



# Concepts and definitions

- Radiation chemistry: the effect of radiation (usually ionising) on chemical compounds
- Hot-atom-chemistry: the effect of radioactive transformations or nuclear reactions on chemical compounds

## Books:

Spinks and Woods: An introduction to radiation chemistry (1991)

Farhataziz and Rodgers: Radiation Chemistry (1987)



# Concepts and definitions

- Average energy for formation of an ion pair ( $W$ ) (not the same as ionisation energy)
- G-value ( $G(X)$ ) -“radiation chemical yield”
  - ▶  $G(X)$  is a measurement of the probability of formation of the product  $X$  in a given radiation chemical reaction
  - ▶  $G(X)$  number of units of  $X$  formed per. 100 eV absorbed radiation energy
  - ▶  $G(-Y)$  number of units of irradiated compound converted per 100 eV radiation energy
  - ▶  $G = (M/N)(100/W)$ 
    - $M$  - number of species formed
    - $N$  - number of original species consumed
    - $W$  - number of eV per ion- or radical pair
- $1 < G < 5$  Simple reactions
- $10 < G < 25$  High values
- $G \sim 10^5$  Extreme values (catalytic effects)



# Radiation chemistry in gases

Gas	H <sub>2</sub>	He	Xe	NH <sub>3</sub>	CH <sub>4</sub>	Air
Ionisation energy (eV)	15.6	24.5	12.1	10.8		
Energy loss pr.ion pair(eV) 5.3 MeV $\alpha$	36.5	43	22	39	29	35
Energy loss pr.ion pair 3-20 keV e <sup>-</sup>	36.3	42	22		27	34
Fraction to ionisation	.43	.58	.55	.28		

Average values for the ion pair energies

Only a part of the energy needed goes to the ionisation itself. The rest goes to thermal transfer and excitation

# “Spurs, blobs and short-tracks”

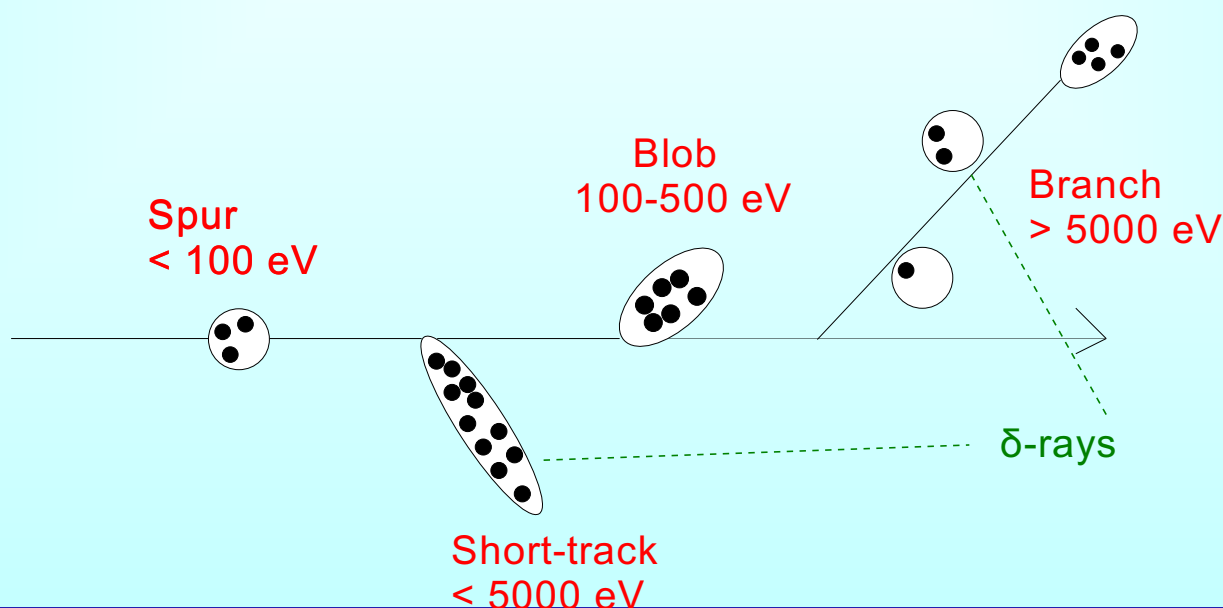
The number of ion pairs formed within a local region is important.

A high number of ion pairs gives a considerably increased possibility for recombination and formation of particular excited states.

Spur:  $< 100$  eV deposited

Blob:  $100 - \sim 500$  eV deposited

Short-track:  $> \sim 500$  eV deposited





# “Spurs, blobs and short-tracks”

In the discussion of the interaction of radiation with matter (Bethe-Bloch) we have used the so-called CSDA - i.e. the continuous slowing down approximation.

This approach does not consider the “fine structure” in the medium slowing down the radiation, nor that biologic material is in effect single molecules

In reality, the interaction is not a continuous process, but a sequence of single events (“spurs”). Each spur gives 2-3 ion pairs which are initially isolated from each other.



## “Spurs, blobs and short- tracks”

For low-LET particles each spur develops by itself and initially independent of what happens elsewhere in the matrix

At high-LET radiation and towards the end of each track for low-LET radiation, a large number of spurs will overlap and give a continuous picture -“short-tracks”.

