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# A Concise Introduction on Radiation Chemistry

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## 1. Introduction

The Laboratory of Chemical and Physico-Chemical Analysis of Drugs (Unité CHAM, Ecole de Pharmacie, UCL), under the supervision of Professor Bernard Tilquin, has dedicated over ten years of research to the study of the radiolysis of drugs; starting with the development of analytical techniques to detect ionized drugs, evolving to the study of radiolytic products formed and finally to establishing the different mechanisms governing the drug stability. Many recent theses of this laboratory studied the radiation chemical effects on drugs in aqueous solutions. The radiolysis of a drug in aqueous solution results from the *indirect effect* of the ionizing radiation; that is via the solvent radiolysis, which forms reactive species. In this case the solvent is water and therefore, a comprehensive introduction on the radiolysis of water is presented here.

## 2. A Few Definitions in Radiation Chemistry

### 2.1. Radiation Chemistry

*Radiation Chemistry* is defined as the study of chemical effects induced by high energy ionizing radiations, such as X-rays, gamma rays, electrons, protons, deuterons,  $\alpha$ -particles and neutrons.

### 2.2. Radiolysis or radiation-chemical change

*Radiolysis* or *radiation-chemical* change is the chemical transformation brought about in the irradiated material by the absorption of the ionizing radiation energy. It thus relies on the interaction of energy with matter, as do photolysis and electrolysis. The chemical transformations are produced by a variety of reactive species such as ions, excited molecules and free radicals, and therefore depend on the chemical composition of the medium. However, the primary interaction between the incident radiation and the molecules is highly similar whether the medium is water, dilute or more concentrated aqueous solutions or more complex media such as biological matter.

### 2.3. Absorbed Dose

Radiolytic processes are often described as a function of the energy absorbed by the irradiated material. The *Absorbed Dose* (A) is the amount of energy absorbed from the ionizing radiation per unit mass of sample. The S.I. unit is the Gray (Gy), which corresponds to the absorption of one joule per kg of irradiated material. Other units conventionally used are the rad and eV g<sup>-1</sup> (1 Gy = 100 rad and 1 Gy = 6.24 x 10<sup>15</sup> eV g<sup>-1</sup>).

### 2.4. Radiation Chemical Yield

In order to quantitatively compare the effects of the absorbed dose, the *Radiation Chemical Yield* (G) is defined as the number of molecules formed or the number of molecules of starting material changed per 100 eV of energy absorbed. The SI unit is the mole J<sup>-1</sup> and 1 molecule / 100 eV = 1.036 x 10<sup>-7</sup> mol J<sup>-1</sup>. For a species X, G<sub>x</sub> and G(X) are used to avoid confusion between the primary radiation chemical yield and the final radiation chemical yield, respectively.

### 2.5. Dose-Rate

The *Dose-rate* (I) is the *intensity* of the ionizing radiation and is defined as the absorbed dose per unit time. The S.I. unit is the Gy s<sup>-1</sup>. Other units commonly used are rad s<sup>-1</sup> and eV g<sup>-1</sup> s<sup>-1</sup>.

### 2.6. Linear Energy Transfer

The *Linear Energy Transfer* or *LET* of the ionizing radiation is the rate of energy loss with distance, per unit length of irradiated material. The S.I. unit is the J m<sup>-1</sup> and more conventionally used units are eV Å<sup>-1</sup> and keV μm<sup>-1</sup>.

$$\text{LET} = -dE / dx$$

## 3. Radiation Chemistry versus Photochemistry

### 3.1. Photochemistry

In photochemistry, the ultraviolet or visible radiation is usually monochromatic and the quantum is totally absorbed by one molecule leading to an excited state, which depends on the allowed optical transitions. Thus, the absorption of radiation is highly specific to molecules having an absorption band in the appropriate region and usually concerns a specific bond. In this way, even in dilute solutions all the radiation energy may be absorbed selectively by the solute. The excited states are produced homogeneously in the solution. The radiation energy is of a few electronvolts and a limited number of excited states are produced. UV radiation is not very penetrating and is stopped by most materials. Thus, only surfaces are irradiated.

### 3.2. Radiation Chemistry

In radiation chemistry, the radiation may or may not be monochromatic. The energy loss is such that it will always pass through a spectrum of lower energy states. The radiation energy is within

the range of keV to MeV. The initial quantum or particle will excite and ionize thousands of molecules indiscriminately. The excitation is not governed by optical transition rules and all excited states are therefore possible. For example, triplet states may be directly produced. The absorption of radiation is non-specific and, in a solution, each component will absorb energy in proportion to its electron fraction. The electron fraction is the number of electrons of a component compared to the total number of electrons in the system. In dilute aqueous solutions, most of the energy is absorbed by the solvent. The excited and ionized solvent molecules are not distributed homogeneously and are formed in clusters or tracks along the path of the ionizing radiation. The complexity of radiation chemical reactions is due to the high concentration of ions and excited species nonhomogeneously formed, and therefore encourages speculation. High energy electrons and gamma rays are very penetrating radiations.

## 4. Energy Loss of Radiation with Matter

### 4.1. Energy Loss of Gamma Rays

Electromagnetic radiation is considered to be "ionizing" when the wavelength is shorter than 250 Å and thus, the photon energy is higher than 50 eV. Gamma rays are electromagnetic radiation of very short wavelength in the range of 0.3 Å to 0.003 Å, which corresponds to a photon energy of 40 keV to 4 MeV.

