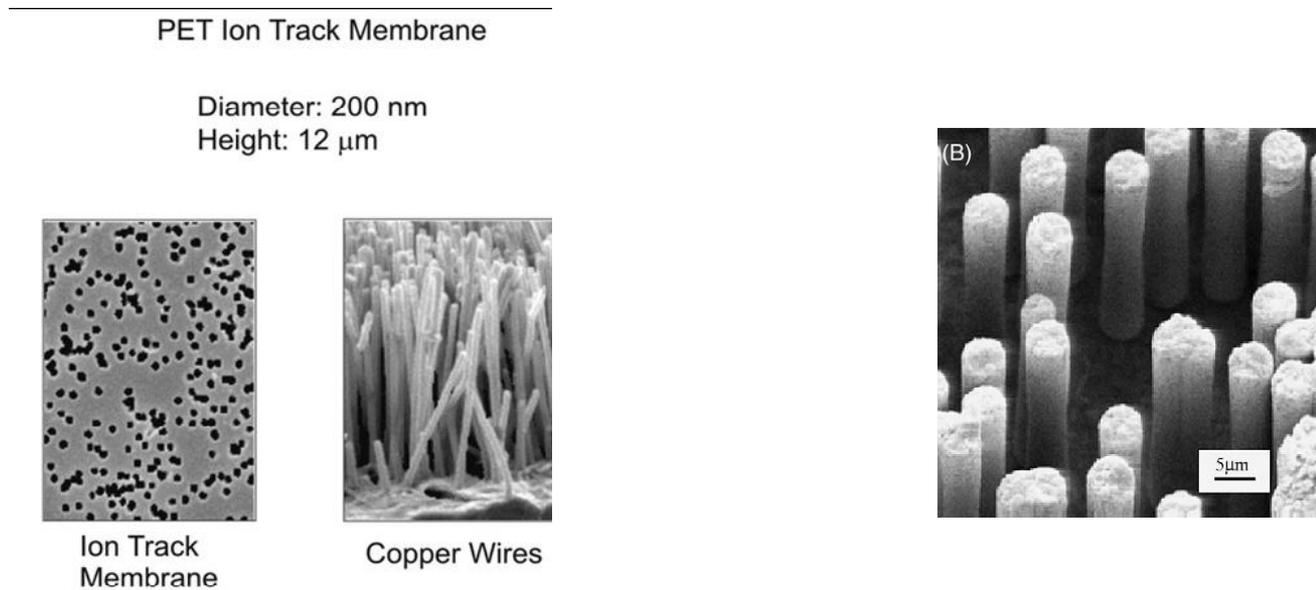
- **Taken from**

P.Yu. Apel et al., *Nucl. Instr. Meth Phys. Res. B*, 2003, **209**,329; *ibid*, 2003, **208**, 11]

Applications: hemodialysis, ultrafiltration, analytical applications, etc.

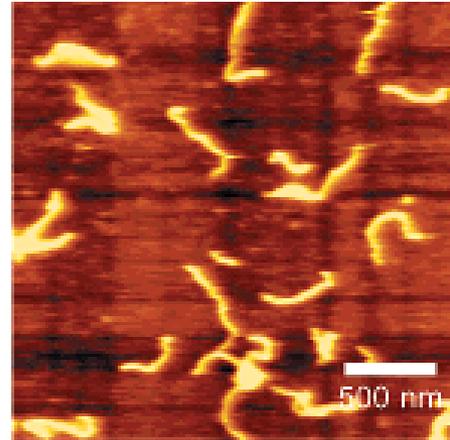
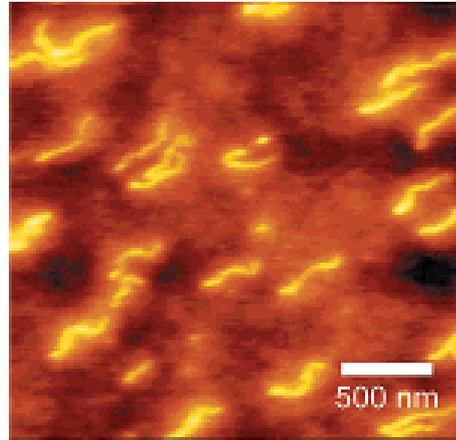
Modification and functionalization of track membranes

- Templates for nanowires
- Precursors for functional membranes
- Fabrication of smart materials



Copper nano- and micro-wires formed within the track membrane pores (taken from:
A.G. Chmielewski et al., *Nucl. Instr. Meth. Phys. Res. B*, 2007, **265**, 339;
P.Yu. Apel et al., *Nucl. Instr. Meth Phys. Res. B*, 2003, **208**, 11)