Low energy electrons give rise to “blobs”.

In some cases, single interactions can give large transfer of energy to one single electron, so-called  $\delta$ -rays, a name originating from a classical scientific misunderstanding.



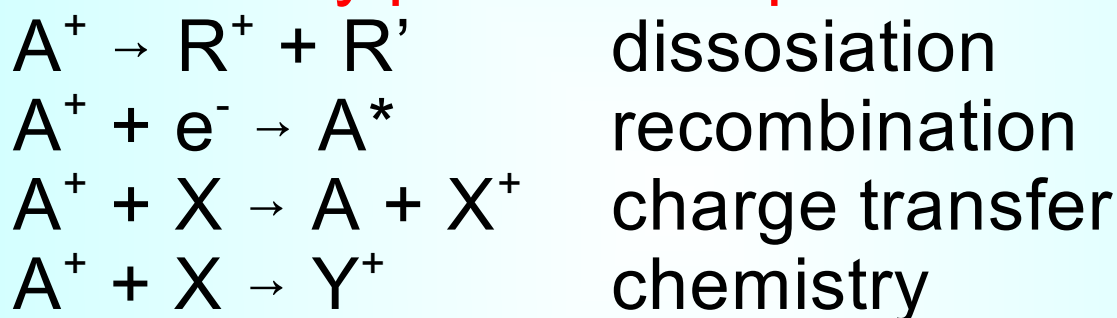
## Radiation chemical reactions

Primary processes:  $(10^{-17} - 10^{-16} \text{ s})$

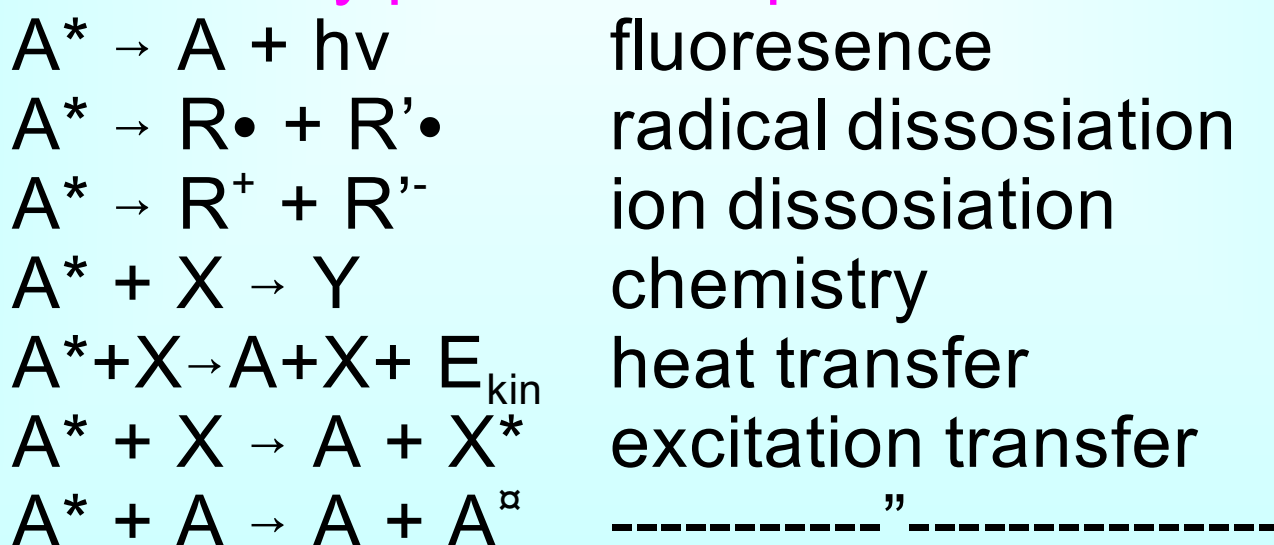


( $\rightsquigarrow$  = ionising radiation)

### Sekundary processes: post-ionisation



### Secondary processes: post-excitation



( $\alpha <^*$ )

Secondary processes:  $10^{-10} - 10^{-7} \text{ s}$



# Radiation chemistry in water

Primary processes:  $(10^{-17} - 10^{-16} \text{ s})$

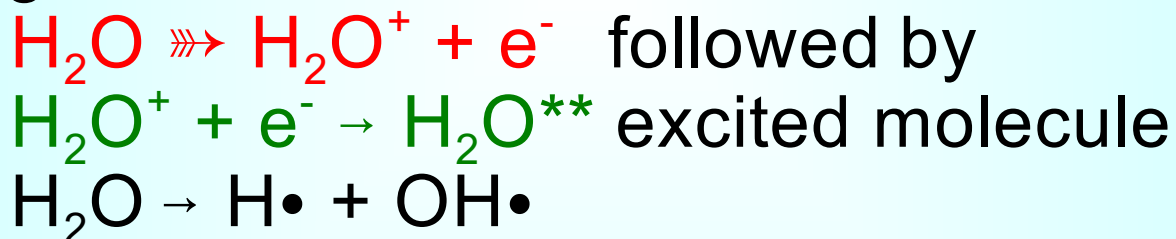


( $\rightsquigarrow$  = ionising radiation)

Originally: two models.