The absorption of gamma rays by matter follows Lambert-Beer's law:

$$I = I_0 e^{-\mu x}$$

$I$  and  $I_0$  are the intensities of the transmitted and incident radiations respectively  
 $x$  is the thickness of the absorber in cm  
 $\mu$  is the *linear absorption coefficient* in  $\text{cm}^{-1}$

The linear absorption coefficient depends on the density of the medium. Therefore, to compare different absorbers the *mass absorption coefficient* is used:

$$\mu_{\text{mass}} = \mu_{\text{linear}} / \rho$$

$\mu_{\text{mass}}$  is the mass absorption coefficient in  $\text{g}^{-1} \text{cm}^2$   
 $\mu_{\text{linear}}$  is the linear absorption coefficient in  $\text{cm}^{-1}$   
 $\rho$  is the density of the medium in  $\text{g cm}^{-3}$

The *mass absorption coefficient* is the same for different physical states (gaseous, liquid and solid) of the absorber. The *total absorption coefficient* is the sum of three separate coefficients representing the main three processes of energy absorption from gamma rays. These processes are the photoelectric effect, the Compton effect and pair production.

Whatever the mechanism of gamma ray absorption, secondary electrons with considerable kinetic energy ( $E_k$ ) are produced. The subsequent energy absorption processes, which account for most of the incident photon energy, will be characteristic of electrons and will therefore be similar to those occurring when the material is bombarded directly with high energy electrons. This explains why gamma rays and high energy electrons produce similar chemical changes in the absorbing material.

### 4.2. Energy Loss of Electrons

Electrons interact with matter by three main phenomena: emission of electromagnetic radiation, elastic and inelastic collisions.

#### 4.2.1. Emission of Electromagnetic Radiation

Electrons may be decelerated when passing close to an atomic nucleus with the consequent emission of energy as an X-ray photon or *Bremsstrahlung* radiation, which in turn may be absorbed leading to chemical changes. Bremsstrahlung radiation is predominant for electron energies of 10-100 MeV but is negligible below 0.1 MeV. In water, this occurs for energies higher than 1 MeV. *Cerenkov* radiation is emitted as a characteristic blue glow when high energy electrons are slowed down to the speed of light in materials of refractive index greater than one. The energy loss is greatest for materials of high atomic number since it is proportional to  $Z^2$ .

#### 4.2.2. Inelastic Collisions of Electrons

Electrons of lower energies lose their energy through inelastic collisions or Coulomb interactions with electrons of the stopping material resulting in *ionizations* (1) and *excitations* (2):



The rate of energy loss with distance, the LET, of an electron by ionization and excitation is described by H.A. Bethe's formula:

$$-dE/dx = 2\pi N e^4 Z / m_0 v^2 [\ln m_0 v^2 E / 2I^2 (1-\beta)^2 - \ln 2 \{ 2(1-\beta^2)^{1/2} - 1 + \beta^2 \} + 1 - \beta^2 + 1/8 \{ 1 - (1-\beta^2)^{1/2} \}^2]$$

$E$  is energy of the electron

$x$  is the distance traveled by the electron in the material

$N$  is the number of atoms per  $\text{cm}^3$

$e$  is the charge on the electron

$Z$  is the atomic number of the stopping material

$m_0$  is the rest mass of the electron

$v$  is the velocity of the electron

$I$  is the mean excitation potential for the atoms of the stopping material

$\beta = v / c$  where  $c$  is the velocity of light

Two important conclusions can be drawn from Bethe's formula. First, the LET of electrons increases as energy decreases or as the electrons are slowed down in the medium. Second, the LET of electrons is proportional to the electron density of the medium ( $NZ$ ).

#### 4.2.3. Elastic Collisions of Electrons

Electrons may be deflected by the Coulomb field of an atomic nucleus. There is no energy loss but these collisions result in a non-linear passage of electrons throughout the medium. Elastic collisions occur for low energy electrons in materials of high atomic number. As a rule of thumb, electrons in the energy range of 1-50 MeV lose their energy over a distance in cm that is approximately half their energy in MeV for irradiated material densities close to one. Thus in water an electron of 1 MeV loses its energy in only 0.5 cm.

## 5. LET in Water

The LET of all particles increases as the energy of the particle decreases, that is, as they are slowed down in the medium. Radiations are therefore characterized by their *mean LET values*, which is the total radiation energy divided by the distance traveled by the radiation before coming to a rest. Table 1 shows mean LET values in water for different radiations.

The LET of high energy electrons and gamma rays are of the same magnitude. For a LET of  $0.02 \text{ eV } \text{\AA}^{-1}$ , characteristic of 2 MeV electrons and 1.25 MeV gamma rays, the spurs will lie on average  $5000 \text{ \AA}$  apart. The track persists for a short time following the passage of an ionizing radiation and then disappears as the molecules are separated by diffusion. A number of fast-reactions, described in chapter 3, may occur before the spurs expand and dissipate.

More densely ionizing radiation, with high LET such as  $\alpha$ -particles, may form spurs that overlap along the primary track. Spurs that overlap form a *column* of ionized and excited species in very high concentration. For a LET higher than  $2.5 \text{ eV } \text{\AA}^{-1}$ , the spurs will lie on average  $40 \text{ \AA}$  apart and will thus overlap.

Table I. Mean LET values for water.

Radiation	Mean LET ( $\text{eV } \text{\AA}^{-1}$ )
2 MeV electrons	0.021
1.25 MeV $\gamma$ -rays ( $^{60}\text{Co}$ )	0.021
0.018 MeV $\beta$ -particles ( $^3\text{H}$ )	0.32
5.3 MeV $\alpha$ -particles ( $^{210}\text{Po}$ )	13.6
1 MeV $\alpha$ -particles	19.9

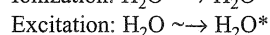
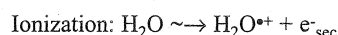
The initial distribution of excited and ionized species is non-homogeneous along the path of the ionizing radiation. The subsequent radiolytic effect is brought about by the reactions of these unstable intermediates with the medium. The entities produced within a spur may recombine to give molecular products or they may diffuse out into the bulk of the solution where they may react with other solutes. The yields of species recombining and diffusing out are known as the *molecular* and *radical yields* respectively.

