Low-linear energy transfer radiolysis of liquid water at elevated temperatures up to 350 °C: Monte-Carlo simulations

par

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ABSTRACT

LOW-LINEAR ENERGY TRANSFER RADIOLYSIS OF LIQUID WATER AT ELEVATED TEMPERATURES UP TO 350 °C: MONTE-CARLO SIMULATIONS

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A re-examination of our Monte-Carlo modeling of the high-temperature radiolysis of liquid water by low-linear energy transfer (LET~0.3 keV/μm) radiation has been undertaken in an attempt to reconcile our computed g-values (primary yields) of the various radiolytic products (e\textsuperscript{-aq}, OH, H\textsuperscript{+}, H\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2}) with recently reevaluated experimental data over the range from 25 up to 350 °C. The temperature dependence of the rate constant for the self-reaction of the hydrated electron (e\textsuperscript{-aq}) measured under alkaline conditions, and in particular the abrupt drop observed above 150 °C, was assumed, in contrast to previous study, to be valid also in near-neutral pH water. To best reproduce the currently available temperature-dependent g-values, we found it necessary to introduce a discontinuity in the temperature dependence at 150 °C of certain parameters that intervene in the physicochemical stage of the radiolysis, including the thermalization distance (r\textsubscript{th}) and the dissociative attachment (DEA) of subexcitation electrons, and the dissociative decay of electronically and vibrationally excited water molecules. With the exception of g(H\textsubscript{2}) above 200 °C, all calculated g-values were consistent with the general observation that when the temperature is increased, the yields of free radicals g(e\textsuperscript{-aq}), g(OH), and g(H\textsuperscript{+}) increase while the molecular yield g(H\textsubscript{2}O\textsubscript{2}) decreases. Although H\textsubscript{2} is a molecular product, g(H\textsubscript{2}) was observed to continue to increase with temperature for a reason that has been a matter of controversy recently. Our simulations show that the reaction of H\textsuperscript{+} atoms with water previously proposed by Swiatla-Wojcik and Buxton can indeed account for the anomalous increase in g(H\textsubscript{2}) at high temperature if we use for the rate constant of this reaction the value of 10\textsuperscript{4} M\textsuperscript{-1} s\textsuperscript{-1} at 300 °C. Finally, as a direct application of the Fricke (ferrous sulfate) dosimeter, we have calculated the spur lifetime (\tau\textsubscript{s}) and its temperature dependence. The results show that our calculated \tau\textsubscript{s} value is decreasing from 4.2\times10\textsuperscript{-7} to 5.7\times10\textsuperscript{-8} s over the temperature range 25-350 °C.

Keywords: Monte-Carlo simulation, Radiolysis of water, High temperature, g-values, Free radical and molecular yields, LET, Electron thermalization distance, Dissociative electron attachment (DEA), Time of spur expansion, Fricke dosimeter.
RESUMÉ

RADIOLYSE DE L’EAU LIQUIDE À FAIBLE TRANSFERT D’ÉNERGIE LINÉAIRE POUR DES TEMPÉRATURES ÉLEVÉES JUSQU’À 350 °C : SIMULATIONS MONTE-CARLO

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Une réexamination de notre modèle de simulation Monte-Carlo de la radiolyse de l’eau liquide à haute température par des radiations à faible transfert d’énergie linéaire (TEL~0,3 keV/μm) a été effectuée dans une tentative de réconcilier nos valeurs G simulées (rendement primaire) des différents produits radiolytiques (e\textsubscript{aq}, OH, H\textsuperscript{•}, H\textsubscript{2} et H\textsubscript{2}O\textsubscript{2}) avec les récentes données expérimentales réévaluées entre 25 et 350 °C. La dépendance en température de la constante de vitesse de la réaction bimoléculaire de e\textsubscript{aq} (électron "hydraté") mesuré sous conditions alcalines, et en particulier la chute abrupte de celle-ci au-dessus de 150 °C, est assumé, à l’opposé des études précédentes, être valide également dans l’eau à pH quasi-neutre. Pour mieux reproduire les valeurs G disponibles récemment en fonction de la température, nous avons trouvé qu’il est nécessaire d’introduire une discontinuité dans la dépendance en température à 150 °C de certains paramètres qui interviennent au stade physicochimique de la radiolyse, incluant la distance de thermalisation (r\textsubscript{th}) et l'attachement dissociatif (DEA) des électrons de sous-excitation, et la dégradation dissociative des molécules d'eau excitées électroniquement et vibrationnellement. À l'exception de GH\textsubscript{2} au-dessus de 200 °C, toutes les valeurs G calculées sont cohérentes avec l'observation générale que lorsque la température est augmentée, la quantité (rendement) de radicaux libres G\textsubscript{e\textsubscript{aq}}, G\textsubscript{OH} et G\textsubscript{H\textsuperscript{•}} augmente tandis que le rendement moléculaire GH\textsubscript{2}O\textsubscript{2} diminue. Bien que H\textsubscript{2} est un produit moléculaire, GH\textsubscript{2} a été observé comme augmentant avec la température pour une raison qui est présentement controversée. Nos simulations montrent que la réaction de l’atome d’hydrogène avec l’eau proposée par Swiatla-Wojcik et Buxton en 2005 peut expliquer l’augmentation anormale de GH\textsubscript{2} à haute température si l’on utilise une valeur de 10\textsuperscript{8} M\textsuperscript{-1} s\textsuperscript{-1} à 300 °C pour la vitesse de cette réaction. Enfin, comme application directe du dosimètre de Fricke (sulfate ferreux), nous avons déterminé le temps de vie (τ\textsubscript{s}) des grappes et sa dépendance en température. Les résultats montrent que nos valeurs calculées de τ\textsubscript{s} diminuent de 4,2×10\textsuperscript{-7} à 5,7×10\textsuperscript{-8} s pour les températures allant de 25 à 350 °C.

Mots clés : Simulation Monte-Carlo, Radiolyse de l'eau, Haute température, Valeurs G, Radicaux libres et produits moléculaires, TEL, Distance de thermalisation de l'électron, Attachement dissociatif de l'électron, Temps de vie des grappes, Dosimètre de Fricke.
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$g(H_2)$ values computed with the rate constant predicted by Bartels $(2.2 \times 10^3 \text{ M}^{-1} \text{s}^{-1} \text{ at } 300 \degree C)$ [8,49]. The solid line shows our simulated results of $g(H_2)$ obtained with the value of $10^4 \text{ M}^{-1} \text{s}^{-1} \text{ at } 300 \degree C$ recently inferred by Ghandi et al. [45] from muon spin spectroscopy experiments. Experimental data are the same as in Figs. 1 and 4e.

Chapter IV – Article No. 2

Figure 1: Time evolution of $G(\text{Fe}^{3+})$ (in molec./100 eV) for 300-MeV incident protons (LET ~ 0.3 keV/μm at 25 °C) in air-saturated solutions of 5 mM FeSO$_4$ in aqueous 0.4 M H$_2$SO$_4$ at different temperatures in the range 25-350 °C. The different lines correspond to our theoretical simulations at 25 °C (solid line), 50 °C (dotted line), 100 °C (dashed line), 200 °C (dash-dot line), and 350 °C (dash-dot-dot line) (see text). The arrow on the right of the figure shows the accepted value (15.6 molec./100 eV) of the yield of the Fricke dosimeter for $^{60}$Co γ-rays and fast electrons at room temperature (see, for example, refs. 1, 15, 19, 21, and 50).

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Chapter V

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Figure V.11: Spur lifetime $\tau_s$ as a function of temperature in the low-LET radiolysis of liquid water, as calculated using the same procedure based on the radiolysis of the Fricke dosimeter described above but with Eq. (57) instead of Eq. (18), for the three different concentrations of $\text{Fe}^{3+}$ ions 1, 5, and 10 mM.

Figure V.12: Comparison between the lifetimes of spur obtained by different methods. The solid line illustrates the spur lifetime, obtained from Eq. (59). The dash and dot lines represent the spur lifetimes obtained by using the procedure based on the radiolysis of the Fricke dosimeter (5 mM $\text{FeSO}_4$) before and after corrections were taken into account, respectively.
LIST OF ABBREVIATIONS

<table>
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<th>Symbol</th>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>( \sigma )</td>
<td>Cross section</td>
<td></td>
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<tr>
<td>D</td>
<td>Diffusion coefficient</td>
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<tr>
<td>DEA</td>
<td>Dissociative electron attachment</td>
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<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
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<tr>
<td>e(_{aq})</td>
<td>Hydrated electron</td>
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<td>eV</td>
<td>Electronvolts</td>
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<tr>
<td>( G_x ) or ( g(X) )</td>
<td>Primary yield of the radiolytic species X</td>
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<td>( G(X) )</td>
<td>Experimental 100-eV yield of the final product X</td>
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<td>IRT</td>
<td>Independent reaction times</td>
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<td>( k )</td>
<td>Reaction rate constant</td>
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<tr>
<td>keV</td>
<td>Kilo-electronvolts</td>
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<tr>
<td>LET</td>
<td>Linear energy transfer</td>
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<td>MC</td>
<td>Monte-Carlo</td>
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<tr>
<td>MeV</td>
<td>Mega-electronvolts</td>
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<td>molec./100 eV</td>
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I. INTRODUCTION

1.1 The importance of radiation chemistry

In order to develop a better understanding of chemical and biological effects of ionizing radiations, one should be able to describe their action in liquid water, which is a major constituent of all living matter, representing 70-85% of the weight of cells. For this reason, water plays a major role in radiobiology, because its radiolysis produces reactive species which are responsible for indirect effects. Its absorption properties are very similar to those of human body. It is also of importance in nuclear technology, such as in water-cooled nuclear power reactors (where water, used both as moderator and as a heat transport medium, is circulating around the reactor core at temperatures of 250-310 °C), and in order to control water chemistry to mitigate the effects of water radiolysis and thus minimize corrosion (that occurs through the radiolytic production of oxidizing species, such as 'OH, H$_2$O$_2$, O$_2$, etc.), the yields and activities of decomposition products of water must be well understood. In fact, the radiolysis of water and aqueous solutions has been the subject of numerous experimental and theoretical investigations, but some general points concerning the initial yields of the species generated in the ionisation event, their initial distribution in space and the mechanisms of their formation are still not fully resolve. A good summary of aqueous radiation chemistry is given in the review articles of BUXTON (1987), FERRADINI and JAY-GERIN (1999), and LAVERNE (2004).

Monte-Carlo simulation techniques have been used to model the complex sequence of events that are generated by the interaction of ionizing radiations with pure liquid water. These simulation methods have permitted detailed studies of the relationship between track structure and radiation-induced chemical change. On the theoretical side, the entire water radiolysis process can be efficiently modeled, using Monte-Carlo computer codes, to simulate the primary interactions and to describe the fast kinetics of reactive radicals and ions as a function of the linear energy transfer (LET) of the ionizing radiation, pH, and temperature. Such a modeling can also be done in a nuclear reactor, where the cooling water undergoes radiolytic decomposition induced by neutrons, γ-rays, and fast electrons in the core. As experiments at high temperatures and pressures and in mixed radiation fields
are extremely difficult to perform, computer simulations in this condition are a particularly important route of investigation to predict the detailed of radiation chemistry in the nuclear reactor core and the consequences for material used.

In the present work, Monte-Carlo simulations are used to determine the radiolytic yields for the radiolysis of water at elevated temperature (25-350 °C) by low-LET radiation, and also investigate the anomalous increase of g(H2) in high temperature water radiolysis by considering the sensitivity of the reaction of H' + H2O → H2 + 'OH which has been postulated by SWIATLA and BUXTON (2005) and still be a matter of controversy about its rate constant. Finally, we have been determined the lifetime of spur expansion as a function of temperature which is the time required for the changeover from nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution by using a direct application of Monte-Carlo simulations of the ferrous sulfate (Fricke) dosimeter.

I.2 Energy deposition events and interaction of ionizing radiation with matter

Ionizing radiations are defined as those types of energetic particles and electromagnetic radiations that, either directly or indirectly, cause ionization of a medium, that is, the removal of a bound orbital electron from an atom or a molecule and, thereby, the production of a residual positive ion. Some molecules, instead of being ionized, may also be excited to upper electronic states (see, for example: EVANS, 1955; ANDERSON, 1984; IAEA-TECDOC-799, 1995; MOZUMDER, 1999; TOBUREN, 2004). Directly ionizing radiations are fast moving charged particles (e.g., electrons, protons, α-particles, stripped nuclei, or fission fragments) that produce ionizations through direct Coulomb interactions. In this case, note that particle-particle contact is not necessary since the Coulomb force acts at a distance. Indirectly ionizing radiations are energetic electromagnetic radiations (like X- or γ-ray photons) or neutrons that can also liberate bound orbital electrons, but secondarily to a preliminary interaction. For photons, this interaction is predominantly via production of Compton electrons and photoelectrons (and, if the incident photon energy is greater than 1.02 MeV, the production of electron-positron pairs). Neutrons interact with matter through elastic nuclear scattering resulting in the production of energetic recoil protons or other positively charged nuclei (ions), characteristic of the irradiated medium, which can go on to
generate ionized and excited molecules along their paths. Regardless of the type of ionizing radiation, the final common result in all modes of absorption of ionizing radiation is thus the formation of tracks of physical energy-loss events in the form of ionization and excitation processes and in a geometrical pattern that depends on the type of radiation involved.