Samuel-Magee:

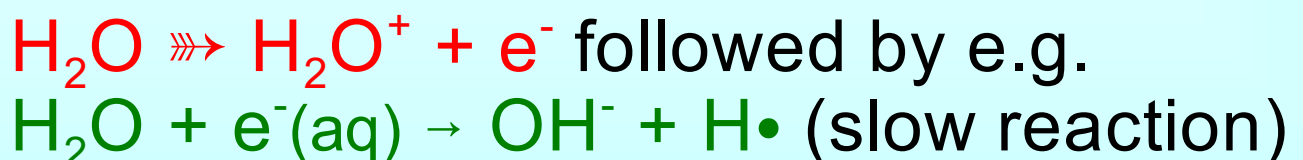
High recombination:



Electrons must have short range

Lea-Gray-Platzman

Formation of “solvatised electron”



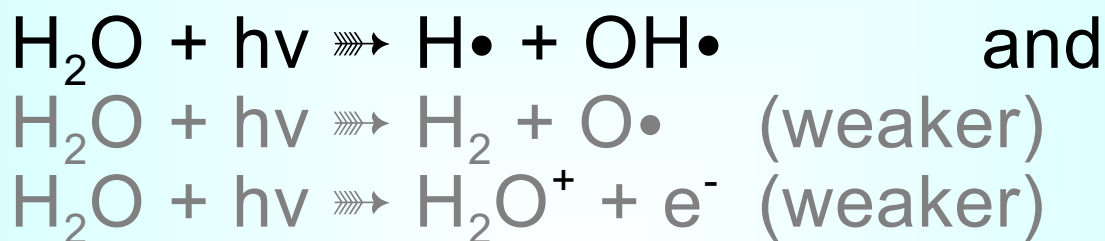
Electrons must have longer range





## Radiation chemistry of water

Radiation chemistry developed largely from the experiences in water vapour, where one has the primary processes:



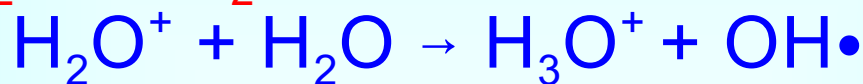
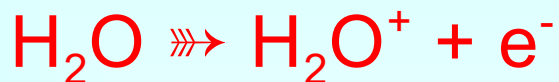
It is also possible to excite the water molecule and the product into different quantum states with different probability, depending on the wavelength of the electromagnetic radiation.

The conditions in water vapour will of course be quite different from a liquid.



# Radiation chemistry of water

Main reactions:



The species  $\text{H}_2\text{O}^+$  is very reactive and disappears instantaneously from the system, i.e. within  $10^{-17}$  -  $10^{-16}$  s.

In liquid form, all thermal species are hydrated within  $10^{-11}$  s, excitation energy is more rapidly transferred than in gases, and diffusion is much slower than in gases.

Species formed close to each other, will have a large probability to influence each other.



## Further important species

$e^-(aq)$  - the solvatised electron - a well defined and well characterised “chemical compound”, with its own reactions

$H\bullet$  - hydrogen radical

$OH\bullet$  - hydroxyl radical

$H_2O_2$  - hydrogen peroxide  
formed in several ways

$HO_2^-$  - hydroperoxide ion  
corresponding base

$O_2^{2-}$  - peroxide ion  
corresponding base

$O_2^-$  - superoxide ion  
formation:  $e^-(aq) + O_2 \rightarrow O_2^-$

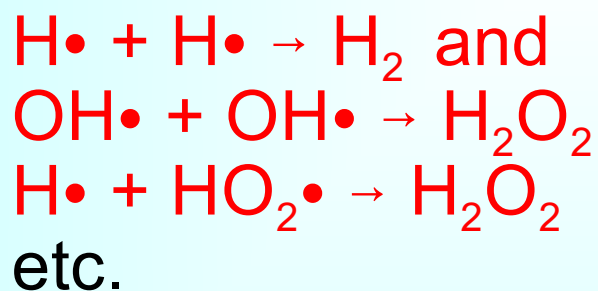
$HO_2\bullet$  - hydroperoxyl radical  
corresponding acid  
formation:  $H\bullet + O_2 \rightarrow HO_2\bullet$   
or:  $O_2^- + H^+ \rightarrow HO_2\bullet$



## Further important species

When solutions are irradiated,  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  are formed, often close to the ratio 2:1. Other gases may also be formed, depending upon the chemical content of the sample

Neutral, non-radical radiation chemical species are assumed to form in radical/radical reactions, e.g.