## 6. The Radiolysis of Water

The radiolysis of water forms radicals,  $\cdot\text{OH}$ ,  $\cdot\text{H}$  and  $\text{e}_{\text{aq}}^-$ , and molecular products,  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ , in three stages. They are the physical stage, the physico-chemical stage and the chemical stage.

### 6.1. Physical Stage

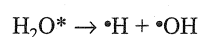
The primary interaction of the ionizing radiation with water results in the ionization and excitation of water molecules along the path of the ionizing radiation. The excitation potential for water is 7.3 eV.



Excited water molecules, water radical-cations and secondary electrons are formed in nonhomogeneous zones, called *spurs*, along the path of the ionizing radiation after  $\sim 10^{-15} \text{ s}$ .

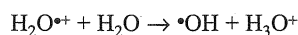
### 6.2. Physico-Chemical Stage

Approximately  $<10^{-12} \text{ s}$  after the primary interaction of the ionizing radiation with water, there is no diffusion. The energy transfer occurs through rotational and vibrational motion. The radiolytic species are transformed into more stable intermediates. Excited water molecules in the singlet state may undergo homolytic dissociation:



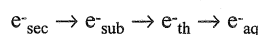
The bond dissociation energy of H-OH is 5.16 eV and thus singlet states, which have an energy of 6.6 eV in their lowest level, are favorable to homolytic dissociation, whilst triplet states have insufficient energies of 4.2-4.5 eV.

The water radical-cation stabilizes itself through a proton-transfer with an adjacent water molecule also known as an *ion-molecule reaction* by analogy to mass spectrometry reactions:

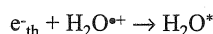


There is thus a slight local acidification of the medium.

The only movement in the medium is that of the secondary electrons that are slowed down as they lose energy. When their energy is below the excitation potential of water they are called *subexcitation electrons* ( $E < 7.3 \text{ eV}$ ). Finally, inelastic collisions slow them down and they are called thermalized electrons ( $E < 0.02 \text{ eV}$ ). *Thermalized electrons* stabilize themselves in a water cavity and are called *aqueous electrons* or *hydrated electrons*:



The electron solvation in water takes  $0.1\text{-}0.5 \times 10^{-12} \text{ s}$ . Thermalized electrons may undergo geminate recombination:



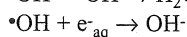
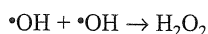
The net effect of the prediffusional stage is the formation of the hydroxyl radical, the aqueous electron, the hydrogen atom and a proton in the nonhomogeneous zones.

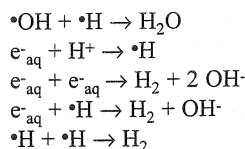
### 6.3. Chemical Stage

The concentration of the radiolytic species in the nonhomogeneous zones decreases by three competing phenomena: recombination reactions that are favored by the high local concentration in radicals in the nonhomogeneous zones, diffusion into the bulk of the solution until homogenization is reached, and reactions with a solute molecule.

#### 6.3.1. Recombination Reactions

The radical recombination reactions lead to the formation of water, hydroxyl ions and the molecular products,  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ , of water radiolysis:





## 6.3.2. Diffusion

The rates of the radical recombination reactions decrease as the concentration in radicals decreases through diffusion, the reaction rates are said to be diffusion-controlled. In the homogeneous phase of the solution it is very difficult to determine the proportion of radicals that have escaped recombination and diffused into the bulk of the solution to that of radicals having recombined to form molecular products. Many mathematical solutions have been applied to try and solve this problem and the evolution of the concentration of the radiolytic species as a function of time in space is approximated by:

$$\partial c_i / \partial t = D_i \nabla^2 c_i - \sum k_{ij} c_i c_j$$

$c_i$  is the concentration of the radiolytic species  
 $\nabla^2 c_i$  is the Laplacien operator =  $\partial^2 c_i / \partial x^2 + \partial^2 c_i / \partial y^2 + \partial^2 c_i / \partial z^2$ ; it defines the spatial position of the radiolytic species (nonhomogeneous zones)  
 $D_i$  is the diffusion constant  
 $\sum k_{ij} c_i c_j$  expresses the loss in radiolytic species due to recombination reactions with the other species  $j$  in the medium with reaction rate constant  $k$

Samuel, Magee and Kuppermann have made an approximation in which the radiolytic species maintain a Gaussian distribution at all times. The nonhomogeneous zones vary in shape, size and energy and therefore the initial concentration in radiolytic species varies. An average spur of 10 Å and 100 eV, with the formation of 4-6 radical pairs, is considered to solve the differential equations. This is called Jaffé's approximation. Today, chemical simulators such as Monte Carlo programs are used to solve these complex equations.

## 6.3.3. Reaction with a Solute

A solute may compete with radical recombination and diffusion if its concentration is high enough.  $-k_i c_i [S]$  is added in the formula,  $k_i$  is the reaction rate constant of the solute with a radical from water radiolysis in  $\text{M}^{-1} \text{s}^{-1}$  and  $[S]$  is the molar concentration of the solute. A solute will compete for radicals in the nonhomogeneous zones if its *scavenging strength*,  $k [S]$  is greater than  $\sim 10^7 \text{ s}^{-1}$ . For example, a solute with a reaction rate constant of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  may intervene in the nonhomogeneous zones if its concentration is greater than  $10^{-3} \text{ M}$ . If its concentration is lower it will react with the radicals and products of water radiolysis in the homogeneous phase.

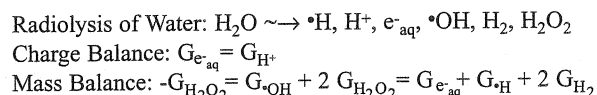
## 6.3.4. Homogeneous Phase

Approximately  $10^{-7} \text{ s}$  after the passage of the ionizing radiation, the radicals ( $\bullet\text{OH}$ ,  $e_{\text{aq}}^-$ ,  $\bullet\text{H}$ ) and molecular products ( $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ ) of water radiolysis are homogeneously distributed in the bulk of the solution.