Generally, the electrons ejected in the ionization events may themselves have sufficient energy to ionize one or more other molecules of the medium. In this way, the primary high-energy electron can produce a large number (~4 x 10^4 by a 1 MeV particle) of secondary or higher-order generation electrons (it is customary to refer to all electrons that are not primary as "secondary") along its track as it gradually slows down (ICRU REPORT 31, 1979). From atomic physics it is known that most energy-loss events by fast electrons involve small transfers of energy. In fact, the probability of a given energy transfer Q varies inversely with the square of that energy loss (EVANS, 1955). "Distant" or "soft" collisions, in which the energy loss is small, are therefore strongly favored over "close" or "hard" collisions, in which the energy loss is large (MOZUMDER, 1999). The vast majority of these secondary electrons have low initial kinetic energies with a distribution that lies essentially below 100 eV, and a most probable energy below 10 eV (LAVERNE and PIMBLOTT, 1995; SANCHE, 2002; AUTSAVAPROMPORN, 2006). In most cases, they lose all their excess energy by multiple quasi-elastic (i.e., elastic plus phonon excitations) and inelastic interactions with their environment, including ionizations and/or excitations of electronic, intramolecular vibrational or rotational modes of the target molecules (MICHAUD et al., 2003), and quickly reach thermal equilibrium (i.e., they are "thermalized"). Determining exactly which of these competing interaction types will take place is a complex function of the target medium and the energy range of the incident electron. By definition, a measure of the probability that any particular one of these interactions will occur is called the "cross section" (expressed in units of area) for that particular interaction type (see, for example: JOACHAIN, 1975). The total interaction cross section σ, summed over all considered individual processes i, is used to determine the distance to the next interaction, and the relative contributions σ_i to σ are used to determine the type of
interaction. Actually, the mean distance between two consecutive interactions or "mean free path" $\lambda$ is defined by

$$\lambda = \frac{1}{N \sigma},$$  \hspace{1cm} (1)

where $N$ is the number of atoms or molecules per unit volume, and

$$\sigma = \sum_i \sigma_i.$$ \hspace{1cm} (2)

In a dilute aqueous environment, thermalized electrons undergo trapping and hydration in quick succession (within $\sim 10^{-12}$ s) as a result of the water electric dipoles rotating under the influence of the negative charge (BERNAS et al., 1996). Some electrons that have kinetic energies lower than the first electronic excitation threshold of the medium, the so-called "subexcitation" electrons (PLATZMAN, 1955), may also undergo, prior to thermalization, prompt geminate ion recombination (FREEMAN, 1987) or induce the production of energetic (~1-5 eV) anion fragments via formation of dissociative negative ion states (resonances) (i.e., dissociative electron attachment, or DEA) (CHRISTOPHOROU et al., 1984; BASS and SANCHE, 2003). As a consequence of the energy gained by the medium, a sequence of very fast reactions and molecular rearrangements lead to the formation of new, highly nonhomogeneously distributed chemical species in the system, such as charged and/or neutral molecular fragments, reactive free radicals, and other excited chemical intermediates. The trail of the initial physical events, along with the chemical species, is generally referred to as the track of a charged particle, and its overall detailed spatial distribution, including contributions from secondary electrons, is commonly known as "track structure" (see, for example: PARETZKE, 1987; MAGEE and CHATTERJEE, 1987; KRAFT and KRÄMER, 1993; PARETZKE et al., 1995; MOZUMDER, 1999; LAVERNE, 2000, 2004).

I.3 Structure of proton tracks in liquid water

I.3.1 Track structure in radiation chemistry and radiobiology
A great many experimental and theoretical studies have shown that the quantities and proportions of the chemical products formed in the radiolysis of water are highly dependent on the distances separating the primary radiolytic species from each other along the track of the ionization radiation. The distribution of separations, referred to as the “track structure” (see above), is determined to a large extent by the distribution of the physical energy deposition events and their geometrical dispositions, or, in other words, by the quality of the radiation. In fact, track-structure effects are also usually called “LET effects” as most of the early studies used this parameter to characterize the different radiation chemical yields (or “g-values”) for various irradiating ions in liquid water. The radiation track structure is of crucial importance in specifying the precise spatial location and identity of all the radiolytic species and free-radical intermediates generated in the tracks, and their subsequent radiobiological action at the molecular and cellular levels. Track structure, coupled with a reaction scheme and yields of primary species, forms the basis of radiation-chemical theory (MOZUMDER, 1999). It is now well accepted by the scientific community that differences in the biochemical and biological effects (e.g., damage to DNA, changes in cell signaling, etc.) of different qualities of radiation must be analyzed in terms of track structure (CHATTERJEE and HOLLEY, 1993; MUROYA et al., 2006).

1.3.2 Low-LET radiation and track entities

The average LET of a 1-MeV electron in water is ~0.3 keV/µm. The track-averaged mean energy loss per collision event by such a fast electron is in the region ~48–65 eV (LAVERNE and PIMBLOTT, 1995; MOZUMDER, 1999; AUTSAVAPROMPORN, 2006). This means that the energy-loss events are, on the average, separated by distances of about 2000 Å. Historically, this nonhomogeneous distribution of energy deposition events in space gave rise to the development of the “spur” model for low-LET track structure (KARA-MICHAILOVA and LEA, 1940; ALLEN, 1948; SAMUEL and MAGEE, 1953; MAGEE, 1953; GANGULY and MAGEE, 1956), according to which the entire track is to be viewed as a random succession of (more or less spherical) spurs (sometimes called the “string-of-beads” model of a track), or spatially localized energy-loss events (it is assumed that irradiating particles are isolated from each other, an assumption not necessarily correct
at very high dose rates or with very short pulses of intense beams). The few tens of electronvolts deposited in a spur cause a secondary electron to be ejected from a molecule. As the ejected electron moves away, it undergoes collisions with surrounding water molecules, loses its excess energy, and becomes thermalized (~0.025 eV) within about 80–120 Å of its geminate positive ion (GOULET and JAY-GERIN, 1988; MUROYA et al., 2002; MEESUNGNOEN et al., 2002a; PIMBLOTT and MOZUMDER, 2004). This electron thermalization distance or “penetration range” can be viewed as an estimate of the average radius of the spurs in the first stages of their development. Thus, the individual spurs produced by a radiation of low LET (so-called “sparsely” ionizing radiation) are so far apart along the track that they are not initially overlapping (but they will overlap somewhat later as they develop in time).

![Diagram of track structure classification](image)

**Figure 1.1** Track structure classification by track entities so-called spurs (spherical entities, up to 100 eV), blobs (spherical or ellipsoidal, 100–500 eV), and short tracks (cylindrical, 500 eV–5 keV) for a primary high-energy electron (not to scale; Adapted from BURTON, 1969). The energy partition between the three track entities strongly depends on the incident particle energy, dividing approximately as the ratio of 0.75:0.12:0.13 between the spur, blob, and short track fractions for a 1-MeV electron in liquid water (PIMBLOTT et al., 1990).

In their pioneering work to apply the “spur” model to the radiation chemical consequences of the different energy-loss processes, MOZUMDER and MAGEE (1966a,b) considered, somewhat arbitrarily, a low-LET track as composed of a random sequence of
three types of essentially nonoverlapping entities: "spurs, blobs, and short tracks" (Figure. 1.1). The spur category contains all track entities created by the energy losses between the lowest excitation energy of water and 100 eV; in most cases, there are one to three ion pairs in such isolated spatial areas and about the same number of excited molecules (PIMBLOTT and MOZUMDER, 1991). Blobs are defined as track entities with energy transfers between 100 and 500 eV, and short tracks as those with energy transfers between 500 eV and 5 keV. Secondary electrons produced in energy transfers above 5 keV are considered as "branch tracks". Short and branch tracks are, collectively, described as δ-rays. This old concept of track entities proved to be very helpful in greatly facilitating the visualization of track processes and in modeling radiation-chemical kinetics. It is still a useful approach for the classification of track structures, since it takes into account the spatial arrangements of initial species, which affect their subsequent reactions.

![Simulated tracks](image)

**Figure 1.2** Simulated tracks (projected into the $XY$ plane of figure) of five 150-keV electrons in water, showing the stochastic nature of paths. Each electron is generated at the origin and starts moving vertically upwards.

To illustrate the low-LET tracks, Figure. 1.2 shows an example of the complete tracks of five 150-keV electrons and the secondary electrons they produce in water, calculated by our Monte-Carlo simulation program.
1.4 Radiolysis of liquid water and aqueous solutions

1.4.1 The radiolysis of water

The complex sequence of events that are generated by using ionizing radiation with water is usually divided into three stages (PLATZMAN, 1958): (1) deposition of radiant energy and formation of initial products in a specific, highly nonhomogeneous track structure geometry ("physical" stage), (2) establishment of thermal equilibrium in the bulk medium with reactions and reorganization of initial products to give stable molecules and chemically reactive species such as free atoms and radicals ("physicochemical" stage), and (3) thermal chemistry during which the various reactive species diffuse and react with one another (or with the environment) ("chemical" stage). Briefly, the radiolysis of pure deaerated liquid water by low-LET radiation (such as $^{60}$Co $\gamma$-rays, hard X-rays, fast electrons, or high-energy protons) principally leads to the formation of the radicals and molecular products $e^-_{aq}$ (hydrated electron), $H^+$ (hydrogen atom), $H_2$ (molecular hydrogen), $'OH$ (hydroxyl radical), $H_2O_2$ (hydrogen peroxide), $HO_2^-/O_2^-$ (hydroperoxyl/superoxide anion radicals, $pK_a = 4.8$), $H^+$, $OH^-$, etc. (for a review, see: SPINKS and WOODS, 1990). Under ordinary irradiation conditions, these species are generated nonhomogeneously on subpicosecond time scales in small, spatially isolated regions of dense ionization and excitation events, referred to as "spurs" (MAGEE, 1953), along the track of the radiation. Owing to diffusion from their initial positions, the radiolytic products then either react within the spurs as they expand or escape into the bulk solution. At ambient temperature, this spur expansion is essentially complete by about $10^{-6}$-$10^{-7}$ s after the initial energy deposition. The so-called "primary" radical and molecular yields ("long-time" or "escape" yields) $g(e^-_{aq})$, $g(H^+)$, $g(H_2)$, $g('OH)$, $g(H_2O_2)$, etc., represent the numbers of species of each kind formed or destroyed per 100 eV of absorbed energy that remain after spur expansion and become available to react with added solutes (treated as spatially homogeneous) at moderate concentrations.

The radiolysis of pure deaerated (air-free) liquid water for low-LET radiation can be described by the following global equation, written for an absorbed energy of 100 eV
(FERRADINI and JAY-GERIN, 1999) (the symbol $\nearrow$ is used to distinguish reactions brought about by the absorption of ionizing radiation):

$$G_{H_2O} H_2O \nearrow Ge^{-}_{aq} e^{-}_{aq} + G_{H^+} H^+ + G_{H_2} H_2 + G_{H_2^+} H^2 + G_{OH^-} OH^-$$

$$+ G_{OH}^\cdot OH + G_{H_2O_2} H_2O_2 + G_{HO_2^-/O_2^-} HO_2^-/O_2^- + ... , \quad (3)$$

where the coefficients $G_X$ – also written as $g(X)$ – are the "primary" radical and molecular yields of the various radiolytic species $X$, and $G_{H_2O}$ denotes the corresponding yield for net water decomposition. For $^{60}$Co $\gamma$-rays (photon energies of 1.17 and 1.33 MeV), hard X-rays or fast electrons of the same energies, at neutral pH and 25 °C (average LET ~ 0.3 keV/\mu m), the most recently reported values of the primary yields are (LAVERNE, 2004) (in units of molecules per 100 eV): \(^1\)

$$Ge^{-}_{aq} = 2.50 \quad G_{H^+} = 0.56 \quad G_{H_2} = 0.45$$

$$G_{OH}^\cdot = 2.50 \quad G_{H_2O_2} = 0.70 \quad (4)$$

These primary yield values, including the contribution of $HO_2^-/O_2^-$ [note that, for low-LET radiolysis, $HO_2^-/O_2^-$ is a minor radiolytic product because its very small yield of ~0.02 molec./100 eV (HART, 1955; BJERGBAKKE and HART, 1971) accounts for less than 1% of the other primary radiolytic species], are linked by the following equations:

$$Ge^{-}_{aq} + G_{OH}^\cdot = G_{H^+}$$

$$Ge^{-}_{aq} + G_{H^+} + 2 G_{H_2} = G_{OH}^\cdot + 2 G_{H_2O_2} + 3 G_{HO_2^-/O_2^-} \quad (5)$$

expressing the charge conservation and material balance of Eq. (3).

The yields of the radical and molecular species produced by the irradiation within the lifetime of a spur vary with time, and also depend on the radiation type (or LET) and the added solute (scavenger) concentration. One of the main goals in the study of the radiation

\(^1\) These units (abbreviated as "molec./100 eV") for $g$-values are used throughout in this work. For conversion into SI units (mol J\(^{-1}\)): 1 molec./100 eV $\approx 1.0364 \times 10^{-7}$ mol J\(^{-1}\).
chemistry of water is the determination of those yields and their dependences as a function of those different parameters.

**I.4.2 Time scale of events and formation of primary radical and molecular products in neutral water radiolysis**

The overall process of producing chemical changes by ionizing radiation can be usually divided into three, more or less clearly delineated, consecutive, temporal stages (PLATZMAN, 1958; KUPPERMANN, 1959) (the time scale of events that occur in the radiolysis of water and aqueous solutions is shown in Figure. I.3) that are briefly described below.