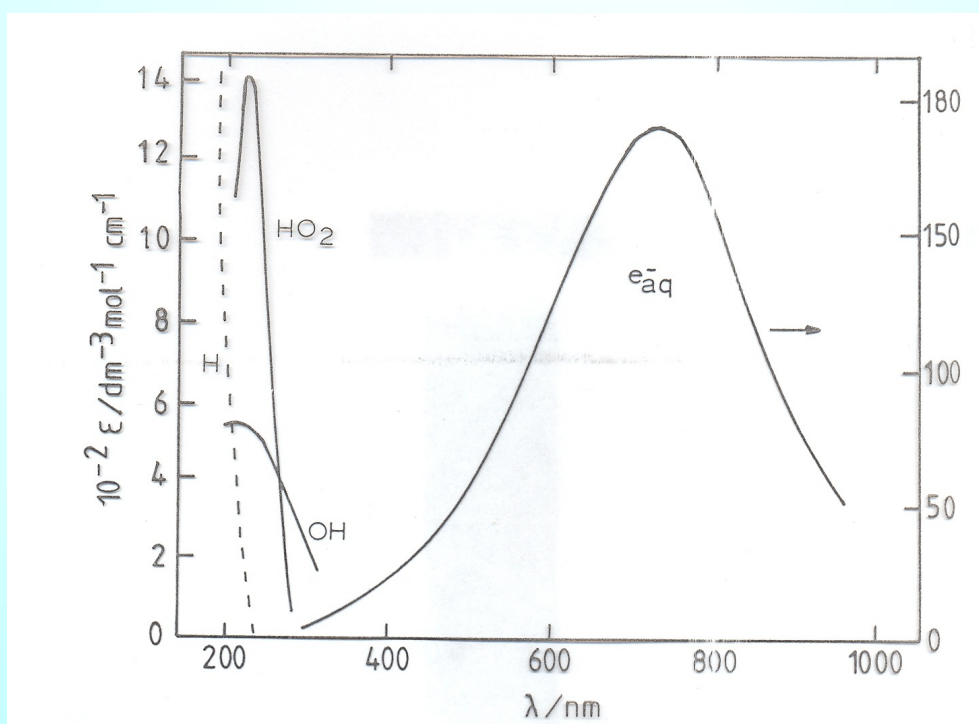
Molecular species are most easily formed where the radical concentration is highest, in “short-tracks “ and “blobs”.



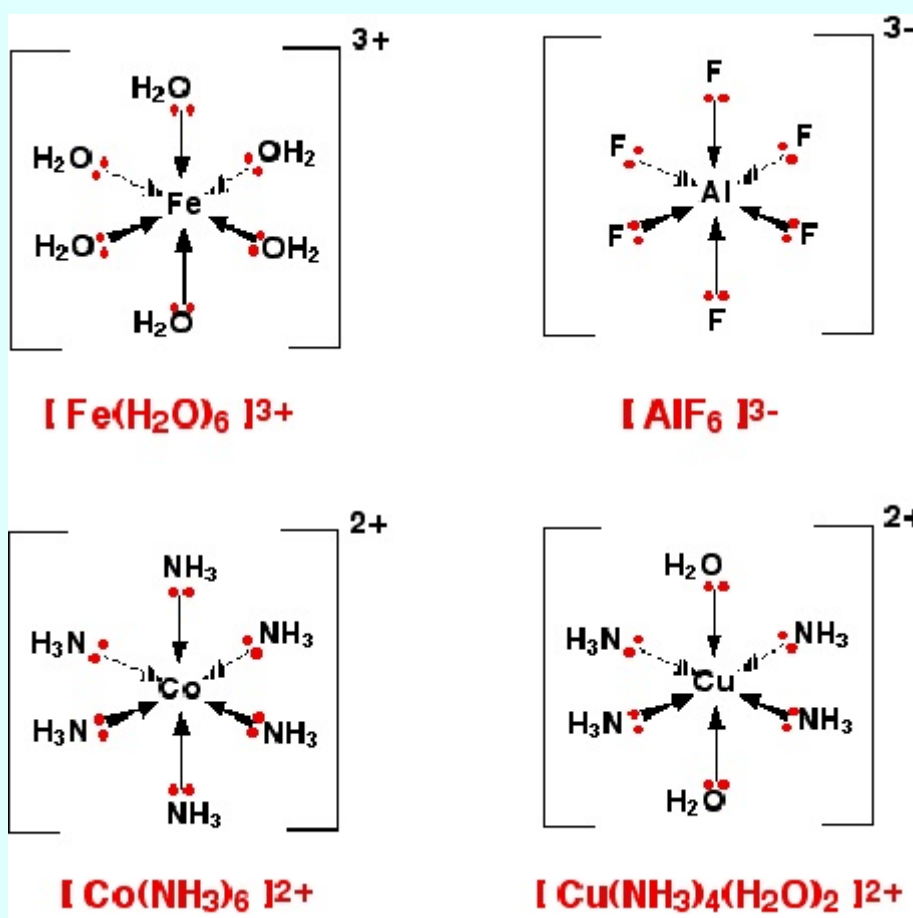
# The solvatised electron, $e^-_{aq}$

The presence of solvatised electrons in solutions was proposed due to relationships found between reaction rates and PH or ion strength which could not be explained by acid/base considerations.

The solvatised electron has a characteristic absorption spectrum.



## Metal ions in different conditions



Metal ions in solution are shown for comparison to the solvatised electron.  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  (aq) is normally just called  $\text{Fe}^{3+}$  (aq), but this is a simplification.