The physical stage, physico-chemical stage and chemical stage of water radiolysis are summarized in Table II.

## 6.3.5. Charge and Mass Balance

From the charge and mass balance of water radiolysis reactions, we can derive the following relationship between the primary radiation chemical yields of radicals and molecular products:



The rate of formation of radicals and molecular products of the water radiolysis is proportional to the primary radiation chemical yield of each species:  $G_{\bullet\text{OH}}$ ,  $G_{e_{\text{aq}}^-}$ ,  $G_{\text{H}}$ ,  $G_{\text{H}^+}$ ,  $G_{\text{H}_2\text{O}_2}$  and  $G_{\text{H}_2}$ . The primary radiation chemical yields result from the competition between the diffusion out of the nonhomogeneous zones and the radical recombination. As long as the nonhomogeneous zones do not overlap and solutes don't intervene in the nonhomogeneous zones, the primary radiation chemical yields remain constant. Therefore, the primary radiation chemical yields are highly similar for diffuse ionizing radiation that have similar LET, such as X-rays, gamma rays and high energy electrons.

Table II. Summary of the time scale of events in the radiolysis of water

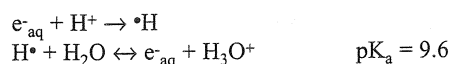
	Events	Reactions	Species Present	Time
Physical Stage	Primary interaction of the radiation:		Nonhomogeneous zones:	$10^{-15} \text{ s}$
	Excitation Ionization	$\text{H}_2\text{O} \xrightarrow{\sim} \text{H}_2\text{O}^*$ $\text{H}_2\text{O} \xrightarrow{\sim} \text{H}_2\text{O}^{*+} + e^-$	$\text{H}_2\text{O}^* \text{H}_2\text{O}^{*+} e^-$	
Physico-chemical Stage	No diffusion			$10^{-12} \text{ s}$
	Energy transfer through: Rotational and vibrational motion			
	Homolytic dissociation:	$\text{H}_2\text{O}^* \rightarrow \bullet\text{H} + \bullet\text{OH}$	Nonhomogeneous zones:	
	Ion-molecule reaction:	$\text{H}_2\text{O}^{*+} + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}_3\text{O}^+$	$\bullet\text{OH} e_{\text{aq}}^- \text{H}^+$	
Chemical Stage	Electron solvation:	$e_{\text{aq}}^- \rightarrow e_{\text{sub}}^- \rightarrow e_{\text{th}}^- \rightarrow e_{\text{aq}}^-$		$10^{-7} \text{ s}$
	Geminate recombination:	$e_{\text{th}}^- + \text{H}_2\text{O}^{*+} \rightarrow \text{H}_2\text{O}^*$		
	Competition between: Diffusion	$\bullet\text{OH} + \bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$ $\bullet\text{OH} + e_{\text{aq}}^- \rightarrow \text{OH}^-$ $\bullet\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$	Homogeneous solution:	
Recombination reactions:		$e_{\text{aq}}^- + \text{H}^+ \rightarrow \bullet\text{H}$ $e_{\text{aq}}^- + e_{\text{aq}}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$ $e_{\text{aq}}^- + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$ $\bullet\text{H} + \text{H} \rightarrow \text{H}_2$	$\bullet\text{OH} e_{\text{aq}}^- \text{H}^+$ $\text{H}_2\text{O}_2 \text{H}_2$	
	Reaction with a solute molecule if $k [S] > 10^7 \text{ s}^{-1}$			

## 6.4. Influence of $\text{H}^+$ and $\text{O}_2$ on the Reactive Species

The two solutes that play a major role in the radiolysis water are the hydronium ion and oxygen.

### 6.4.1. $\text{H}^+$ as a Solute

In an acidic solution, the aqueous electron reacts with a proton to form its conjugate acid, the hydrogen atom:

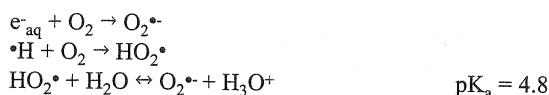


Thus, the hydrated electron does not exist in acidic solutions and the reactive species of water radiolysis will be different in neutral and acidic solutions.

Neutral deaerated solutions:  $\text{H}_2\text{O} \rightsquigarrow \bullet\text{OH}, e_{\text{aq}}^-, \bullet\text{H}, \text{H}_2, \text{H}_2\text{O}_2$   
 Acidic deaerated solution:  $\text{H}_2\text{O} \rightsquigarrow \bullet\text{OH}, \bullet\text{H}, \text{H}_2, \text{H}_2\text{O}_2$

#### 6.4.2. $\text{O}_2$ as a Solute

In the presence of air, there is a solute concentration of  $2.2 \times 10^{-4}$  M in oxygen. Oxygen reacts readily with the aqueous electron and the hydrogen atom to form the superoxide anion and the perhydroxyl radical respectively:



The proportion of the perhydroxyl radical and its conjugate base, the superoxide anion, will depend on the pH of the solution.

Neutral aerated solution:  $\text{H}_2\text{O} \rightsquigarrow \bullet\text{OH}, \text{O}_2^{\bullet-}, \text{H}_2, \text{H}_2\text{O}_2$   
 Acidic aerated solution:  $\text{H}_2\text{O} \rightsquigarrow \bullet\text{OH}, \text{HO}_2^{\bullet}, \text{H}_2, \text{H}_2\text{O}_2$

## 7. The Radiolysis of Aqueous Solutions

All solutes are found to play an important role in the radiolysis of water. Furthermore, they contributed significantly to the description of the radiolysis mechanisms and the model for the nonhomogeneous zones of water radiolysis. The solute transformation will depend on its reactions with the radicals and products of water radiolysis. Chemical and physical parameters influence the radiolysis of aqueous solutions. Chemical parameters include the solute concentration and the pH of the solution. Physical parameters include the absorbed dose, the radiation intensity, the temperature, the LET and the pressure. Both the chemical and physical parameters are extrinsically linked. They determine whether or not chemical reactions follow homogeneous kinetics and because of them radiation chemical yields may or may not be constant and the nature of the reactive intermediates vary. The radiolysis mechanism of aqueous solutions is very complex.