(i) The "physical stage" consists of the phenomena by which energy is transferred from the incident ionizing radiation (energetic photons, for example, γ-rays from $^{60}$Co or X-ray photons, or charged particles, such as fast electrons, protons or heavy ions generated by a particle accelerator, or neutron radiation, or high-energy α-particles from suitable radioactive nuclides) to the system. It lasts not more than $\sim 10^{-16}$ s. The result of this energy absorption is the production, along the path of the radiation, of a large number of ionized and electronically excited water molecules (denoted $H_2O^+$ and $H_2O^{*\text{elec}}$, respectively; note that $H_2O^{*\text{elec}}$ represents here the many excited states, including the so-called superexcitation states (PLATZMAN, 1962a) and the collective electronic oscillations of the "plasmon" type (HELLER et al., 1974; KAPLAN and MITEREV, 1987; WILSON et al., 2001). The earliest processes in the radiolysis of water are:

$$H_2O \xrightarrow{\text{ionization}} H_2O^+ + e^- \quad (6)$$

$$H_2O \xrightarrow{\text{excitation}} H_2O^{*\text{elec}} \quad (7)$$

Generally, the electron ejected in the ionization event has sufficient energy to ionize or excite one or more other water molecules in the vicinity, and this leads, as mentioned above, to the formation of track entities, or "spurs", that contain the products of the events. For low-LET radiation, the spurs are separated by large distances relative to their diameter and the track can be viewed, at this stage, as a random succession of isolated spherical spurs.
(ii) The "physicochemical stage" consists of the processes that lead to the establishment of thermal equilibrium in the system. Its duration is about $10^{-12}$ s for aqueous solutions. During this stage, the ions and excited-state water molecules dissipate their excess energy by bond rupture, luminescence, energy transfer to neighboring molecules, etc. The ionized water molecules are unstable. They are allowed to undergo a random walk during their very short lifetime ($\sim 10^{-14}$ s) (MOZUMDER and MAGEE, 1975) via a sequence of electron transfers (about 20, one the average, over a few molecular diameters; COBUT et al., 1998) from neighboring water molecules to the H$_2$O$^{+}$ hole (i.e., electron-loss center) (OGURA and HAMILL, 1973). These short-lived H$_2$O$^{+}$ radical cations subsequently decompose to form 'OH radicals by transferring a proton to an adjacent H$_2$O molecule:

$$ \text{H}_2\text{O}^{+} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{+} + \cdot\text{OH}, \tag{8} $$

where H$_3$O$^{+}$ (or equivalently, H$_{\text{aq}}^{+}$) represents the hydrated hydrogen ion.

The energetic (or "dry") secondary electrons lose their kinetic energy via a sequence of interactions with the medium until they attain thermal energies ($\sim 0.025$ eV at 25 °C) after about $4 \times 10^{-14}$ s (MEESUNGNOEN et al., 2002a). In the course of their thermalization, "dry" electrons can be recaptured by their parent ions due to the Coulomb attraction of the latter which tends to draw them back together to undergo electron-cation "geminate" recombination:

$$ \text{e}^- + \text{H}_2\text{O}^{+} \rightarrow \text{H}_2\text{O}_{\text{vib}} \tag{9} $$

As the electron is recaptured, the parent ion is transformed into a (vibrationally) excited neutral molecule.

The electron released in the ionization event can cause further ionization and excitation to occur if it has sufficient kinetic energy. Eventually, its energy falls below the
**Event**

$H_2O + H_3O^+ + e^- + H_2O$

- $H_2O^+_{vib}$ (Geminate recombination ($< 10^7 fs$))
- $H_2O^-$ (proton transfer ($10^7-40 fs$))
- $H' + 'OH$ (Dissociation of excited water molecule)
- $H_2 + 0(1D)$ (Nonradiative decay back to ground-state water)

**Approximate time scale**

- Physical stage ($<10^{-12} s$)
- Physico-chemical stage ($10^{-12} - 10^{-12} s$)
- Nonhomogeneous chemical stage ($10^{-12} - 10^{-6} s$)

**Examples of spur reactions:**

- $e^-_{eq} + e^-_{eq} \rightarrow 2H_2O \rightarrow H_2 + 2 OH^-$
- $'OH + H_2O_2 \rightarrow HO_2 + H_2O$
- $H' + H' \rightarrow H_2$
- $H' + H_2O_2 \rightarrow 'OH + H_2O$

(more than 60 reactions...)

**Figure 1.3** Time scale of events that occur in the low-LET radiolysis of neutral, deaerated water (Adapted from MEESUNGNOEN, 2007).
first electronic excitation threshold of water (~7.3 eV; see: MICHAUD et al., 1991), forming the so-called “subexcitation electron” (PLATZMAN, 1955). This latter loses the rest of its energy relatively slowly by exciting vibrational and rotational modes of water molecules. Once thermalized ($e'_{th}$), it can be localized or “trapped” (then forming the so-called “wet” electron whose exact physical nature is still the subject of investigation) ($e'_{tr}$) in a pre-existing potential energy well of appropriate depth in the liquid before it reaches a fully relaxed, hydrated state ($e'_{aq}$) as the dipoles of the surrounding molecules orient under the influence of the negative charge of the electron. In liquid water at 25 °C, thermalization, trapping, and hydration can then follow in quick succession in less than ~10^-12 s (for example, see: JAY-GERIN et al., 2008, and references therein):

$$e^- \rightarrow e^{-}_{th} \rightarrow e^{-}_{tr} \rightarrow e^{-}_{aq} \quad (10)$$

In the course of its thermalization, the ejected electron can also temporarily be captured by a water molecule to form a transient anion

$$e^- + H_2O \rightarrow H_2O^- \quad (11)$$

This anion then undergoes dissociation mainly into $H^-$ and $'OH$ according to

$$H_2O^- \rightarrow H^- + 'OH, \quad (12)$$

followed by the reaction of the hydride anion with another water molecule through a fast proton transfer reaction:

$$H^- + H_2O \rightarrow H_2 + OH^- \quad (13)$$

Reactions (11) and (12) correspond to the so-called “dissociative electron attachment” (or DEA) process, which has been observed in amorphous solid water at ~20 K for electron energies between about 5 and 12 eV (ROWNTREE et al., 1991). DEA to water was suggested to be responsible, at least in part, for the yield of “nonscavengeable” molecular hydrogen in the radiolysis of liquid water at early times (PLATZMAN, 1962b; FARAGGI and DÉSALOS, 1969; GOULET and JAY-GERIN, 1989; KIMMEL et al., 1994; COBUT et al., 1996). This proposed mechanism for the production of $H_2$ has received strong
support from recent experiments that have shown that the previously accepted nonscavengeable yield of H₂ is due to precursors of e⁻aq and it can be lowered with appropriate (dry electron) scavengers at high concentration (PASTINA et al., 1999).

Excited molecules may be produced directly in an initial act [reaction (7)] or by neutralization of an ion [reaction (9)]. We have little knowledge about the channels through which the excited water molecules in the liquid phase decay and the branching ratios associated with each of them. Fortunately, the contribution of the water excited states to the primary radical and molecular products in the water radiolysis is of relatively minor importance in comparison with that of the ionization processes, so that the lack of information about their decomposition has only limited consequences. Consequently, the competing deexcitation mechanisms of H₂O* are generally assumed to be essentially the same as those reported for an isolated water molecule (it should be noted here that the same decay processes have been reported to occur for the electronically and vibrationally excited H₂O molecules in the gas phase), namely (see, for example: SWIATLA-WOJCIK and BUXTON, 1995; COBUT et al., 1998; MEESUNGNOEN and JAY-GERIN, 2005a):

\[
\begin{align*}
H₂O^* & \rightarrow H^+ + \cdot OH \quad (14a) \\
H₂O^* & \rightarrow H₂ + O(^1D) \quad (14b) \\
H₂O^* & \rightarrow 2H^+ + O(^3P) \quad (14c) \\
H₂O^* & \rightarrow H₂O + \text{release of thermal energy} \quad (14d)
\end{align*}
\]

where O(^1D) and O(^3P) represent oxygen atoms produced in their singlet ^1D excited state and triplet ^3P ground state, respectively (see Figure. 1.3). Note that the dissociation of H₂O* via reaction (14a) is the main source of the “initial” (at \(\sim 10^{-12}\) s, i.e., at the end of the physicochemical stage, prior to spur or track expansion) yield of hydrogen atoms. As for the different branching ratios (or decay probabilities) associated with reactions (14a-d), they are chosen in order to consistently match the observed picosecond G-values of the various spur species (MUROYA et al., 2002; MEESUNGNOEN and JAY-GERIN, 2005a). It should also be noted here that the O(^1D) atoms produced in reaction (14b) react very
efficiently with water to form H₂O₂ or possibly also 2°OH (TAUBE, 1957; BIEDENKAPP et al., 1970). By contrast, ground-state oxygen atoms O(³P) in aqueous solution are rather inert to water but react with most additives (AMICHAI and TEININ, 1969).

(iii) The "nonhomogeneous chemical stage" consists of the period after ~10⁻¹² s, during which the radiolytic species generated previously in a nonhomogeneous track structure (e⁻aq, 'OH, H', H₂O⁺, H₂, H₂O₂, OH', 'O', ...) undergo chemical reactions as they diffuse away from the site where they were originally produced. These species react together to form molecular or secondary radical products, or with dissolved solutes (if any) present at the time of irradiation, until all spur/track reactions are complete. Table 1 gives the principal reactions that are likely to occur while the spurs expand. The time for completion of spur processes is generally taken to be ~10⁻⁷-10⁻⁶ s. By this time, the spatially nonhomogeneous distribution of reactive species has relaxed. Beyond a few microseconds, the reactions which occur in the bulk solution at room temperature can usually be described with conventional homogeneous chemistry methods (for example, see: PASTINA and LAVERNE, 2001).

1.5 The effect of pH

For the ⁶⁰Co γ-irradiated 0.4 M sulphuric acid aqueous solutions at room temperature (pH 0.46), representative values of the primary free-radical and molecular product yields (expressed in units of molec./100 eV) are (HOCHANADEL and LIND, 1956; FERRADINI and PUCHEAULT, 1983):

\[
\begin{align*}
G_{\text{e}^\text{-aq}} + G_{\text{H}} & = 3.70 \\
G_{\text{H}_2} & = 0.40 \\
G_{\text{2OH}} & = 2.9 \\
G_{\text{H}_2\text{O}_2} & = 0.80
\end{align*}
\]