# The solvatised electron, $e^-(aq)$

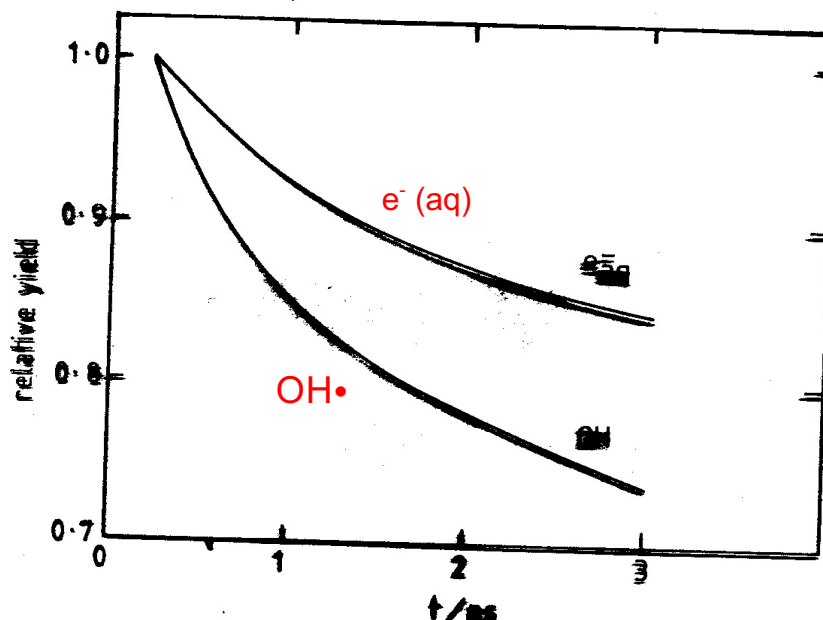


Figure 10-3. Decay of  $e_{aq}^-$  and OH produced by a 30-ps pulse of 20-MeV electrons in water. (Reproduced with permission.<sup>39</sup>)

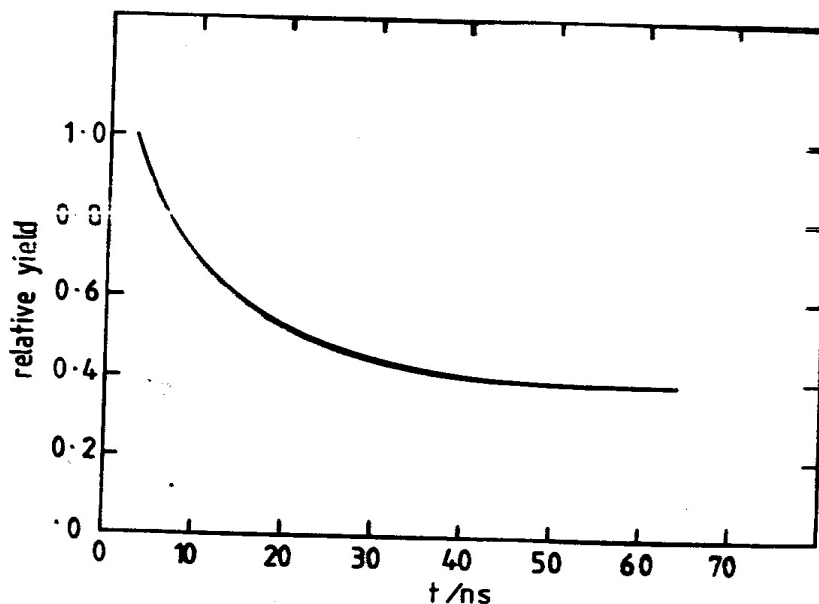


Figure 10-4. Decay of  $e_{aq}^-$  produced by a 1-ns pulse of 3-MeV protons in water. (Reproduced with permission.<sup>39</sup>)



## The solvatised electron, $e^-(aq)$

Table 10-1. Spur Reactions in Water	
Reactions	$10^{-10} k/M^{-1} s^{-1}$
(10-1) $e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	0.54
(10-2) $e_{aq}^- + \cdot OH \rightarrow OH^-$	3.0
(10-3) $e_{aq}^- + H_3O^+ \rightarrow \cdot H + H_2O$	2.3
(10-4) $e_{aq}^- + \cdot H \rightarrow H_2 + OH^-$	2.5
(10-5) $\cdot H + \cdot H \rightarrow H_2$	1.3
(10-6) $\cdot OH + \cdot OH \rightarrow H_2O_2$	0.53
(10-7) $\cdot OH + \cdot H \rightarrow H_2O$	3.2
(10-8) $H_3O^+ + OH^- \rightarrow 2 H_2O$	14.3

Some typical chemical reactions of the solvatised electron





## Two main mechanisms

We concentrate in this course the attention to radiation chemistry in:

- 1) Water
- 2) Biologically interesting molecules in aqueous medium.

Radiation chemical reactions can be classified as **direct** or **indirect**

At **indirect reactions**, ionisations and excitations from primary radiations leads to formation of radicals and reactive chemical species in a solvent (water). These will in turn react with the biologic material.

By **direct reactions**, the primary radiation destroys the biologic material itself, the intermediate stadium (radicals) is insignificant or non-existent.