### 7.1. Influence of the Solute Concentration

#### 7.1.1. The Indirect Effect

In the radiolysis of solutions, the solute transformation occurs when it reacts with radicals ( $e_{\text{aq}}^-$ ,  $\bullet\text{H}$ ,  $\bullet\text{OH}$ ) and molecular products ( $\text{H}_2$  and  $\text{H}_2\text{O}_2$ ) formed by water radiolysis. The effect of the ionizing radiation on the solute is thus indirect because it occurs via the solvent radiolysis. The hydroxyl radical is an oxidizing species and the hydrogen atom and the aqueous electron are reducing species. Hydrogen is not very reactive and hydrogen peroxide may either be reduced or oxidized.

#### 7.1.2. The Solute Dilution Curve

The indirect effect is illustrated by the solute dilution curve shown in Figure 1, which plots the radiation chemical yield of the solute transformation,  $G(-S)$ , as a function of the solute concentration,  $[S]$ . Generally, in very dilute aqueous solutions, the radiation chemical yield of the solute transformation is proportional to its concentration. As the solute concentration increases, the com-

petition for the radicals and products of water radiolysis in the homogeneous phase increases until their capture is complete and a plateau is reached. At the plateau, the radiation chemical yield in solute transformation is independent of the solute concentration.

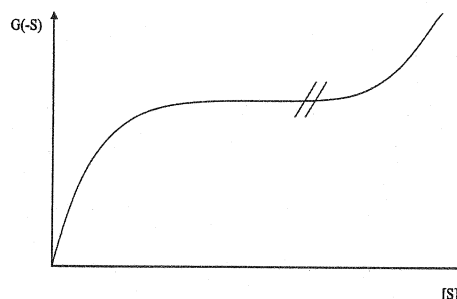


Figure 1. Solute dilution curve

As is shown in Figure 1, the yield of solute transformation for very dilute aqueous solutions is a linear function and  $G(-S) = m[S]$ , where  $m$  is the slope of the tangent to the origin. In this range of solute concentration, the same percentage is transformed regardless of the solute concentration.

The plateau of a solute dilution curve generally extends from  $10^{-5}$  M to  $10^{-3}$  M and this range of solute concentration is interesting because the capture of the radicals of water radiolysis is complete, without the solute intervening in the nonhomogeneous zones. The  $G$  values of various solutes at the plateau are used to calculate the primary radiation chemical yields of radicals and molecular products formed by water radiolysis.

If the solute concentration is increased beyond a certain concentration, the radiation chemical yield of the solute transformation increases. The solute then scavenges radicals in the nonhomogeneous zones of water radiolysis and competes with the formation of the molecular products.

#### 7.1.3. Schwarz's Curve

Schwarz's curve best illustrates the solute intervention in the nonhomogeneous zones of water radiolysis. The ratio of the primary radiation chemical yield of a molecular product,  $\text{H}_2$  or  $\text{H}_2\text{O}_2$ , in the presence of a solute ( $G_M$ ) and in the absence of a solute ( $G_{M0}$ ) is plotted as a function of the solute scavenging strength,  $k[S]$ .

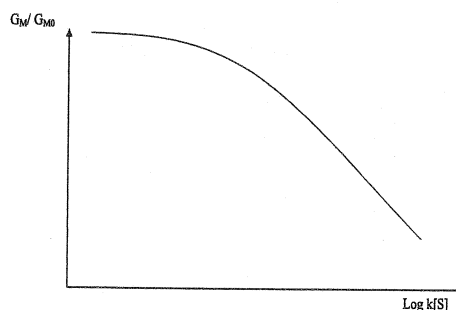
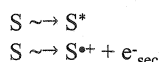


Figure 2. Schwarz's curve

## 7.1.4. Direct effect

The direct effect becomes non negligible for solute concentrations higher than 1 M. The energy of the ionizing radiation is directly absorbed by the solute resulting in excitations and ionizations.



## 7.1.5. Direct and indirect effects

The radiolysis mechanism of concentrated aqueous solutions is highly complex. The reactive intermediates originate from the direct effect, as well as the indirect effect of the ionizing radiation on the solute. All the radicals and molecular products formed by the water radiolysis and the solute radiolysis are in competition. The solute may react in the picosecond time scale and thus, reactions with other reactive intermediates of water radiolysis are possible. Furthermore, at such high solute concentration changes in the dielectric constant and ionic force of the medium may influence the reaction rate kinetics.

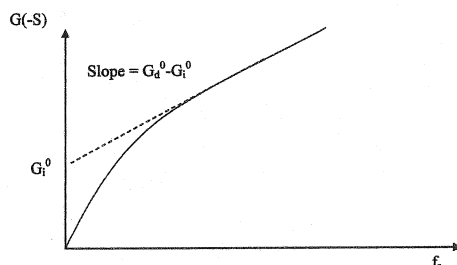


Figure 3. Schematic representation of the direct and indirect effects

If the direct and indirect effects are cumulative, the global transformation of the solute, shown in Figure 3, may be represented by:

$$G(-S) = f_s G_d^0 + (1-f_s) G_i^0 \varphi [S]$$

$f_s$  is the ratio between the energy directly absorbed by the solute to the total energy absorbed in the system. It is proportional to the electron density of the solute.  $G_d^0$  is the yield of the direct effect, a supposition is made that it is independent of the solute concentration.  $G_i^0$  is the maximum yield of the indirect effect.  $\varphi [S]$  is the fraction of primary products used for the solute transformation.