In fact, radiolysis experiments concerning acidic solutions were carried out before those for neutral solutions [the most commonly used acid was H₂SO₄ in 0.4 M aqueous solutions, although a few other acids such as HCl, HClO₄, and (COOH)₂ were also
Table 1  Main spur/track reactions and rate constants \((k)\) for the radiolysis of pure liquid water at 25 °C (from MEESUNGNOEN, 2007). Some values of \(k\) have been updated by using the most recently available data of ELLIOT and BARTELS (2009).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(k (M^1 s^{-1}))</th>
<th>Reaction</th>
<th>(k (M^1 s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H^+ + H^+ \rightarrow H_2)</td>
<td>5.2 \times 10^8</td>
<td>(e^- \rightarrow e^- + H_2 + 2 \text{ OH}^-)</td>
<td>7.3 \times 10^9</td>
</tr>
<tr>
<td>(H^+ + \text{OH} \rightarrow \text{H}_2\text{O})</td>
<td>1.6 \times 10^9</td>
<td>(e^- + H^+ \rightarrow H^\cdot)</td>
<td>2.1 \times 10^10</td>
</tr>
<tr>
<td>(H^+ + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{OH}^-)</td>
<td>3.6 \times 10^7</td>
<td>(e^- + \text{O}_2^- \rightarrow \text{H}_2\text{O}_2 + 2 \text{ OH}^-)</td>
<td>1.3 \times 10^10</td>
</tr>
<tr>
<td>(H^+ + e^- \rightarrow \text{H}_2 + \text{OH}^-)</td>
<td>2.8 \times 10^10</td>
<td>(e^- + \text{HO}_2^- \rightarrow \text{O}_2^- + \text{OH}^-)</td>
<td>3.51 \times 10^9</td>
</tr>
<tr>
<td>(H^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^-)</td>
<td>2.4 \times 10^7</td>
<td>(e^- + \text{O}_2^- \rightarrow 2 \text{ OH}^-)</td>
<td>2.31 \times 10^10</td>
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<td>(H^+ + \text{O}_2^- \rightarrow \text{HO}_2^-)</td>
<td>1.3 \times 10^10</td>
<td>(e^- + \text{H}_2\text{O} \rightarrow H^\cdot + \text{OH}^-)</td>
<td>15.8</td>
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<td>(H^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2)</td>
<td>1.1 \times 10^10</td>
<td>(e^- + \text{O}_2 \rightarrow \text{O}_2^-)</td>
<td>2.3 \times 10^10</td>
</tr>
<tr>
<td>(H^+ + \text{HO}_2^- \rightarrow \text{OH}^- + \text{OH}^-)</td>
<td>1.1 \times 10^9</td>
<td>(e^- + \text{HO}_2^- \rightarrow \text{HO}_2^-)</td>
<td>1.3 \times 10^10</td>
</tr>
<tr>
<td>(H^+ + e^\text{aq} \rightarrow \text{OH}^-)</td>
<td>1.5 \times 10^8</td>
<td>(e^- + \text{O}_2 \rightarrow \text{O}_2^-)</td>
<td>2.0 \times 10^10</td>
</tr>
<tr>
<td>(H^+ + O^\cdot \rightarrow OH^-)</td>
<td>2.0 \times 10^9</td>
<td>(e^- + \text{O}_2 \rightarrow \text{O}_2^-)</td>
<td>3.6 \times 10^10</td>
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<td>(H^+ + \text{O}_2^- \rightarrow \text{OH}^- + \text{O}_2)</td>
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<td>(H^+ + \text{O}_2^- \rightarrow \text{HO}_2^-)</td>
<td>5.0 \times 10^10</td>
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<tr>
<td>(\text{OH}^- + \text{OH} \rightarrow \text{H}_2\text{O}_2)</td>
<td>6.3 \times 10^6</td>
<td>(H^+ + \text{OH}^- \rightarrow \text{H}_2\text{O})</td>
<td>1.2 \times 10^11</td>
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<tr>
<td>(\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O})</td>
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<td>(H^+ + \text{O}_2^- \rightarrow \text{OH}^- + \text{O}_2)</td>
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<tr>
<td>(\text{OH}^- + \text{H}_2 \rightarrow H^\cdot + \text{H}_2\text{O})</td>
<td>4.0 \times 10^7</td>
<td>(\text{OH}^- + e^\text{aq} \rightarrow \text{OH}^-)</td>
<td>4.2 \times 10^8</td>
</tr>
<tr>
<td>(\text{OH}^- + e^\text{aq} \rightarrow \text{OH}^-)</td>
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<td>(\text{OH}^- + \text{HO}_2^- \rightarrow \text{O}_2^- + \text{H}_2\text{O})</td>
<td>1.3 \times 10^10</td>
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<td>(\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^- + \text{H}_2\text{O})</td>
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<td>(\text{O}_2 + \text{O}_2^- \rightarrow \text{O}_3^-)</td>
<td>3.7 \times 10^8</td>
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<td>(\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O})</td>
<td>9.0 \times 10^10</td>
<td>(\text{O}_2 + \text{O}_2^\text{aq} \rightarrow \text{O}_3)</td>
<td>4.0 \times 10^9</td>
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<td>(\text{OH}^- + \text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-)</td>
<td>1.1 \times 10^10</td>
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<td>9.7 \times 10^7</td>
</tr>
<tr>
<td>(\text{OH}^- + \text{HO}_2^- \rightarrow \text{HO}_2^- + \text{OH}^-)</td>
<td>8.3 \times 10^9</td>
<td>(\text{HO}_2^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2)</td>
<td>1.94 \times 10^8</td>
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<tr>
<td>(\text{OH}^- + e^\text{aq} \rightarrow \text{OH}^-)</td>
<td>2.02 \times 10^9</td>
<td>(\text{HO}_2^- + e^\text{aq} \rightarrow \text{HO}_2^- + \text{O}_2)</td>
<td>2.02 \times 10^10</td>
</tr>
<tr>
<td>(\text{OH}^- + e^\text{aq} \rightarrow \text{OH}^-)</td>
<td>1.0 \times 10^9</td>
<td>(\text{HO}_2^- + \text{H}_2\text{O} \rightarrow H^\cdot + \text{O}_2^-)</td>
<td>1.4 \times 10^8</td>
</tr>
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<td>(\text{OH}^- + \text{O}_2^- \rightarrow \text{O}_2^- + \text{OH}^-)</td>
<td>8.5 \times 10^9</td>
<td>(\text{O}_2^- + \text{O}_2^- \rightarrow \text{O}_2 + 2 \text{ OH}^-)</td>
<td>6.0 \times 10^8</td>
</tr>
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<td>(\text{OH}^- + \text{O}_2^- \rightarrow \text{O}_2^- + \text{OH}^-)</td>
<td>1.11 \times 10^10</td>
<td>(\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{OH}^-)</td>
<td>0.155</td>
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<tr>
<td>(\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}^-)</td>
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<td>(\text{O}_2^- + \text{O}_2^- \rightarrow \text{O}_3^- + \text{O}_2)</td>
<td>1.5 \times 10^9</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O})</td>
<td>1.33 \times 10^10</td>
<td>(\text{HO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^-)</td>
<td>1.27 \times 10^8</td>
</tr>
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<td>(\text{H}_2\text{O}_2 + e^\text{aq} \rightarrow \text{HO}_2^- + \text{OH}^-)</td>
<td>1.6 \times 10^9</td>
<td>(\text{HO}_2^- + e^\text{aq} \rightarrow \text{O}_2^- + \text{OH}^-)</td>
<td>8.02 \times 10^8</td>
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<td>(\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{HO}_2^- + \text{OH}^-)</td>
<td>5.55 \times 10^8</td>
<td>(\text{HO}_2^- + e^\text{aq} \rightarrow \text{O}_2^- + \text{OH}^-)</td>
<td>5.3 \times 10^8</td>
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<td>(\text{H}_2 + e^\text{aq} \rightarrow \text{H}^\cdot + \text{OH}^-)</td>
<td>4.77 \times 10^7</td>
<td>(\text{O}_2^- + \text{O}_2^- \rightarrow \text{2 O}_2^-)</td>
<td>7.0 \times 10^8</td>
</tr>
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<td>(\text{H}_2 + \text{O}_2^- \rightarrow \text{H}^\cdot + \text{OH}^-)</td>
<td>1.3 \times 10^8</td>
<td>(\text{O}_2^- + \text{O}_2^- \rightarrow \text{2 O}_2^-)</td>
<td>7.0 \times 10^8</td>
</tr>
<tr>
<td>(e^\text{aq} + \text{O}_2^- \rightarrow \text{O}_3)</td>
<td>2.2 \times 10^10</td>
<td>(\text{O}_2^- + \text{OH}^- \rightarrow \text{OH} + \text{OH}^-)</td>
<td>1.3 \times 10^8</td>
</tr>
<tr>
<td>(\text{O}_2^- + \text{H}_2\text{O} \rightarrow 2 \text{ OH}^-)</td>
<td>1.9 \times 10^9</td>
<td>(\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{O}^- + \text{O}_2)</td>
<td>46.5</td>
</tr>
</tbody>
</table>
employed in radiation yield determinations at low pH) for historical reasons related to the early development of the standard aerated ferrous sulphate (Fricke) dosimeter (FRICKE and MORSE, 1929). One of the reasons that dictated the choice of sulphuric acid came from the fact that the dominant anion HSO$_4^-$ was then considered to not intervene in the course of the radiolysis. The concentration of 0.4 M H$_2$SO$_4$ was originally selected to provide the same mass absorption for X-rays in the dosimeter solution as in air (FRICKE and HART, 1966). At such a high concentration of H$_2$SO$_4$, the H$^+$ ions very rapidly scavenge most, if not all, of the e$^{-}_{aq}$ radicals in the spurs/tracks to form H$^*$ atoms (HAYON, 1968; BUXTON, 1967, 1968; DRAGANIC and DRAGANIC, 1971):

$$e^{-}_{aq} + H^+ \rightarrow H^*$$

with a bimolecular rate constant $k_{16} = 1.12 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ (value corrected to take into account the effects of the ionic strength at this acid concentration) (ELLIOT, 1994; JONAH et al., 1977). Figure 1.4 shows the variation of the primary yields of radicals and molecular products in the γ-radiolysis of (air-free) water as a function of pH in the range 1.3-13 (DRAGANIC et al., 1969; DRAGANIC and DRAGANIC, 1971).

**Figure 1.4** The effect of pH on the primary radical and molecular yields in γ-radiolysis of water. There is a relatively small increase (~7%) in the water decomposition when the pH is varied from 3 to 1.3 (Adapted from DRAGANIC et al., 1969).
As we can see, above pH 4 up to strongly alkaline solutions, the radical and molecular yields are essentially constant and independent of pH. In acid solutions with pH < 4, the yield of the “reducing” free radicals $g(e^-_{aq})$ and $g(H')$, represented by the sum $g(e^-_{aq}+H') = g(e^-_{aq}) + g(H')$, increases as the proportion of $H'$ increases through reaction (16). An increase in acidity below pH 4 also leads to slight increases in the primary yields of “oxidizing” products $g(OH)$ and $g(H_2O_2)$, while there is a slight decrease in $g(H_2)$ (for example, see: FERRADINI and JAY-GERIN, 2000).

At high acidities (pH < 1), a certain proportion of the $'OH$ radicals react with hydrogen sulfate anions $HSO_4^-$ to form the sulfate radical $SO_4^{2-}$ according to

$$'OH + HSO_4^- \rightarrow . H_2O + SO_4^{2-}$$

with a rate constant taken to be $k_{17} = 1.5 \times 10^5 \ M^{-1} \ s^{-1}$ (MEESUNGNOEN et al., 2001; AUTSAVAPROMPORN et al., 2007). As a result of reaction (17), $g(OH)$ reaches a weakly pronounced maximum around pH 1 and then diminishes steeply as the pH is reduced below 1. This has been well reproduced by AUTSAVAPROMPORN et al. (2007) who used Monte-Carlo simulations to investigate the influence of acidity on the primary yields of chemical species produced in the radiolysis of deaerated aqueous sulfuric acid solutions over the range from neutral solution to 0.4 $M$ $H_2SO_4$.

### I.6 The Fricke, or ferrous sulfate, chemical dosimeter

One of the most extensively studied systems in radiation chemistry is the aerated dilute (1-10 mM) solution of FeSO$_4$ in aqueous 0.4 $M$ $H_2SO_4$, which is called the Fricke dosimeter after Hugo Fricke, who first published an account of its properties in 1927 (FRICKE & MORSE, 1927, 1929). The Fricke dosimeter is widely accepted in radiation-chemical work because of the accuracy, reproducibility, and linearity of its response as a function of dose (with care, Fricke dosimetry is capable of 0.1% precision for $^{60}$Co $\gamma$-rays, high-energy X-rays or fast electrons) (KLASSEN et al., 1999). The chemistry of this system is based on the oxidation of ferrous ions (Fe$^{2+}$) to ferric ions (Fe$^{3+}$) by the oxidation
species 'OH, HO2*, and H2O2 that are produced in the radiolytic decomposition of water at low pH and in the presence of oxygen (ALLEN, 1961; SPINKS and WOODS, 1990). The Fricke dosimeter is a broadly used chemical dosimeter because the production of ferric ions is well reproducible and has been accurately calibrated (FRICKE and HART, 1966). In fact, at the present time, its well understood characteristics are a standard in radiation chemical work for comparison of yields under various conditions, both for experiment and for theoretical calculations. The radiation chemical yields of ferric ions, G(Fe3+), can be expressed in terms of the primary free radical and molecular yields g(H'), g(OH), g(H2O2), and g(HO2*) of the radiolysis of aqueous 0.4 M H2SO4 solutions by the following stoichiometric equations (SPINKS and WOODS, 1990):

$$G(Fe^{3+}) = 3 [g(e_{aq}^- + H^') + g(HO_2^*)] + g(OH) + 2 g(H_2O_2)$$  \hspace{1cm} (18)

This relationship, which has been confirmed by experiment, shows that the production of Fe3+ ions is highly sensitive to factors that alter the free-radical yields, especially the yield of H' atoms. In particular G(Fe3+) depends on LET or the type of the radiation used. Data by a number of different authors have shown that G(Fe3+) steadily decreases with increasing LET, this dependence reflecting the lower yields of radicals that escape the high-LET track as compared with low-LET radiolysis (for example, see: AUTSAVAPROMPORN et al., 2007, and references therein). The recommended value of the limiting yield of the Fricke dosimeter, obtained for 60Co γ-rays or fast electrons at room temperature, is ~15.6 molec./100 eV. Representative values of G(Fe3+) for low-LET radiation are shown in Table 2.

The part played by sulfuric acid and its anions is generally ignored when the ferrous sulfate system is described, although with the standard dosimeter solution (0.4 M H2SO4) a certain proportion of the hydroxyl radicals react with HSO4- ions to form the sulfate radical SO4^2- [see reaction (17)]. However, this does not affect the overall ferric ion yield G(Fe3+), which remains the same as given by Eq. (16), since SO4^2- (or, equivalently, its protonated
Table 2 Values of ferric-ion yields $G(\text{Fe}^{3+})$ (in molec./100 eV) for the Fricke dosimeter irradiated with different types of radiation, at room temperature.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>LET $^{(a)}$ (keV/μm)</th>
<th>$G(\text{Fe}^{3+})$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co $\gamma$-rays</td>
<td>~0.3</td>
<td>15.6 ± 0.3</td>
<td>Hochanadel &amp; Ghormley (1953)</td>
</tr>
<tr>
<td>2-MeV cathode rays</td>
<td>~0.3</td>
<td>15.45 ± 0.11</td>
<td>Schuler &amp; Allen (1956)</td>
</tr>
<tr>
<td>(electrons)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20-MeV X-rays</td>
<td>~0.2</td>
<td>15.55 ± 0.1</td>
<td>Klassen et al. (1999)</td>
</tr>
</tbody>
</table>

$^{(a)}$ "Mean" LET values, taken from WATT (1996) and AUTSAVAPROMPORN et al. (2007).

Form HSO$_4^-$, although no pK$_a$ value has been determined) is stoichiometrically equivalent to ·OH, oxidizing one ferrous ion to a ferric ion (Neta et al., 1988):

$$\ce{Fe^{2+} + SO4^- -> Fe^{3+} + SO4^{2-}} \quad (19)$$

($k_{19} \approx 2.79 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, taking into account ionic strength effects; see below)

(note that, contrary to HSO$_4^-$, the sulfate ion SO$_4^{2-}$ has been reported to be unreactive toward ·OH or dimerizing to a product (S$_2$O$_8^{2-}$) that, like H$_2$O$_2$, oxidizes two ferrous ions (Spinks and Woods, 1990).

The usual range of the Fricke dosimeter is from ~30 to 400 Gy. The upper limit is set by oxygen depletion [when oxygen is consumed, $G(\text{Fe}^{3+})$ decreases to ~8.2 molec./100 eV for fast electrons and $^{60}$Co $\gamma$-radiation; see, for example: Fricke and Hart, 1966] and the lower limit by the analytical method. By suitable modifications of the composition of the system or of its analysis, it is possible to extend the useful range beyond these limits. Higher doses can be measured by means of the "super" Fricke dosimeter, which consists of 10 mM Fe$^{2+}$ in 0.4 M H$_2$SO$_4$ and is saturated with pure oxygen ($\sim 1.25 \times 10^{-3} \text{ M O}_2$). This system can be used up to 2000 Gy.
I.7 The effect of temperature

A knowledge of the radiation chemistry of water at high temperature became important when water-cooled reactors came into use. The cooling water is, of course, subjected to an intense radiation field comprising low-LET $\gamma$-radiation and also fast neutrons which interact with water molecules to produce recoil high-LET protons. In operational reactors it is necessary to select conditions such that the radiolytic decomposition of the water is suppressed in order to reduce deleterious corrosion, hydriding, and cracking processes both in the core and in the associated piping components (BURNS and MOORE, 1976; COHEN, 1980; HICKEL, 1991; ELLIOT, 1994; ELLIOT et al., 1996a; McCRACKEN et al., 1998; BUXTON, 2001; STUART et al., 2002; KATSUMURA, 2004; CHRISTENSEN, 2006; EDWARDS et al., 2007), and this is achieved most efficiently when the radiation chemistry of water under reactor conditions is understood. However, direct measurement of the chemistry in reactor cores is extremely difficult. The extreme conditions of high temperature, pressure, and mixed neutron/gamma radiation fields are, of course, not compatible with normal chemical instrumentation. For these reasons, theoretical calculations and chemical models have been used, with some simplifying assumptions, to simulate and predict the detailed radiation chemistry of the water in the core and the consequences for materials.