## Two main mechanisms (ctd.)

**Direct reactions** dominate by irradiation with **high LET** radiation, and the domination is complete at values e.g. LET  $\sim 100$  keV/ $\mu\text{m}$  (typical value for an  $\alpha$ -particle of 5 MeV)

**Indirect reactions** dominate by irradiation with **low-LET** radiation, and the domination is complete at values e.g. LET  $\sim 0.2$  keV/ $\mu\text{m}$  (typical value for a  $\beta$ -particle of 1 MeV)

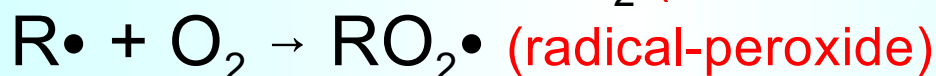
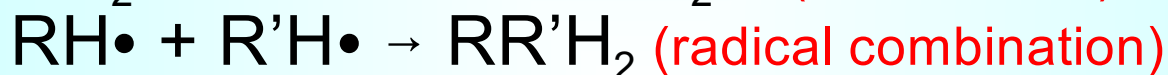
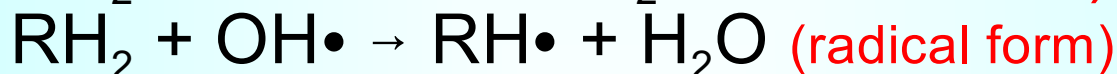
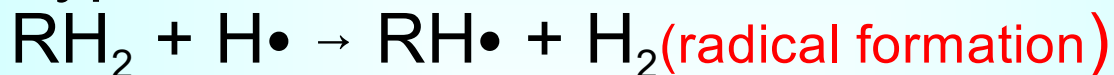
For direct mechanism, the chemical conditions are not important. By indirect mechanism, chemistry is very important.



## Radical reactions

Radicals formed by irradiation of water in biologic material may react further chemically with more complex biologic molecules:

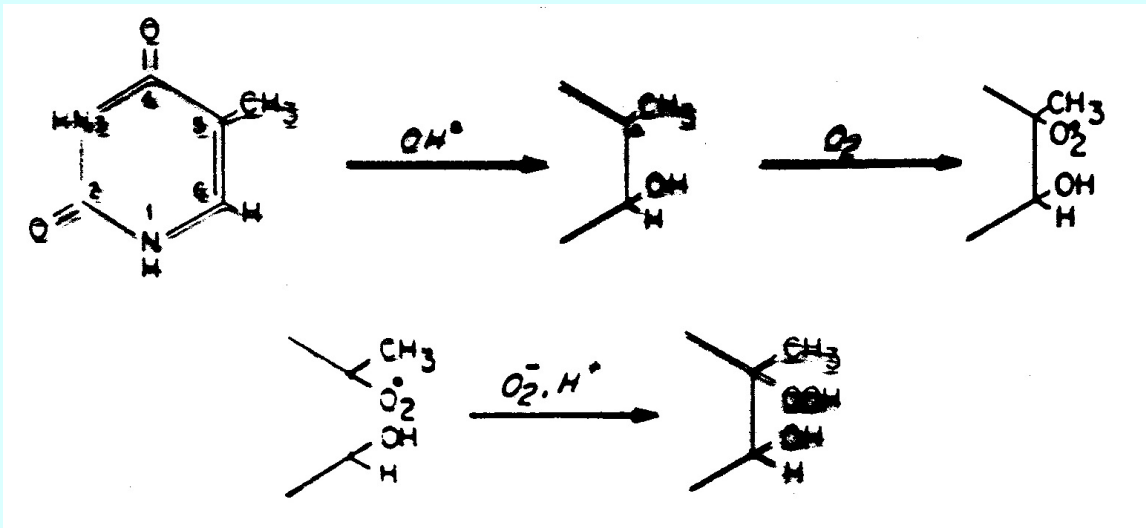
Typical reactions:



+ others

The presence of oxygen is in order to form peroxides and hydroperoxides, which are very cellularly toxic, and for formation of  $\text{HO}_2\cdot$ . **Oxygen increases the degree of radiation damage and functions thus a “radiosensitizer”**

# Radical reactions



A radiation chemical mechanism suggested for thymine (one of the DNA bases)



# Radiosensitizers

**Radiosensitizers:** compounds increasing the effect of ionising radiation on biologic material.

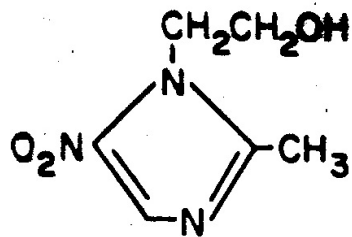
Already mentioned:  $O_2$

Others:

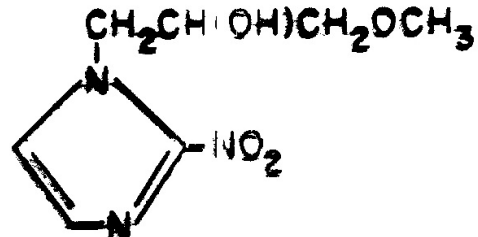
Halogenated pyrimidines:  
Can replace “correct” building-blocks in the DNA synthesis and weaken the DNA when incorporated

Nitroimidazoles  
Replace oxygen in radical mechanisms by irradiation. These compounds metabolise much slower than oxygen and are therefore able to penetrate better into hypoxic tissue.