For very high solute concentrations,  $\varphi [S] = 1$  and a linear equation of the asymptote to the curve is obtained:

$$G(-S) = G_i^0 + (G_d^0 - G_i^0) f_s$$

From the slope of the asymptote, the contribution of the direct effect and the indirect effect on the solute transformation may be approximated.

## 7.2. Influence of the pH of the Solution

The primary radiation chemical yields remain constant between pH 4-10. The values of the primary radiation chemical yields in acidic and neutral solutions are described in the first part of the article.

### 7.2.1. Acidic Solutions

The hydrated electron is converted into hydrogen atoms in the nonhomogeneous zones, influencing the radical recombination reactions. Hydrogen atoms are less reactive than aqueous electrons, especially towards hydroxyl radicals. There is an increase in  $G_{\bullet\text{OH}}$  and thus an increase in  $G_{\text{H}_2\text{O}_2}$ . Since the reducing entity is less reactive there is an increase in  $(G_{e_{\text{aq}}} + G_{\bullet\text{H}})$ . Therefore  $G_{\text{H}_2\text{O}}$  is higher for acidic solutions than neutral solutions.

### 7.2.2. Basic Solutions

The hydroxyl radical is converted into its conjugate base, the oxide radical ion. The oxide radical ion does not react well with aqueous electrons and an increase in  $(G_{e_{\text{aq}}} + G_{\bullet\text{H}})$  is expected. The dismutation of the oxide radical ion is less favorable and thus  $(G_{\text{H}_2\text{O}_2} + G_{\text{HO}_2})$  is expected to decrease and  $(G_{\bullet\text{OH}} + G_{\bullet\text{O}})$  increase compared to the neutral media.  $G_{\text{H}_2\text{O}}$  is higher for basic solutions than neutral solutions. However, in basic media the oxide radical ion could give rise to other reactions and the radiolysis mechanism of basic aqueous solutions is not yet fully elucidated.

## 7.3. Influence of the Absorbed Dose

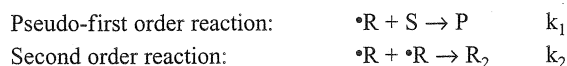
The greater the absorbed dose, the greater the amount of reactive species of water radiolysis formed and the greater the solute degradation. The amount of solute transformation is proportional to the absorbed dose multiplied by its radiation chemical yield of transformation.

However, if the absorbed dose is increased beyond a certain point, the radiolytic products accumulating in the solution may react also with the reactive species of water radiolysis. This "dose effect", the dose at which the radiolysis of radiolytic products is not negligible anymore, has seldom been studied.

## 7.4. Influence of the Dose Rate

### 7.4.1. Solute Transformation

A dose rate effect is observed when a pseudo-first order reaction, such as that of a solute with a radical, is in competition with a second order reaction, such as radical-radical reactions, in the water radiolysis.



From the stationary concentration of the radical  $\bullet\text{R}$  and the radiation chemical yield in the solute transformation the following relationship is derived:

$$G(-S) = k_1^2 [S]_0^2 / (4k_2 I) \{ (1 + 8k_2 I G_{\bullet R} / k_1^2 [S]_0^2)^{1/2} - 1 \}$$

Therefore, the solute transformation is a function of the dose rate of the ionizing radiation (I) as is shown in Figure 4. For low dose rates, the radiation chemical yield of solute transformation,  $G(-S)$ , tends towards the yield in radicals,  $G_{\bullet R}$ , and is independent of the dose rate. For high dose rates,  $G(-S)$  tends towards zero following an asymptote of  $I^{-1/2}$ :

$$G(-S) = \{ k_1^2 [S]_0^2 G_{\bullet R} / (2k_2 I) \}^{1/2}$$

As the dose rate is increased, the solute transformation will be inversely proportional to the square root of the dose rate.

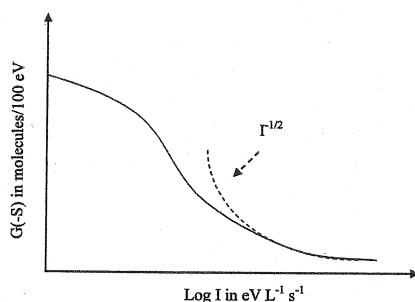


Figure 4. Influence of the dose-rate on the solute transformation

#### 7.4.2. Solute Dilution Curve

A similar effect of the dose rate is found on solute dilution curves, described in section 7.1.2., because these also illustrate the competition between first and second order processes. The plateau of the solute dilution curve is reached at a lower solute concentration for low dose rates compared to high dose rates. At the plateau, the solute captures all the radicals of water radiolysis and  $G(-S)$  is independent of the dose rate for a very large range of radiation intensities.

#### 7.4.3. Nonhomogeneous Zones Overlapping

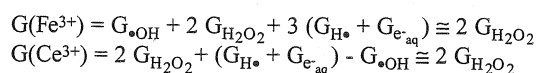
For extremely high dose rates, higher than  $10^7 \text{ Gy s}^{-1}$ , the nonhomogeneous zones overlap in the bulk of the solution. The high concentration of radicals favors the formation of the molecular products, which are then more or less homogeneously distributed. The primary radiation chemical yield in molecular products is increased and that of radicals decreased for very high dose rates. They should not be confused with the primary radiation chemical yields calculated experimentally using gamma rays of cobalt-60. Low solute concentrations will only react with hydrogen peroxide and hydrogen, and very high solute concentrations are needed to scavenge the radicals.