To predict the effect of radiation at elevated temperature, it is necessary to know the temperature dependence on chemical yields of oxidizing ($\cdot$OH, H$_2$O$_2$) and reducing ($e_{aq}^\cdot$, H$^-$, H$_2$) radiolytic products as well as the temperature dependence of rate constants for the reactions taking place in spurs and tracks that result in these primary yields. The $g$-values for the primary yields formed by using low-LET (gamma or fast electrons) radiation at ambient temperature up to $\sim$300 °C have been determined by several groups of experimentalists (KENT and SIMS, 1992a,b; ELLIOT et al., 1993, 1996a,b; ELLIOT, 1994; SUNARYO et al., 1995a,b; ISHIGURE et al., 1995; KATSUMURA et al., 1998; ŠTEFANIĆ and LAVERNE, 2002). The yields of free radicals increase with temperature, which can readily be explained from the fact that many important reactions are not diffusion controlled and therefore have rate constants that increase less steeply with
temperature than do the diffusion coefficients of the individual species (for example, see: ELLIOT et al., 1996b; HERVÉ DU PENHOAT et al., 2000).² In other words, as the temperature is raised, diffusion of free radical species out of spurs/tracks increases more rapidly than recombination, and one should have less molecular recombination products (namely, water, H₂, and H₂O₂) (ELLIOT et al., 1993; JANIK et al., 2007). Deterministic diffusion-kinetic modeling of spur processes (KABAKCHI and BUGAENKO, 1992; LAVERNE and PIMBLOTT, 1993; SWIATLA-WOJCIK and BUXTON, 1995, 1998, 2000) and stochastic Monte-Carlo simulations (HERVÉ DU PENHOAT et al., 2000, 2001) have also reproduced those experimental data satisfactorily. One difficulty, however, appears in explaining the experimentally observed monotonic increase of the H₂ yield. In fact, although the above calculations have explained an increase of g(H₂) up to about 200 °C as resulting from the bimolecular reaction of e⁻\(_{aq}\) (SWIATLA-WOJCIK and BUXTON, 1995; HERVÉ DU PENHOAT et al., 2000), above 200 °C the computed g(H₂) tends to decrease with increasing temperature (see Figure. 1.3). The fact that g(H₂) continues to increase with temperature (even though the yield of the other molecular recombination product, H₂O₂, decreases) raises interesting questions about the physicochemical stage of the radiolysis of water such as, for example, the need to postulate an additional channel for H₂ formation (SWIATLA-WOJCIK and BUXTON, 2005; BARTELS, 2009).

In order to update our computational results, we have used a most recent report compiled by ELLIOT and BARTELS (2009) which reviews the radiolysis data now available and, where possible, corrected the reported g-values and rate constants to provide a recommendation for the best values to use in the high-temperature modelling of light water radiolysis up to 350 °C. In this work, the authors have re-measured or re-evaluated the g-values for the primary radiolysis species for low-LET radiation as well as many of the reaction rate constants. Generally, they have been able to extend the measurements to

² Just recall here that, most generally, the yield of a species that escapes the spur/track depends on the competition between reactions in the spur/track and escape by diffusion out of the spur/track.
higher temperatures than the original investigations, thereby reducing or eliminating the need to "extrapolate" the data to the temperatures of interest.

I.8 Research objectives

A number of experiments have reported the radiolytic yields for the low-LET radiolysis of water as a function of temperature from 25-350 °C. It is shown that \( g(e^-_{aq}) \), \( g(H^+) \), \( g(\cdot OH) \), and \( g(H_2) \) continuously increase, while \( g(H_2O_2) \) decreases, with increasing temperature. As mentioned above, the temperature dependences of the \( g \)-values can be explained by the fact that many important reactions are partially diffusion controlled. In other words, as the temperatures increase, diffusion of free radical species out of spurs/tracks increases more rapidly than recombination, and one should have less molecular recombination products. This explanation, unfortunately, cannot be used for the temperature dependence of \( g(H_2) \) which increases as a function of temperature instead of decreasing. The fact that we cannot explain the anomalous increase of the \( H_2 \) yield as a function of temperature is of course a very strong motivation to enlarge our understanding of the effect of temperature on the radiolysis of water at elevated temperature.

In the present work, Monte-Carlo simulations have been performed in an attempt to study the effect of temperature on the low-LET radiolysis of pure liquid water. More specifically, the principal aims of this work are:

(1) To re-examine our Monte-Carlo simulations of the high-temperature water radiolysis at low LET in an attempt to reconcile our computed \( g \)-values of the various radiolytic species with the most recent experimental data up to 350 °C.

(2) To quantify the contribution of the reaction of hydrogen atoms with water \( H^+ + H_2O \rightarrow H_2 + \cdot OH \), a reaction that has been proposed to explain the anomalous increase in the primary yield of \( H_2 \) in the low-LET radiolysis of water at elevated temperature.

(3) To determine the temperature dependence of the lifetime of the spur (\( \tau_s \)) which is the time required for the changeover of nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution, in the low-LET radiolysis of water over the temperature range 25-350 °C by using a simple method based on the direct application of the Fricke dosimeter.
II. MONTE CARLO SIMULATIONS

II. 1 Overview of our Monte-Carlo simulations

Monte-Carlo simulation techniques were used to model the complex sequence of events that are generated in liquid water and aqueous solutions after the absorption of ionizing radiation. Such a procedure is well adapted to account for the *stochastic* nature of the phenomena, provided that realistic probabilities and cross sections for all possible events are adequately known. The simulation then allows one to reconstruct the intricate action of the radiation. It also offers a powerful tool for appraising the validity of different assumptions, for making a critical examination of proposed reaction mechanisms, and for estimating some unknown parameters. The accuracy of these calculations is best determined by comparing their predictions with experimental data on well-characterized chemical systems that have been examined with a wide variety of incident radiation particles and energies.

TURNER and his coworkers (1981, 1983, 1988) at the Oak Ridge National Laboratory (Oak Ridge, Tennessee, U.S.A.) jointly with MAGEE and CHATTERJEE at Lawrence Berkeley Laboratory (Berkeley, California, U.S.A.) were the first to use Monte-Carlo simulations to derive computer-plot representations of the chemical evolution of a few keV electron tracks in liquid water at times between \( \sim 10^{-12} \) and \( 10^{-7} \) s. Following this pioneering work, stochastic simulation codes employing Monte Carlo procedures were used with success by a number of investigators to study the relationship between the initial track structure and the ensuing chemical processes that occur in the radiolysis of both pure water and water containing solutes (for a comprehensive list and reviews, see, for example: BALLARINI et al., 2000; UEHARA and NIKJOO, 2006). Two main approaches have been widely used: (1) the "step-by-step" (or random flights Monte Carlo simulation) method, in which the trajectories of the diffusing species of the system are modeled by time-discretized random flights and in which reaction occurs when reactants undergo pairwise encounters, and (2) the "independent reaction times" (IRT) method (CLIFFORD et al., 1986; PIMBLOTT et al., 1991; PIMBLOTT and GREEN, 1995), which allows the calculation of reaction times without having to follow the trajectories of the diffusing species.
Among the stochastic approaches, the most reliable is certainly the full random flights simulation, which is generally considered as a measure of reality. However, this method can be exceedingly consuming in computer time when large systems (such as complete radiation tracks or track segments) are studied. The IRT method, a computer efficient stochastic simulation technique, has been devised to achieve much faster realisation than are possible with the full Monte-Carlo model. In essence, it relies on the approximation that the distances between pairs of reactants evolve independently of each other, and therefore the reaction times of the various potentially reactive pairs are independent of the presence of other reactants in the system.

In a program begun in the early 1990's, the Sherbrooke group has also developed and progressively refined with very high levels of detail several Monte Carlo codes that simulate the track structure of ionizing particles in water, the production of the various ionized and excited species, and the subsequent reactions of these species in time with one another or with available solutes (COBUT et al., 1994, 1998; FRONGILLO et al., 1996, 1998; HERVÉ DU PENHOAT et al., 2000; MEESUNGNOEN et al., 2001, 2003; MEESUNGNOEN and JAY-GERIN, 2005a,b; MUROYA et al., 2002, 2006; PLANTE et al., 2005; AUTSAVAPROMPORN et al., 2007). A most recent version of the Sherbrooke codes, called IONLYS-IRT (MEESUNGNOEN and JAY-GERIN, 2005a,b), has been used in the present work. Briefly, the IONLYS step-by-step simulation program models all the event of the physical and physicochemical stages in the track development. The third and final nonhomogeneous chemical stage is covered by the program IRT, which employs the "independent reaction times" (IRT) method (CLIFFORD et al., 1986; GREEN et al., 1990; PIMBLOTT et al., 1991) to model the chemical development that occur during this stage and to simulate the formation of measurable yields of chemical products. The detailed description and implementation of the IONLYS-IRT has already been given (MEESUNGNOEN and JAY-GERIN, 2005a,b, and references therein), and will not be reproduced here, only a brief overview of the most essential features of the simulation methodology and reaction scheme, pertinent to the current calculations, is given below.
II.1.1 The IONLYS code

The IONLYS simulation code is used to simulate the early "physical" and "physicochemical" stages of radiation action up to \( \sim 10^{12} \) s (see Sect. 1.4.2). It is actually composed of two components, one (named TRACPRO) for transporting the investigated incident charged particle (proton or any other heavy ion projectile) and another (named TRACELE) for transporting all of the energetic electrons (collectively named "secondary electrons") that result from the ionization of the water molecules. The code models, event by event, all the basic physical interactions (energy deposition) and the subsequent establishment of thermal equilibrium in the system (conversion of the physical products created locally after completion of the physical stage into the various "initial" chemical species of the radiolysis). For code structure of TRACPRO and TRACELE, see Figure. II.1 and Figure II.2.

In particular, IONLYS provides the detailed distribution of coordinates of all physical events that occur locally during the slowing-down of the irradiating charged particle and of all the secondary electrons that it has generated. The particle will interact with water based on the probability per unit distance of each particle’s energy or cross section. The code begins by selecting a particular distance to the first interaction site for the incident particle. The calculation continues with the random choice of the type of interaction (ionization, excitation of electronic, vibrational and rotational levels of single water molecules, excitation of plasmon-type collective modes, and elastic scattering) that occurs. If an inelastic collision is an ionization, the particle’s energy is reduced by the energy loss selected. The secondary electron produced is given a kinetic energy equal to this energy loss minus the binding energy (or ionization energy) of the target electron. Delta rays are produced at sites of high energy loss. Each time a secondary electron is produced, the code proceeds by transporting it until its energy falls below the threshold for electronic excitations, equal to \( \sim 7.3 \) eV for liquid water (MICHAUD et al., 1991) (these electrons we denote as "subexcitation" electrons). If a collision is elastic, an angle of scatter is selected and the flight distance for the next collision site is chosen. The probabilities or cross sections for all of the individual molecular processes and their alternatives are entered as input data in Monte-Carlo code, based on direct measurements (where available, as cross
section data in the case of liquid water are scarce) or on the theoretical estimations (COBUT et al., 1998; MEESUNGNOEN and JAY-GERIN, 2005a). These collision cross sections are needed to follow the history of an energetic charged particle and its products, covering all ranges of energy transferred in individual collisions. Most importantly, they provide the mean free path used to determine the distance to the next interaction, the type of interaction at each event, energy loss, and the angle of emission of the scattered particle (for example, see: DINGFELDER and FRIEDLAND, 2001; NIKJOO et al., 2006; DINGFELDER et al., 2008). The computer simulation thus provides complete information on the spatial distribution of ionized and excited water, H2O+ and H2O*, and subexcitation electrons, e_sub (energy < 7.3 eV), produced along the incident charged particle trajectory during the physical stage of the radiation action. This stage is concluded in ~10^-15 s. Full details of the cross-section database used in the IONLYS code can be found in the references cited (COBUT, 1993; COBUT et al., 1998; MEESUNGNOEN and JAY-GERIN, 2005a).

The simulations performed with IONLYS consist in the generation of short high-energy proton (ion) track segments in water. The primary particle is simulated until it has penetrated the chosen length of the track segment into the medium. Note that, due to its large mass, the proton (or the impacting heavy ion) is almost not deflected by collisions with the target electrons. In the present simulations, these deflections are simply neglected. The use of small path segments is particularly useful as the instantaneous LET of the incident particle is nearly constant over such segments and can be varied simply by changing its energy. All of the produced energetic (dry) secondary electrons are explicitly transported spatially from their initial energies until they reach the subexcitation energy region below ~7.3 eV, the threshold assumed for electronic excitation in liquid water (see Sect. 1.4.2).  

Recall here that most energy-loss events by the fast primary charged particle involve small transfers of energy. In fact, Monte-Carlo simulations have shown that the most probable energy loss for liquid water is 15-20 eV, while the track-averaged mean energy loss is around 50-60 eV, depending on the authors (LAVERNE and PIMBLOTT, 1995;
transferred are determined by the IONLYS code, event by event. All physical details about the various elastic and energy-loss processes involved and the corresponding scattering cross sections employed by IONLYS for the simulation can be found in COBUT (1993), COBUT et al. (1998), and MEESUNGNOEN and JAY-GERIN (2005a). The time that it takes a secondary electron to reach a subexcitation energy is $<10^{-15}$ s.