Nanowires from carbosilanes

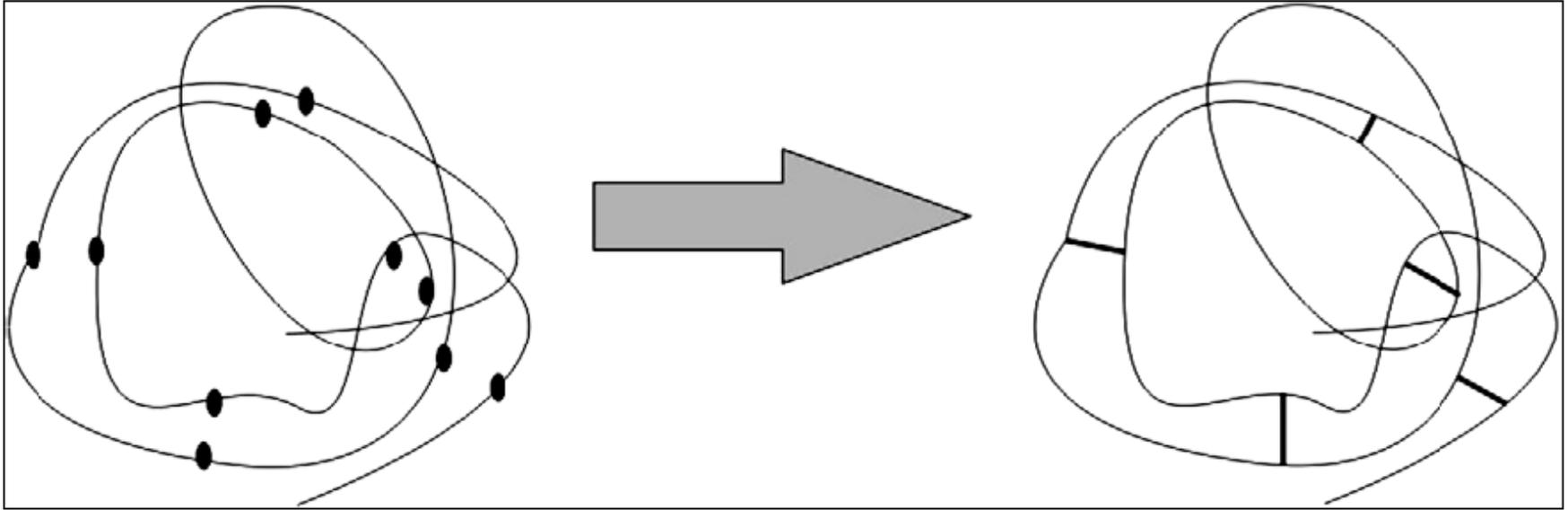


- AFM images of carbon-silicon wires obtained by superdense cross-linking of polycarbosilane and poly(vinyl silane) – polycarbosilane mixture at the boundary of a $^{129}\text{Xe}^{23+}$ track. The non-crosslinked polymers were dissolved after irradiation

- $d = f(\text{LET})$

- (from S.Tsukuda et al., *J. Phys. Chem. B*, 2004, **108**, 3407)

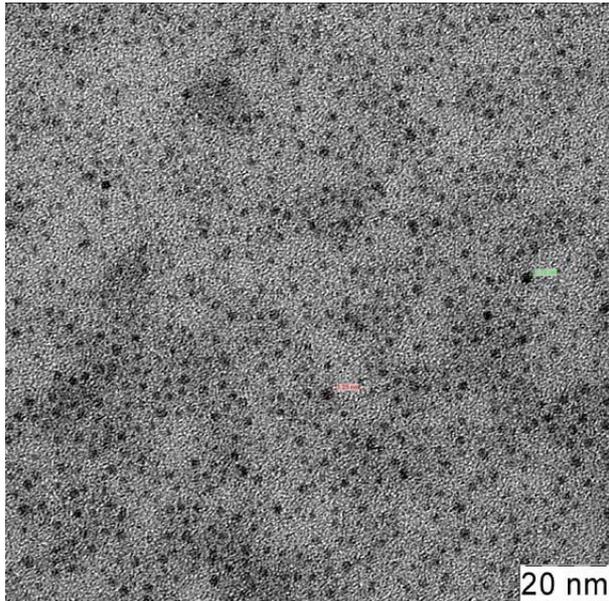
Secondary nanostructures: from microgels to nanogels