For example, at a very high dose rate of  $8.0 \times 10^{11} \text{ Gy s}^{-1}$  reached by a 2 MeV electron-beam irradiation with a pulse of duration of 50 ns, the radiation chemical yield of ferric ions is found to equal that of ferrous ions when very low solute concentrations are used ( $10^{-3} \text{ M}$ ):

$$G(\text{Fe}^{3+}) = G(\text{Ce}^{3+}) = 1.4 \text{ molecules} / 100 \text{ eV}$$

This may only occur if hydrogen peroxide is the only product

formed by water radiolysis and it reacts with the solute:



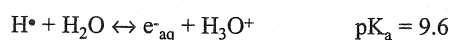
For very high solute concentrations,  $G(\text{Fe}^{3+})$  tends towards 4.6 molecules / 100 eV, corresponding to the complete capture of  $\bullet\text{OH}$  radicals in the nonhomogeneous zones.

## 8. Properties of the Reactive Species of Water Radiolysis

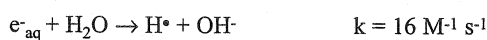
The radiolysis of aqueous solutions will depend on the nature of the solute and its reactions with the radicals and molecular products of water radiolysis.

### 8.1. Properties of the Hydrated Electron and the Hydrogen Atom

#### 8.1.1. Acid-Base Equilibrium



The reaction of aqueous electrons with water to form its conjugate acid, the hydrogen atom, is so slow that even in neutral solutions the reactions of hydrated electrons may be studied:



From pH 5-10, the acid-base equilibrium does not have time to establish itself and the hydrogen atom and the aqueous electron react as they are formed by water radiolysis.

At lower pH the hydrated electron is converted rapidly into the hydrogen atom:



At pH > 10, the hydrogen atom may react with  $\text{OH}^-$ :



#### 8.1.2. Absorption Spectra

The aqueous electron has an intense absorption spectrum with a maximum at 720 nm with a molar absorptivity coefficient equal to  $1.58 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The hydrated electron may be observed by pulse radiolysis with a time-resolved optical absorption system. The hydrogen atom has a very weak absorption spectrum in the ultraviolet range from 200 to 240 nm. At 200 nm, the molar absorptivity coefficient is  $9 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$  but decreases to zero at 240 nm.

#### 8.1.3. Reduction Potentials

The hydrated electron and the hydrogen atom are strong reducing agents:





They may act as oxidizing agents in dismutation reactions of water radiolysis.

### 8.1.4. Reactivity of $e^-_{aq}$

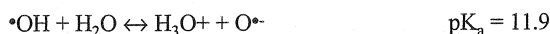
- Reduction reactions:  $Cu^{2+} + e^-_{aq} \rightarrow Cu^+$   
The hydrated electron is a very powerful reductant. The alkali and alkaline earth metals ions are usually unreactive though most other cations are reactive. The higher the positive charge on the cation, the greater the reactivity. Inorganic cations are generally more reactive than inorganic anions. Rate constants are very high and in some cases correspond to those for the diffusion-controlled reaction.
- Acid-base reactions:  $H_2PO_4^- + e^-_{aq} \rightarrow HPO_4^{2-} + \cdot H$   
With some acids, the hydrated electron may act as a proton acceptor.
- Nucleophilic Reagent.  
Aliphatic compounds are reactive only if they contain the groups C-Halogen, C=O, C=S or S-S. Attack on alkene double bonds is enhanced by adjacent electron-withdrawing substituents. Reactions with aromatic compounds depend on the  $\pi$ -electron density in the aromatic ring. The reactivity of hydrated electrons with organic compounds is summarized in Table III.

### 8.1.5. Reactivity of $\cdot H$

- Electron-transfer reactions:  $Cu^{2+} + \cdot H \rightarrow Cu^+ + H^+$   
 $Fe^{2+} + \cdot H + H^+ \rightarrow Fe^{3+} + H_2$   
The hydrogen atom may act either as a reducing or oxidizing agent.
- Hydrogen-atom abstractions:  $CH_3OH + \cdot H \rightarrow \cdot CH_2OH + H_2$   
The reaction with saturated organic compounds is non-specific and many sites of H-abstraction are possible.
- Addition reactions:  $C_6H_6 + \cdot H \rightarrow C_6H_7\cdot$   
These occur with unsaturated and aromatic compounds and the site of addition is not specific. The reactivity of hydrogen atoms with organic compounds is summarized in Table III.

## 8.2. Properties of the Hydroxyl Radical and the Oxide Radical Ion

### 8.2.1. Acid-Base Equilibrium



The acid-base equilibrium is fast and the proportion of hydroxyl radicals to oxide radical ions is a function of the pH.

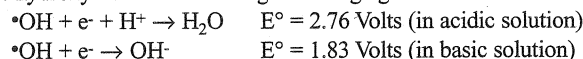
### 8.2.2. Absorption Spectra

The hydroxyl radical absorbs very weakly in the ultraviolet range, from 200 to 400 nm. The molar absorptivity coefficient is  $5.3 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$  at 230 nm and  $3.7 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$  at 260 nm. The oxide radical ion also absorbs very weakly in the ultraviolet region. The molar absorptivity coefficient is  $2.4 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$  at 240 nm. The reactions with hydroxyl radicals and oxide radicals ions are measured by pulse radiolysis, following the formation of

a product with a high molar absorptivity coefficient, or by competition methods.

### 8.2.3. Reduction Potentials

The hydroxyl radical is a strong oxidizing agent:



Rarely, it may act as a reducing agent in dismutation reactions and with very strong oxidizing agents such as  $MnO_4^-$  and  $S_2O_8^{2-}$ .

### 8.2.4. Reactivity of $\cdot OH$

- Electron-transfer reactions:  $Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$   
It acts as an oxidizing agent with many inorganic compounds.
- Hydrogen-atom abstractions:  
 $CH_3OH + \cdot OH \rightarrow \cdot CH_2OH + H_2O$   
H-abstraction occurs with saturated organic compounds including those containing carbonyl groups. Weaker H-C bonds are attacked in preference to stronger bonds such as the H-C bonds in alpha to a carbonyl or alcohol functional group. However, hydroxyl radical H-abstractions are not very selective.
- Addition reactions:  $CH_2=CH_2 + \cdot OH \rightarrow HOCH_2CH_2\cdot$   
Unsaturated and aromatic compounds react by addition reactions. The hydroxyl radical is an electrophilic reagent and reacts preferentially at sites of high electron density. The reactivity of hydroxyl radicals with organic compounds is summarized in Table III.