**Figure II.1** Algorithm of the TRACPRO simulation program

The thermalization of subexcitation electrons is treated by IONLYS using the distribution of thermalization distances obtained from Monte-Carlo track-structure calculations (GOULET and JAY-GERIN, 1989; GOULET et al., 1990, 1996; COBUT et al., 1998; AUTSAVAPROMPORN, 2006). COBUT et al. (1998) also calculated that, if we sum all the electrons ejected directly by the primary particle and by the successive generations of secondary electrons, 88% of them have kinetic energies less than 20 eV.
MEESUNGNOEN et al., 2002b) based on experimental scattering cross sections of slow (~1-100 eV) electrons in amorphous ice films at 14 K (MICHAUD et al., 2003) with corrections to account for the liquid phase. Given the initial position of the subexcitation electron, its position is simply displaced in a randomly selected, isotropic direction by the corresponding, energy-dependent mean penetration distance. At this new position, the electron is regarded as thermalized and subsequently trapped and hydrated where it is, an approximation likely to be valid in a highly polar medium such as liquid water in which very-low energy (e.g., “subvibrational”) electrons have a strong tendency - due to the presence of a large density of possible electron trapping sites - to get instantly trapped prior to thermalization (MOZUMDER, 1999). As mentioned in Sect. I.4.2, the time scale of thermalization, trapping, and hydration of a subexcitation electron in liquid water at 25 °C is less than ~10^{-12} s. Finally, it is worth recalling here that a certain proportion of subexcitation electrons will actually never get thermalized, but will instead undergo prompt recombination with their positive parent ion H_2O^+ or dissociative attachment onto a surrounding H_2O molecule (see Figure. 1.3). All details about the various parameters intervening in the IONLYS code to describe this competition between thermalization, geminate recombination, and dissociative attachment, as well as the values of the branching ratios used in the code for the different dissociative decay channels of the electronically and

\[ \text{29} \]

\[ \text{4 About 25.5% of the subexcitation electrons are found to initially recombine with H}_2\text{O}^+ (\text{MEESUNGNOEN and JAY-GERIN, 2005a}), \text{with an average recombination time as short as a few femtoseconds (GOULET et al., 1990). This average recombination time shows that the recombination process mainly occurs on the water cation and not on H}_3\text{O}^+, \text{that is, before the proton transfer reaction H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + ^{1}\text{OH takes place (~10 fs) (which would change the nature of the cation and therefore affect the values of the recombination cross section). In other words, the subexcitation electron recombines quickly (in the first steps of its random walk) on H}_2\text{O}^+. If it does not recombine quickly, it will never recombine, and will thus become thermalized (unless, of course, it makes a dissociative attachment on a water molecule) (~56 fs), trapped (~50-300 fs), and hydrated (~240 fs-1 ps) (MEESUNGNOEN and JAY-GERIN, 2005a; JAY-GERIN et al., 2008 and references therein).} \]
vibrationally excited H$_2$O molecules, will be explained in the article No. 1 (SANGUANMITH et al., 2011α).

**Figure II.2** Algorithm of the TRACELE simulation program

- $E_c$: lowest electronic excitation energy
- $E_{sec}$: secondary electron
- $E_{loss}$: energy loss
II.1.2 The IRT code

This code begins at $10^{12}$ s in the calculations, after the end of the physicochemical stage ($\sim 10^{12}$ s; we assume that this time also marks the beginning of diffusion), which is provided as an output of the IONLYS program, is then used directly as the starting point for the subsequent nonhomogeneous chemical stage. This third and final stage, during which the individual reactive species diffuse randomly at rates determined by their diffusion coefficients and react with one another (or with any added solutes present at the time of irradiation) until all spur or track processes are complete, is covered by the IRT program. Algorithm of the IRT simulation program is shown in Figure II.3.

Figure II.3 Algorithm of the IRT simulation program
This program employs a Monte-Carlo simulation technique, the so-called "independent reaction times" (IRT) method (CLIFFORD et al., 1986; GREEN et al., 1990; PIMBLOTT et al., 1991), a computer efficient stochastic simulation technique that is used to simulate reaction times without following the trajectories of the diffusing species. This method is based on the approximation that the distances between pairs of reactants evolve independently of each other, and therefore the reaction times of the various potentially reactive pairs are independent of the presence of other reactants in the system. In essence, the simulation begins by considering the initial, or "zero-time", spatial distribution of the reactants (given by the IONLYS program). The separations between all the pairs of reactants are first calculated. Overlapping pairs (i.e., pairs formed in a reactive configuration) are assumed to combine immediately. For each remaining pair, a reaction time is stochastically sampled according to the reaction time probability distribution function (GREEN et al., 1990; GOULET and JAY-GERIN, 1992; FRONGILLO et al., 1998) that is appropriate for the type of reaction considered. This function depends upon the initial distance separating the species, their diffusion coefficients, their Coulomb interaction (for reactions between ionic species), their encounter distance, and the probability of reaction during one of their encounters. The competition between the various reactions is taken into account by realizing them in the ascending order of sampled reaction times. When a reaction occurs, the reactants become unavailable for the competing reactions that are sampled to occur at longer times but one must then consider the possible reactions of the newly formed products with the species that have survived up to that point. Since the IRT method is solely based on a comparison of reaction times, it does not follow the trajectories of the diffusing species. Therefore, a special procedure must be devised to sample the positions of the reaction products and of the species with which newly formed species can in turn react (CLIFFORD et al., 1986). The inclusion of a scavenger in the system does not affect the general simulation technique. In fact, the IRT program allows one to incorporate in a simple way pseudo first-order reactions of the radiolytic products with various scavengers that are homogeneously distributed in the

\[ \text{The "encounter distance" (} \alpha_{A,B} \text{) for each pair of interacting species } A \text{ and } B \text{ can be derived from the Smoluchowski equation (see Sect. II.4).} \]
solution, such as $\text{H}^+$, $\text{OH}^-$, and $\text{H}_2\text{O}$ itself, or more generally any solutes for which the relevant reaction rates are known. Similarly, the truly first-order fragmentations of the species are easily simulated. Finally, the IRT method is very well suited for the description of reactions that are only partially diffusion-controlled (most reactions that occur in irradiated water are not diffusion-controlled even at room temperature), an adequate description of the activation processes that are involved in those reactions is a prerequisite for the modeling of the effects of high temperature on water radiolysis), in which the species do not react instantaneously on encounter but experience, on the average, many encounters and separations before they actually react with each other. The ability of the IRT method to give accurate time-dependent chemical yields under different irradiation conditions has been well validated by comparison with full random flights (or "step-by-step") Monte-Carlo simulation, which does follow the particle trajectories in detail (PIMBLOTT et al., 1991 and references cited therein; GOULET et al., 1998; PLANTE, 2009).

![Diagram](image)

**Figure II.4** Diffusion coefficients ($D$) for the various track species involved in our simulations (ELLIOT and BARTELS, 2009).
Compared to the original version of our IRT program some diffusion coefficients \( (D) \) of reactive species and temperature dependence of reaction rate constants have been updated. Figure II.1 shows the diffusion coefficients of various species as a function of temperature which have been updated in our Monte-Carlo simulations.

The list of the main spur/track chemical reactions and values of reaction rate constants considered in our pure liquid water radiolysis simulations as a function of temperature (ELLIOT and BARTELS., 2009) has been illustrated in Appendix 3.

II.2 Simulation of the effects of acidity

To simulate the radiolysis of water under acidic conditions, we have used aqueous solutions of 0.4 \( M \) sulfuric acid \((\text{pH} \sim 0.46)\). Many experimental works and theoretical works have been done over many decades on the radiation chemistry of aqueous \( \text{H}_2\text{SO}_4 \) solutions (especially, in 0.4 \( M \) \( \text{H}_2\text{SO}_4 \)) because of the fact that sulfuric acid was widely employed in the early development of the Fricke and other chemical dosimeters. For aqueous \( \text{H}_2\text{SO}_4 \) (a diprotic acid), we have:

\[
\text{H}_2\text{SO}_4 \xleftrightarrow{\text{pK}_{a1}} \text{H}^+ \text{HSO}_4^- \xleftrightarrow{\text{pK}_{a2}} \text{SO}_4^{2-} \tag{20}
\]

with \( \text{pK}_{a1} \approx -3 \) and \( \text{pK}_{a2} = 1.987 \) at 25 °C (DEAN, 1987). Hence, \( \text{H}_2\text{SO}_4 \) is virtually completely dissociated when dissolved in water above \( \text{pH} \approx 0 \), and the solution contains mainly \( \text{H}^+ \), \( \text{HSO}_4^- \), and a certain amount of \( \text{SO}_4^{2-} \). The concentration of each species changes as the total acid concentration changes. The model assumptions and procedures employed to carry out the Monte-Carlo simulations of the radiolysis of 0.4 \( M \) \( \text{H}_2\text{SO}_4 \) aqueous solutions with IONLYS-IRT have already been given (MEESUNGNOEN et al. 2001; MEESUNGNOEN and JAY-GERIN, 2005b; AUTSAVAPROMPORN et al., 2007). In brief, as noted before, the effects of the background concentration of \( \text{H}^+ \) in solutions are added to the IRT program as pseudo first-order reactions. We have also supplemented the pure-water reaction scheme to include the reactions listed in Table 3, which account for the species present in irradiated sulfuric acid solutions.
Table 3 Reactions added to the pure water reaction scheme to simulate the radiolysis of aqueous H_2SO_4 solutions, at 25 °C (from AUTSAVAPROMPORN et al., 2007).^{(a)}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 'OH + HSO$_4^-$ → H$_2$O + SO$_4^{2-}$</td>
<td>$1.5 \times 10^5$</td>
</tr>
<tr>
<td>21 H$^+$ + SO$_4^{2-}$ → HSO$_4^-$</td>
<td>$1.0 \times 10^{10}$</td>
</tr>
<tr>
<td>22 H$^+$ + S$_2$O$_8^{2-}$ → SO$_4^{2-}$ + HSO$_4^-$</td>
<td>$2.5 \times 10^7$</td>
</tr>
<tr>
<td>23 e'$_{aq}$ + S$_2$O$_8^{2-}$ → SO$_4^{2-}$ + SO$_4^{2-}$</td>
<td>$1.2 \times 10^{10}$</td>
</tr>
<tr>
<td>24 H$_2$O$_2$ + SO$_4^{2-}$ → HO$_2^+$ + HSO$_4^-$</td>
<td>$1.2 \times 10^7$</td>
</tr>
<tr>
<td>25 OH$^-$ + SO$_4^{2-}$ → 'OH + SO$_4^{2-}$</td>
<td>$8.3 \times 10^7$</td>
</tr>
<tr>
<td>26 SO$_4^{2-}$ + SO$_4^{2-}$ → S$_2$O$_8^{2-}$</td>
<td>$4.4 \times 10^7$</td>
</tr>
</tbody>
</table>

^{(a)} Note that the rate constants given here for the reactions between ions are at ionic strength equal to zero.

At high acidities, a certain proportion of the 'OH radicals react with hydrogen sulfate ions to form the sulfate radical SO$_4^{2-}$ according to reaction (17) (AUTSAVAPROMPORN, 2007).

The diffusion coefficients of HSO$_4^-$, SO$_4^{2-}$, and S$_2$O$_8^{2-}$, employed in the simulations are taken to be (in units of 10$^{-9}$ m$^2$ s$^{-1}$) 1.385 (for both HSO$_4^-$ and SO$_4^{2-}$), 1.065, and 1.145, respectively (LIDE, 2008).

In addition, we have introduced, in the IRT program, the effects due ionic strength (see more detail on page 34) in 0.4 M H$_2$SO$_4$ solutions (see, for example: HARRIS, 2001) for reaction (16) (e'$_{aq}$ + H$^+$ → H$^+$) and for the recombination of the proton with the hydroxyl ion (MEESUNGNOEN et al., 2001; MEESUNGNOEN and JAY-GERIN, 2005a):

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad (27)$$

as well as for all reactions between ions, except for the peculiar bimolecular self-recombination of e'$_{aq}$ for which there is no evidence of any ionic strength effect (SCHMIDT and BARTELS, 1995) (including those given in Table 3). To relate rate constant and ionic
strength of the solution over the 25-350 °C temperature range, we used the following equation, obtained from the Brönsted-Bjerrum model of ionic reactions and the extended Debye-Hückel theory of ionic solutions (GUGGENHEIM, 1935; DAVIES, 1938; ROBINSON and STOKES, 1959; CZAPSKI and SCHWARZ, 1962; WESTON and SCHWARZ, 1972; JONAH et al., 1977; ELLIOT et al., 1990):

\[
\log \left( \frac{k}{k_0} \right) = 3.64 \times 10^6 \frac{Z_a Z_b}{(sT)^{1/2}} \left( \frac{I^{1/2}}{1 + I^{1/2}} \right)
\]

(28)

where \( k \) is the rate constant at ionic strength \( I \), \( k_0 \) is the rate constant at infinite dilution of ions (i.e., in the limit of zero ionic strength), \( Z_a \) and \( Z_b \) are the algebraic numbers of charges on the reactants (positive for cations and negative for anions), \( T \) is the absolute temperature (in K), \( \varepsilon \) is the dielectric constant of the medium (for water, \( \varepsilon = 78.5 \) at 25 °C and 13.0 at 350 °C). The ionic strength \( I \) (in M) of the solution is defined as (SOLOMON, 2001):

\[
I = \frac{1}{2} \sum_i Z_i^2 C_i
\]