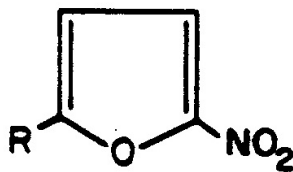
# Radiosensitizers



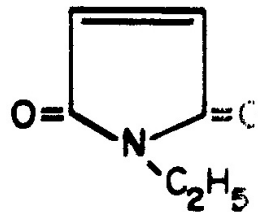
METRONIDAZOLE



MISONIDAZOLE



NITROFURAN



N-ETHYLMALIMIDE

Basic structures for some important radiosensitizers



# Radioprotectors

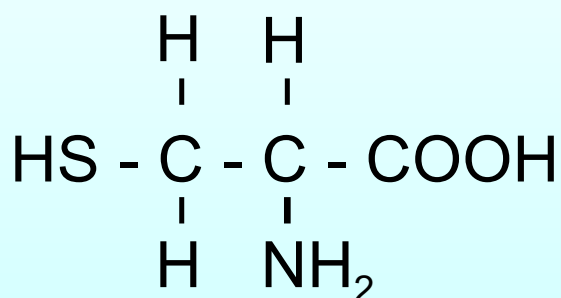
**Radioprotectors:** Compounds decreasing the effect of ionising radiation on biologic material.

General:

Radioprotectors contain thiol-groups (-SH)

The effect of radioprotectors is to function as radical scavengers, i.e. to react with radicals before they can react with vital molecules.

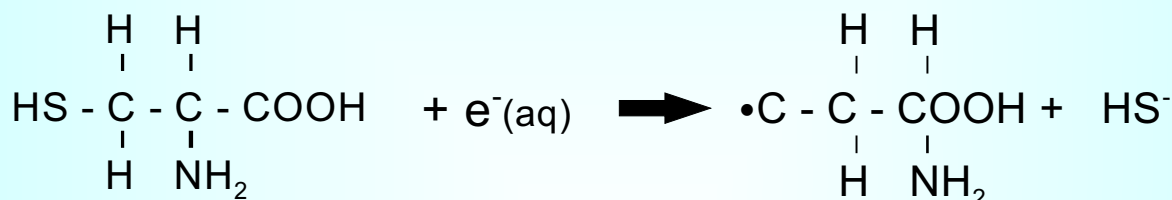
Ex. Cystein:



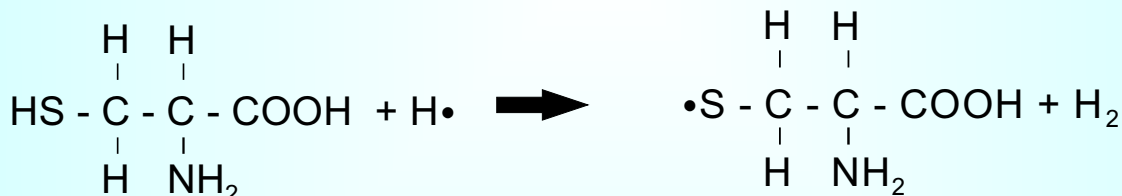


## Radioprotectors

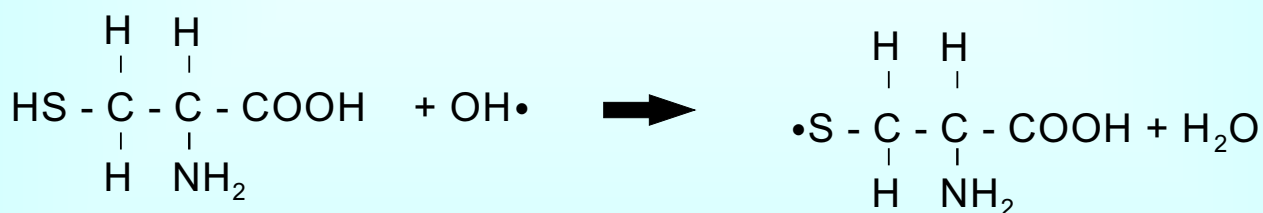
Compounds containing SH-groups can react with different radicals in many ways, e.g.



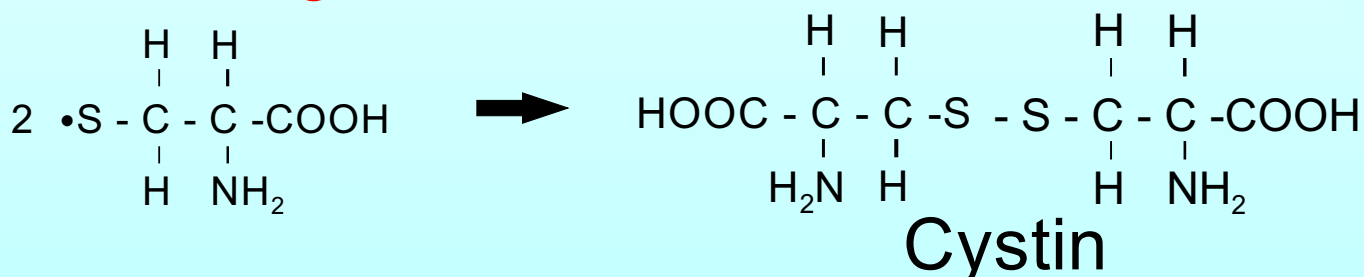
or



or



two can give







# Radiation chemistry and biology

Radiation chemistry has important consequences on radiation biology, radiation biophysics, medical physics, radiology, clinical radio-oncology etc.