Table III. Reactivity of primary radicals with organic functional groups.

Functional Group	Rate Constant Range <sup>a</sup>		$\cdot OH$
	$e^-_{aq}$	$\cdot H$	
H <sup>+</sup>	+++	-	-
O <sub>2</sub>	+++	+++	-
Saturated Carbon	-	++	+++
Alkene	-	+++	+++
Aromatic	+	+++	+++
Pyrimidine	+++	++	+++
Nitrile (R-C≡N)	++	+	++
Carbonyl (R <sub>2</sub> C=O)	+++	+	++
Carboxylic Acid (R-COOH)	++	+	++
Ester (R-CO-O-R)	++	+	++
Amide (R-CO-NH-R)	+	+++	+++
Nitro (R-NO <sub>2</sub> )	+++	++	-
Alcohol (R-OH)	-	++	+++
Ether (R-O-R)	-	++	+++
Chloro (R-Cl)	++	+	
Bromo (R-Br)	+++	++	
Iodo (R-I)	+++	+++	
Thiol (R-S-R)	+++	++	+++
Disulfide (R-S-S-R)	+++	++	+++

<sup>a</sup>+++  $k > 10^6 \text{ M}^{-1} \text{ s}^{-1}$

++  $k = 10^4 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$

+  $k = 10^2 - 10^4 \text{ M}^{-1} \text{ s}^{-1}$

-  $k < 10^2 \text{ M}^{-1} \text{ s}^{-1}$

### 8.2.5. Reactivity of $O^{\cdot -}$

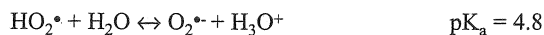
The reactions of oxide radical ions are not well known because solutions having a high pH are needed for their study. It is less reactive in H-abstraction reactions, not as oxidizing as  $\cdot OH$  and acts as a nucleophilic reagent. The mechanism of the radiolysis of basic solutions is yet to be fully elucidated.



### 8.3. Properties of the Peroxyhydroxyl Radical and the Superoxide Anion

These play a major role in the radiolysis of aerated solutions because oxygen is an efficient scavenger of hydrated electrons and hydrogen atoms.

#### 8.3.1. Acid-Base Equilibrium



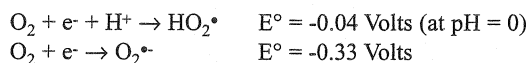
The acid-base equilibrium is fast and the proportion of  $\text{HO}_2^\bullet$  to  $\text{O}_2^{\bullet-}$  depends only on the pH of the solution.

#### 8.3.2. Absorption Spectra

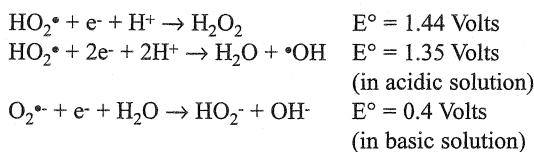
Both the peroxyhydroxyl radical and the superoxide ion absorb sufficiently in the ultraviolet to be observed directly by pulse radiolysis. The molar absorptivity coefficient is  $1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 225 nm for peroxyhydroxyl radicals and  $2.35 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 245 nm for superoxide ions.

#### 8.3.3. Reduction Potentials

The peroxyhydroxyl radical and the superoxide anion may act as reducing agents:

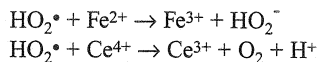


They may also be oxidizing agents:



#### 8.3.4. Reactivity of $\text{HO}_2^\bullet$

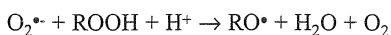
Peroxyhydroxyl radicals act as oxidizing or reducing agents depending on the solute.  $\text{HO}_2^\bullet$  is a stronger oxidizing agent than  $\text{O}_2^{\bullet-}$ .



Organic compounds are inert unless they contain a relatively weakly bonded hydrogen atom, allowing H-abstraction to occur.

#### 8.3.5. Reactivity of $\text{O}_2^{\bullet-}$

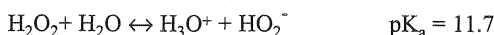
The superoxide anion may act as an oxidizing or reducing agent.  $\text{O}_2^{\bullet-}$  is a stronger reducing agent than  $\text{HO}_2^\bullet$ . Organic compounds are inert unless they contain a relatively weakly bonded hydrogen atom and H-abstraction may occur. The superoxide anion reacts via the Haber-Weiss reaction with hydroperoxides:



### 8.4. Properties of Hydrogen Peroxide

### and the Peroxyhydroxyl Ion

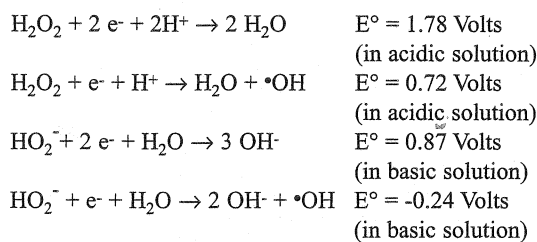
#### 8.4.1. Acid-Base Equilibrium



The acid-base equilibrium is fast and the proportion of hydrogen peroxide to peroxyhydroxyl ions depends entirely on the pH of the solution.

#### 8.4.2. Reduction Potentials

Hydrogen peroxide and the peroxyhydroxyl ion may be reducing or oxidizing agents:



#### 8.4.3. Reactivity of $\text{H}_2\text{O}_2$

Hydrogen peroxide may act as an oxidizing or reducing agent. Hydrogen peroxide is inert towards most organic compounds but may react with some organic radicals.

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