(29)

where \( Z_i \) is the charge number of the \( i \)th ion and \( C_i \) is its molar concentration. The sum extends over all ionic species present in the solution. According to Eq. (28), the rate constant will increase, decrease, or remain the same with increasing ionic strength, depending on whether the reactants have the same sign, opposite signs, or whether one reactant is neutral. For example, in 0.4 \( M \) \( \text{H}_2\text{SO}_4 \) solutions, the rate constants for reactions (16) and (27), corrected for these effects, are \( k_{16} = 1.12 \times 10^{10} \ \text{M}^{-1} \ \text{s}^{-1} \) (see earlier) and \( k_{27} = 5.97 \times 10^{10} \ \text{M}^{-1} \ \text{s}^{-1} \) (instead of 2.11 \times 10^{10} and 11.3 \times 10^{10} \ \text{M}^{-1} \ \text{s}^{-1} \) in neutral water at 25 °C, respectively; see Table 1) (AUTSAVAPROMPORN et al., 2007 and references cited therein). Finally, in our simulations the "direct" action of ionizing radiation on the sulfuric acid anions (mainly \( \text{HSO}_4^- \)) is neglected, which is a reasonably good approximation for 0.4 \( M \) sulfuric acid solutions. In fact, at this concentration of \( \text{H}_2\text{SO}_4 \), only about 3.5% of the total energy expended in the solution is initially absorbed by direct action on \( \text{HSO}_4^- \) ions (rather than on \( \text{H}_2\text{O} \)) (assuming that the energy absorbed by each component is proportional to its electron fraction) (JOHNSON and ALLEN, 1952).
II.3 Simulation of the Fricke dosimeter

To stochastically model the chemistry of the ferrous-sulfate Fricke dosimeter, which is an air-saturated solution of 1-10 mM FeSO₄ in aqueous 0.4 M H₂SO₄ (pH 0.46), we have added the reactions of Fe²⁺ ions with the oxidizing species 'OH, HO₂*, and H₂O₂ that are formed in the water of the irradiated solutions under aerated conditions to the IRT program. The mechanism for the radiolytic oxidation of Fe²⁺ ions to Fe³⁺ is well-understood and the rate constants at 25 °C of the individual reactions taking place are known. The reaction scheme is as follows (Allen, 1961; Fricke and Hart, 1966; Das, 1971; Spinks and Woods, 1990; Lundström et al., 2004):

\[
e^{-} + H^+ \rightarrow H^* \quad k_{16} = 1.12 \times 10^{10} \text{M}^{-1} \text{s}^{-1} \quad (16)
\]
\[
pK_a (H^*/e^-) = 9.59
\]
\[
H^* + O_2 \rightarrow HO_2^* \quad k_{30} = 2.1 \times 10^{10} \text{M}^{-1} \text{s}^{-1} \quad (30)
\]
\[
Fe^{2+} + 'OH \rightarrow Fe^{3+} + OH^- \quad k_{31} = 3.4 \times 10^8 \text{M}^{-1} \text{s}^{-1} \quad (31)
\]
\[
Fe^{2+} + HO_2^* \rightarrow Fe^{3+} + HO_2 \quad k_{32} = 7.9 \times 10^5 \text{M}^{-1} \text{s}^{-1} \quad (32)
\]
\[
HO_2^- + H^+ \rightarrow H_2O_2 \quad k_{33} = 2.66 \times 10^{10} \text{M}^{-1} \text{s}^{-1} \quad (33)
\]
\[
pK_a (H_2O_2/HHO_2) = 11.62
\]
\[
Fe^{2+} + H_2O_2 \rightarrow 'OH + OH^- + Fe^{3+} \quad k_{34} = 52 \text{M}^{-1} \text{s}^{-1} \quad (34)
\]
\[
OH^- + H^+ \rightarrow H_2O \quad k_{27} = 5.97 \times 10^{10} \text{M}^{-1} \text{s}^{-1} \quad (27)
\]
\[
pK_a (H_2O/OH^-) = 13.999
\]

At the acid concentration of 0.4 M H₂SO₄, e⁻ₑaq is rapidly converted to H⁺. The H⁺ atoms created directly by radiolysis and by scavenging of e⁻ₑaq react with oxygen in aerated solutions to form hydroperoxyl radicals (HO₂*) (Begusová and Pimbloy, 2002). Each of these radicals oxidizes three Fe²⁺ ions, one by reaction (32) and two by the reaction sequence (33), (34), and (31). Each 'OH radical oxidizes one Fe²⁺ ion, and each molecule of H₂O₂ oxidizes two Fe²⁺ ions. Summing all sources of Fe³⁺ ions, the yield of ferric ions in an aerated solution G(Fe³⁺) is related to the escape yields of the free radicals and molecular species of (acidic) water radiolysis by Eq. (18).
Note that the values of $k_{27}$ and $k_{33}$ used in the simulations have been corrected using Equations (28) and (29) for the effects due to the ionic strength in the case (under study here) of a solution made of 0.4 M $\text{H}_2\text{SO}_4$ and 5 mM $\text{FeSO}_4$. Note also that, as we have mentioned above, for solutions of 0.4 M in $\text{H}_2\text{SO}_4$ there is a small amount of $'\text{OH}$ radicals that react with $\text{HSO}_4^-$ to form $\text{SO}_4^{2-}$ [reaction (17)]. However, the overall ferric ion yield remains the same as given by Eq. (18) since the sulfate radical reacts with $\text{Fe}^{2+}$ in the same way as $'\text{OH}$ (DAS, 1971; NETA et al., 1988):

$$\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad k_{35} = 2.79 \times 10^8 \, \text{M}^{-1} \text{s}^{-1} \quad (35)$$

Under normal irradiation conditions, the radical concentrations are low compared with the background concentrations of acid, $\text{Fe}^{2+}$ ions, and oxygen ($2.5 \times 10^{-4}$ M) in solution, and the reactions are treated in the IRT program as pseudo first-order. In modeling the Fricke dosimeter, the fastest reaction of $\text{Fe}^{2+}$ ions is with $'\text{OH}$ radicals. The slowest component of the kinetics of $\text{Fe}^{3+}$ formation is due to the Fenton-type reaction (34) (HALLIWELL and GUTTERIDGE, 1999). For example, in the case of 5 mM $\text{FeSO}_4$ solutions considered here, this reaction takes several seconds to go to completion (AUTSAVAPROMPORN et al., 2007), which increases significantly the computer time usually chosen for modeling the radiolysis of water. In the simulations reported here, the time evolution of $G(\text{Fe}^{3+})$ has been followed until ~200 s.

In this work we used Monte-Carlo simulations of the low-LET radiolysis of the ferrous sulphate (Fricke) dosimeter to determine the spur lifetime which is an important indicator for overlapping spurs, giving the time required for the changeover from nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution (see Sect. V, Article No. 2) (SANGUANMITH, 2011b).

II.4 Simulation of the effect of temperature

The radiolysis of liquid water at elevated temperature at low-LET has been modeled by using the updated and extended version of our originally developed Monte-Carlo
simulation codes, TRACPRO, TRACELE, and TRACIRT (HERVÉ DU PENHOAT et al., 2000; MEESUNGNOEN et al., 2002a).

In the present work, we will restrict ourselves to the most essential features of the influence of the temperature on each stage of the radiolysis of water.

In the "physical" stage, the scattering cross sections can be considered as independent of the medium's temperature because the energy of the ionizing particles is much larger than the thermal energies and because the motion of the target (water molecules) can be neglected. However, the density (\( \rho \)) of pressurized water varies with temperature (from \( \rho = 1 \text{ g/cm}^3 \) at room temperature to \( \rho = 0.575 \text{ g/cm}^3 \) at 350 °C), and this influences the particles scattering mean free paths (MFP) which are related to the scattering cross sections through the simple relation \( \text{MFP} = \frac{1}{\sigma N} \), where \( \sigma \) is the total cross section and \( N \) is the number of scatterers per unit volume. The 42.5% decrease in \( N \) that take place when the temperature is increased from 25-350 °C thus causes the energy depositions to become significantly further apart. Since the scattering cross sections is independent of the medium's temperature, the MFP is proportional to the inverse of the density. Physically, this means the temperature brings the water molecules further apart but does not change their ability to interact with the energetic particles.

In the "physicochemical" stage, the influence of the temperature is not well understood. It seems that many parameters intervening in this stage (such as the dissociative decay channels for \( \text{H}_2\text{O}^* \), the migration of the ions \( \text{H}_2\text{O}^+ \) and of the subexcitation electrons) are likely to be sensitive to temperature. It should be mentioned that many authors, such as SWIATLA-WOJCIK and BUXTON (1995), have suggested that the temperature – through a diminution of hydrogen bonding in liquid water – could possibly change the relative contributions of the dissociative decay channels for \( \text{H}_2\text{O}^* \). First of all, the variations of density would act as they did in the physical stage, increasing (on average) each step of the random walk. But any number of other phenomena could come into play. For example, when a "hot" (subvibrational) electron is slowing down before eventually getting trapped, it goes through a stage during which its energy is nearly thermal,
so that it can not only lose energy but also gain some from the surrounding medium. If the duration of this quasi-equilibrium stage depends on temperature, it could affect the electron thermalization distances.

Another temperature effect that could turn out to be the most important one in the physicochemical stage, is its influence on the scattering cross section of the low-energy electrons. In fact, electrons in the subexcitation energy range are known to be sensitive to the structural order of the surrounding medium, owing to their nonnegligible delocalized character. In various media, their scattering cross-sections have been shown to increase rapidly when the degree of order diminishes (HERVÉ DU PENHOAT et al., 2000 and references cited therein). This also seems to be the case for water, since the electron cross sections found in amorphous ice at low incident energy (MICHAUD and SANCHE, 1987) appear to be somewhat smaller (by a factor of ~2) than those that apply to liquid water (COBUT et al., 1998; GOULET et al.,1996) and much smaller (by at least an order of magnitude) than those reported for the gas phase (MICHAUD and SANCHE, 1987). On this basis, one could expect the scattering cross sections of subexcitation electrons to increase with temperature in the range 25-350 °C, since the breaking of the hydrogen bonds gives rise to a decrease of the structural order. It is difficult to estimate to what extent this could affect thermalization distances, but one cannot exclude the possibility that this effect could overcome the 42.5% decrease in the density as temperature increases from 25-350 °C and in turn reduce those distance significantly. A similar conclusion was obtained previously by HOCHANADEL and GHORMLEY (1962), who suggested that, at higher temperature, “subexcitation electrons are thermalized more rapidly”. And it seems that, our simulations are better to reproduce the experimental yields if the electron thermalization distances decrease with increasing temperature.

In the “nonhomogeneous chemical” stage, during which the radiolytic species diffuse and react with one another with a kinetic dictated by their initial nonhomogeneous spatial distribution. At room temperature, this stage is essentially completed at the time of the end of spur expansion after which homogeneous chemistry takes over. It should be noted that the time at the end of spur is depend on temperature. The nonhomogeneous spur/track
expansion is complete by $\sim 4.2 \times 10^{-7}$ s at 25 °C and decrease to $\sim 5.7 \times 10^{-8}$ s at 350 °C (See Sect. V, Article No. 2) (SANGUANMITH et al., 2011b).

Some chemical reactions can take place before any diffusion of species occurs because the latter are formed already “in contact” at the end of the physicochemical stage (COBUT et al., 1998; FRONGILLO et al., 1998). For simplicity, we consider that those “contact reactions” occur at $\sim 10^{12}$ s (i.e., the starting point of the nonhomogeneous kinetics). The occurrence of all the other reactions depends on the ability of reactants to meet and on the probability that their encounter gives rise to a reaction (most reactions are not diffusion-controlled). The physical parameters that will determine the time-dependent reaction probability of a pair of reactants will therefore be (i) their initial separation, (ii) their diffusion coefficient, (iii) their electrostatic interaction (i.e., their charge and the dielectric constant of the medium), (iv) their reaction radius (the distance between the two species at which they react immediately), and (v) their probability of reaction per encounter.

The temperature of the medium has an influence on many of those parameters. The effect of temperature on the initial position of the species comes from the temperature dependence of the scattering mean free paths mentioned in the first two stages. Its influence on the diffusion coefficient depends on the actual species considered, but this parameter always increases with temperature. In the simulation, the temperature dependences of the diffusion coefficients of $\text{H}_2\text{O}^+$, $\text{OH}^-$, $\text{e}^-_{\text{aq}}$, and $\text{H}_2\text{O}$ are represented by polynomial fits to the experimental data (ELLIOT and BARTELS, 2009). For the other species, whose diffusion coefficients are unknown at elevated temperatures, the following scaling procedure has been adopted:

$$D(t) = D(25^\circ\text{C}) + \frac{D_{\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}(25^\circ\text{C})}$$  \hspace{1cm} (36)$$

where $t$ denotes the temperature in degrees Celsius.