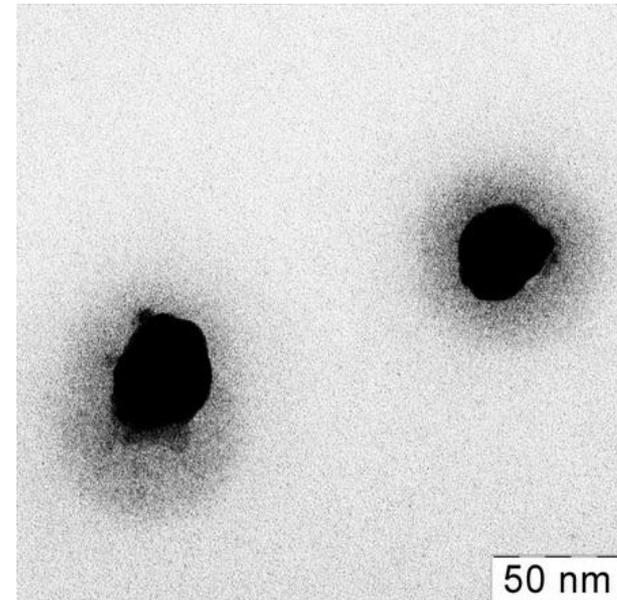
Formation of nanogels under pulsed irradiation: selective intramolecular recombination of radicals in dilute macromolecular solutions (from A.G. Chmielewski et al., *Nucl. Instr. Meth. Phys. Res. B*, 2007, **265**, 339)

Applications: controlled drug release systems, sorbents, smart materials

Secondary nanostructures: radiation-chemical synthesis of metal-polymer nanocomposites

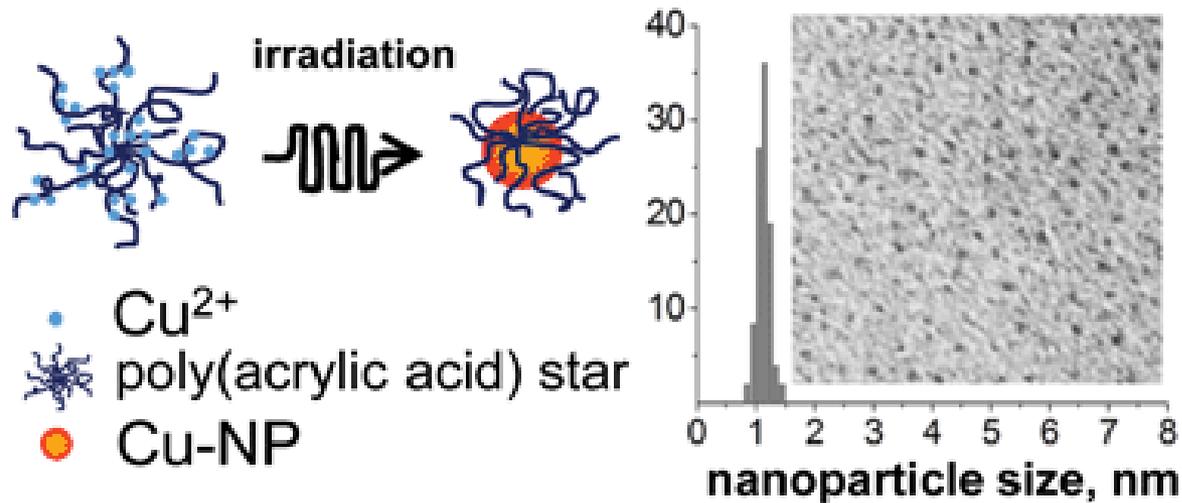


Copper nanoparticles produced by γ -radiation-induced ion reduction in swollen interpolyelectrolyte films (A.A. Zezin et al., *Nucl. Instr. Meth. Phys. Res. B*, 2007, **265, 334)**



“Clouded” silver nanoparticles produced by X-ray-induced ion reduction in swollen interpolyelectrolyte films (V.I. Feldman et al., *J. Phys. Chem. C.*, 2013, **117, 7286)**

A single molecule nanotechnology in solutions: copper nanoparticles from star-shape ion container



Taken from: A.A. Zezin, V.I.. Feldman et al., *Phys. Chem. Chem. Phys.*, 2015, **17**, 11490

Conclusions and outlook

- High-energy chemistry is an alternative way of initiating chemical processes
- - reagent free (ideally)
- - selective and controllable
- - no need for high temperatures
- - intrinsically producing nanostructures of different types

A basis for new cost-efficient and environment friendly technologies

- Prospective areas
- - new technologies for biomedical applications, membranes and smart materials
- - creation of advanced hybrid-type composite materials
- - nanolithography

! It is a scalpel rather than bludgeon, but we still need to learn more, how does it work...