The effect on more or less complex systems (from humans to cells in culture) depend not only on the radiation dose, but also on parameters e.g:

**Doserate**

**Repetition frequency**

**Oxygenation - hypoxia**

**LET-value.**

**Cell phase and radiation sensitivity**

All this determines the general radiation chemical status of the system

(Much) more details, see  
C. von Sonntag: "The chemical basis of radiation biology"



# Hot-atom chemistry

Chemical effects of nuclear reactions or nuclear transformations.

- **Recoil effects**

- ▶ Breaking of chemical bond by incoming projectile
- ▶ Breaking of chemical bond by recoil due to emission of outgoing particle (Szilard Chalmers)
- ▶ Breaking of chemical bond due to recoil from emission of  $\alpha$ -particle

- **Shake-off effects**

- ▶ Removal of inner shell electrons due to electron capture, followed by the emission of outer shell electrons
- ▶ Removal of inner shell electrons due to conversion electron emission

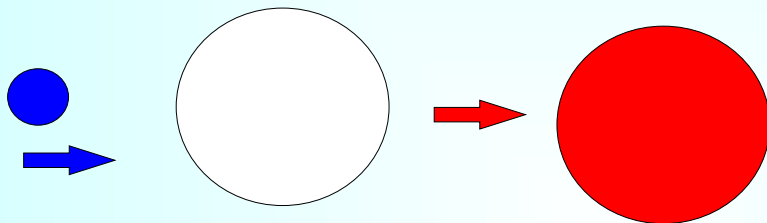
- **Re-modulation effects**

- ▶ In case of insufficient recoil energy or absence of shake-off, the remaining atom may be left in a “weird” and reactive chemical state.



# Szilard-Chalmers reaction

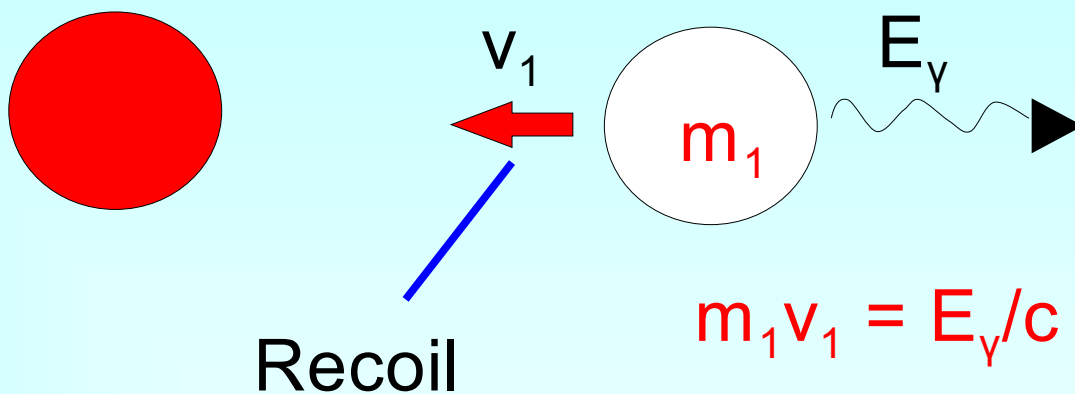
When a thermal neutron is captured in a target nucleus, only thermal energies are involved, far from sufficient to cause chemical changes:



But when a  $\gamma$ -ray is emitted from the slow-moving compound nucleus, chemical changes may occur. This effect (Szilard-Chalmers-effect) can cause persistent chemical changes



# Szilard-Chalmers reaction



The recoil to the nucleus provided at the emission of the photon may break a chemical bond, provided that the energy is high enough (which is normally the case).



# Szilard-Chalmers

$$m_1 v_1 = E_\gamma / c$$

$$m_1^2 v_1^2 = E_\gamma^2 / c^2 \quad \frac{1}{2} m_1 v_1^2 = \frac{1}{2} E_\gamma^2 / (m_1 c^2)$$

$$E_r = \frac{1}{2} E_\gamma^2 / (M m_{\text{nucleon}} c^2) \approx \frac{1}{2} E_\gamma^2 / (A m_{\text{nucleon}} c^2)$$

$$E_r \approx \frac{1}{2} E_\gamma^2 / (A m_{\text{nucleon}} c^2) \approx \frac{1}{2} E_\gamma^2 / 931.5 \text{ MeV}(A)$$

If all energies are in MeV:

$$E_r \approx 0.000537 E_\gamma^2 / A$$

Normally, this is enough to break every chemical bond available, and the radioactive isotopes end up in a different chemical state.