Rate constants are sensitive functions of temperature and for this reason are important parameters in predictive modeling of high-temperature water chemistry. What is generally known is the temperature dependence of the “observed” reaction rate constant ($k_{\text{obs}}$), from
which it is possible to extract information on the temperature dependences of the "activation" and "diffusion" processes that are involved in the reaction. For reactions whose rates are nearly diffusion-controlled at room temperature, $k_{\text{obs}}$ is best described by the Noyes equation:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{act}}},$$  \hspace{1cm} (37)

where $k_{\text{diff}}$ is the rate constant for a truly diffusion-controlled reaction and $k_{\text{act}}$ is the rate constant that would be measured if diffusion had no influence on the reaction rate (NOYES, 1961). A number of reactions pertinent to the radiation chemistry of water have been found to be best described by Eq. (37) (see, for example: ELLIOT, 1994). The Arrhenius equation is used to evaluate $k_{\text{act}}$ empirically:

$$k_{\text{act}} = A \exp(\frac{E_{\text{act}}}{RT}),$$  \hspace{1cm} (38)

where $E_{\text{act}}$ is the activation energy of the process, $A$ is referred to as the pre-exponential factor, $R$ is the gas constant and $T$ is the absolute temperature. $k_{\text{diff}}$ is given by the Smoluchowski equation (see, for example: ELLIOT et al., 1990; ELLIOT, 1994; SWIATLA-WOJCIK and BUXTON, 1995; HERVÉ DU PENHOAT et al., 2000):

$$k_{\text{diff}} = 4\pi \beta N_{\text{Av}} (D_A + D_B) a_{A,B}$$  \hspace{1cm} (39)

where $N_{\text{Av}}$ is Avogadro’s number, $(D_A + D_B)$ is the sum of diffusion coefficients for both reacting species, $\beta$ is a spin statistical factor for radical-radical reactions, and $a_{A,B}$ is the encounter (or reaction) distance. When the reactants are ions, Eq. (38) is multiplied by the Debye factor (DEBYE, 1942):

$$f_D = \frac{\delta}{e^\delta - 1}$$  \hspace{1cm} (40)

where $\delta$ is given by

$$\delta = \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 e(T) a_{A,B} k_B T}.$$  \hspace{1cm} (41)
where $Z_A$ and $Z_B$ are the charges on the ions, $e$ is the electron charge, $\varepsilon_0$ is the permittivity of free space, $\varepsilon(T)$ is the dielectric constant of the medium, and $k_B$ is Boltzmann’s constant.

To reproduce the effect of temperature on the low-LET (~0.3 keV/μm at 25 °C) radiolysis of water from ambient up to 350 °C, we used an extended version of our IONLYS-IRT code which was developed previously (HERVÉ DU PENHOAT et al., 2000; TIPPAYAMONTRI et al., 2009; SANGUANMITH et al., 2011a). In this version, we used the self-consistent radiolysis database, including rate constants, diffusion coefficients, reaction mechanisms, and g-values, compiled by ELLIOT and BARTELS (2009). This new database provides a recommendation for the best values to use in high-temperature modeling of water radiolysis up to 350 °C. In addition, to counterbalance the strong influence of the rapid drop observed in the rate of the self reaction of $e^{-}\text{aq}$ above 150 °C (CHRISTENSEN and SEHESTED, 1986; ELLIOT, 1994; MARIN et al., 2007) and thus obtain a good agreement between model and experiment for the temperature dependence of H₂ yield, we were led to adjust the temperature dependence of some parameters involved in the early physicochemical stage of the radiolysis, namely, the electron thermalization distance ($r_{th}$), the dissociative electron attachment (DEA), and the branching ratios of the different excited water molecule decomposition channels. The details of this adjustment are published elsewhere (SANGUANMITH et al., 2011a) but we briefly summarize them here. In essence, the values of $r_{th}$ were obtained by comparing our simulated time-dependent $e^{-}\text{aq}$ yield data to recent picosecond (~60 ps to 6 ns) and conventional nanosecond (using $e^{-}\text{aq}$ scavenging by methyl viologen MV²⁺) pulse radiolysis measurements of the decay kinetics of $e^{-}\text{aq}$ at several different temperatures between 25 and 350 °C (MUROYA et al., 2010; MUROYA, unpublished data). Using this best fitting procedure, $r_{th}$ was found to remain relatively unchanged below ~100-150 °C (and equal to its value at 25 °C), but to decrease sharply at higher temperatures with $r_{th}/r_{th}(25 °C) \approx 0.4$ at 300 °C. This decrease in $r_{th}$ above 100-150 °C was interpreted as indicating an increase in the scattering cross sections of subexcitation electrons ($e^{-}\text{sub}$) (GOULET and JAY-GERIN, 1989; MOZUMDER, 1999) that accounts for a decrease in the degree of structural order of water molecules due to an increasing breaking of hydrogen bonds with temperature (HERVÉ DU PENHOAT et al., 2000). Building on these findings on $r_{th}$, we incorporated
in our modeling calculations a temperature dependence of the DEA and of the branching ratios of the different decay channels for excited water molecules (as \( r_{th} \), these parameters are sensitive to the local structural order of water) in a form similar to that of \( r_{th} \), that is, unchanged below 100-150 °C and then followed by a marked discontinuity around these temperatures. In the absence of any other detailed experimental information, we assumed that the values of these latter parameters at 350 °C were equal to those observed in water vapor (SWIATLA-WOJCIEK and BUXTON, 1995; SANGUANMITH et al., 2011a).

All Monte-Carlo simulations reported here were performed along the liquid-vapor coexistence curve, the density of the pressurized water decreasing from 1 g/cm\(^3\) (1 bar or 0.1 MPa) at 25 °C to 0.575 g/cm\(^3\) (16.5 MPa) at 350 °C (LINSTROM and MALLARD, 2005). For this range of temperature, calculations show that \( g \)-values vary only little with the applied pressure. Finally, to reproduce the effects of \(^{60}\)Co \( \gamma \)-rays or fast electrons, we used short segments (~150 \( \mu \)m) of ~300-MeV proton tracks, over which the average LET value obtained in the simulations was nearly constant and equal to ~0.3 keV/\( \mu \)m at 25 °C (McCRAKEN et al., 1998; COBUT et al., 1998; FRONGILLO et al., 1998). The number of proton histories (~150) was chosen so as to ensure only small statistical fluctuations when calculating average yields while keeping acceptable computer time limits.
III. ARTICLE No.1

LOW-LINEAR ENERGY TRANSFER RADIOLYSIS OF LIQUID WATER AT ELEVATED TEMPERATURES UP TO 350 °C: MONTE-CARLO SIMULATIONS


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Foreword:

In this work, I updated our IONLYS and IRT programs to take into account the most recent data on the effect of temperature and in particular the best recommended values reported by Elliot and Bartels (2009). I performed all the calculations, incorporating and adjusting the new temperature dependence of certain parameters intervening in the physicochemical stage of the radiolysis. Finally, I had a significant contribution to the main idea of this work and to all the preparation process for the first version of this article.
ABSTRACT

Our Monte-Carlo modeling of the high-temperature radiolysis of water by low-LET radiation was re-examined in an attempt to reconcile our computed g-values of the various radiolytic products (e$^{-}_{aq}$, OH, H', H$_2$, and H$_2$O$_2$) with recently re-assessed experimental data up to 350 °C. The inclusion in our simulations of the abrupt drop in the rate constant for the self-reaction of e$^{-}_{aq}$ above 150 °C led us to re-evaluate the temperature dependence of certain parameters intervening in the physicochemical stage of the radiolysis. A very good agreement was found between model and experiment. The importance of the reaction of H' atoms with water in the unexplained yield of H$_2$ above 200 °C was also briefly discussed.

Key words: Liquid water, high temperature, radiolysis, g-value, spur kinetics, Monte-Carlo simulation.
1. Introduction

The radiolysis of liquid water at elevated temperatures is a subject of considerable interest to nuclear power engineers. In boiling water reactors (BWR) and pressurized water reactors (PWR), the nuclear core is cooled by liquid water that is typically at a temperature in the range of 285-320 °C. The aqueous coolant undergoes radiolytic decomposition induced by an intense ionizing radiation field in the core, comprising low linear energy transfer (LET) γ-rays, fast neutrons whose energy is transferred to protons and oxygen nuclei resulting in the emission of charged particle recoils of high LET, and also much higher LET radiation (recoil of $^7$Li ions and α-particles) associated with the nuclear reactions of thermal neutrons with $^{10}$B (used in PWR as a reactivity control chemical). The aqueous radiolysis products must be assessed because they can induce unwanted deleterious corrosion, hydriding, and cracking of sensitive materials both in the core and in the various piping components of the reactors [1-3]. The basic interest of nuclear power engineers is to know the real concentrations of the oxidizing products and to select conditions at which their formation could be suppressed. However, direct measurement of the chemistry in reactor cores is extremely difficult. The extreme conditions of high temperature, pressure, and mixed neutron/gamma radiation fields are, of course, not compatible with normal chemical instrumentation [4]. For these reasons, theoretical models and computer simulations are an important route of investigation to predict the detailed radiation chemistry of the cooling water in the core and the consequences for materials [5,6].

In this work, we re-examine our Monte-Carlo modeling of the high-temperature radiolysis of liquid water by low-LET radiation [7], in an attempt to reconcile our computed primary or 'escape' yields (or g-values) (throughout this Letter, g-values are given in the units of molecules per 100 eV, abbreviated molec./100 eV; for conversion into SI units: 1 molec./100 eV ≈ 0.10364 μmol/J) of the various radiolytic products with newly measured or recently re-assessed experimental data up to 350 °C. Much of the data
required to model this radiolysis, including reaction rate constants, diffusion coefficients, reaction mechanisms, and g-values, are drawn from a recent compilation by Elliot and Bartels [8]. Contrary to our previous work [7], we incorporate in the simulations the abrupt drop observed in the rate constant for the self-reaction of the hydrated electron (e\textsuperscript{-aq}) above 150 °C (see, for example, [8]). As discussed below, much of the modeling depends on this lack of reaction of e\textsuperscript{-aq} + e\textsuperscript{-aq} at temperatures greater than 150°C. Most importantly, a direct result is the need to re-evaluate the temperature dependence of certain parameters intervening in the early physicochemical stage of the radiolysis. These parameters include, in particular, the thermalization distance (r\textsubscript{th}) and the dissociative attachment (DEA) of ‘subexcitation’ electrons (those electrons that have kinetic energies lower than the first electronic excitation threshold of the medium, i.e., ~7.3 eV in liquid water; they lose energy relatively slowly, the dominant mode of energy loss being the excitation of molecular vibrations [9]), and the branching ratios of the excited water molecule decay channels.

2. Radiolysis of high-temperature water and Monte-Carlo simulations

Monte-Carlo techniques are used to model the complex succession of events that are generated in liquid water under irradiation. The detailed description of our Monte-Carlo code IONLYS-IRT that simulates, in a three-dimensional geometrical environment, the initial production of the various reactive species and the subsequent chemical reactions of these species, has been given previously [10-14]. In brief, the IONLYS program models, event by event, all the events of the early ‘physical’ and ‘physicochemical’ stages of radiation action up to ~10\textsuperscript{-12} s. The complex spatial distribution of reactants at the end of the physicochemical stage, which is provided as an output of the IONLYS program, is then used directly as the starting point for the ‘nonhomogeneous chemical’ stage (from ~10\textsuperscript{-12} s up to ~10\textsuperscript{-7}-10\textsuperscript{-6} s at 25 °C). This third and final stage, during which the various radiolytic species diffuse randomly and react with one another (or with dissolved solutes, if any) until
all spur processes are complete, is covered by our IRT program. This program employs the ‘independent reaction times’ (IRT) method (see, for example, [15]), a computer-efficient stochastic simulation technique that is used to simulate reaction times without having to follow the trajectories of the diffusing species. The IRT method relies on the approximation that the reaction time of each pair of reactants is independent of the presence of other reactants in the system. Its implementation and validation have been described in detail [11,16,17].

In the current Letter, we use an extended version of our IONLYS-IRT code [7,13,18] to examine the effect of temperature on the low-LET radiolysis of liquid water in the range from ambient up to 350 °C. The important parameters are the yields of the primary products of water radiolysis and the rate constants of their inter-reactions. In this version of IONLYS-IRT, we use the self-consistent radiolysis database, including rate constants, reaction mechanisms, and g-values, recently compiled by Elliot and Bartels [8]. This new database provides a recommendation for the best values to use in high-temperature modeling of water radiolysis up to 350 °C.

All Monte-Carlo simulations reported here are performed along the liquid-vapor coexistence curve, the density of the pressurized water decreasing from 1 g/cm$^3$ (1 bar or 0.1 MPa) at 25 °C to 0.575 g/cm$^3$ (16.5 MPa) at 350 °C [19]. For this range of temperature, calculations show that g-values, to a large extent, depend relatively little on the applied pressure. Finally, to reproduce the effects of $^{60}$Co γ-rays or fast electrons, we used short segments (~150 μm) of ~300-MeV proton tracks, over which the average LET value obtained in the simulations was nearly constant and equal to ~0.3 keV/μm at 25°C [1,11]. The number of proton histories (~150) was chosen so as to ensure only small statistical fluctuations when calculating average yields while keeping acceptable computer time limits.
3. Results and discussion

3.1 Temperature dependence of the bimolecular self-reaction of the hydrated electron

Of particular significance, we have adopted in this work the temperature dependence of the rate constant for the self-reaction of $e^{-}_{\text{aq}}$ as recently measured in alkaline water by Marin et al. [8,20]. Overall, this rate constant exhibits a behavior similar to that previously reported by other groups [21-23], i.e., it increases with temperature in accordance with an Arrhenius relationship up to $\sim 150$ °C and then decreases sharply as the temperature is further increased. The mechanism behind this inverse temperature dependence above 150°C is not understood, but it is generally thought to involve the formation of some transient intermediate [24], such as a hydride ion (H\textsuperscript{−}) or a hydrated electron dimer or dielectron ($e_{2\text{aq}}$) sharing the same solvent cavity [20,21,25]. The applicability of this abrupt drop in the rate constant above 150 °C to near-neutral solution, however, has long been a subject of discussion on the pretext that it could be a function of the pH of the solution [26]. In fact, until recently, most computer modelers of the radiolysis of water at high temperatures have employed, in neutral solution, an extrapolation procedure previously proposed by Elliot [22], assuming that such an abrupt change does not occur and that this reaction is diffusion controlled at temperatures above 150 °C. This assumption was justified mainly by the good agreement obtained between model and experiment [7,13,27].

In their reports (and personal communication), Bartels and coworkers [8,20] emphasized that the measured temperature behavior of the rate of the bimolecular decay of $e^{-}_{\text{aq}}$ in alkaline solution should in fact be regarded as independent of pH. As a consequence, the incorporation of the drop in reaction rate at temperatures greater than $\sim 150$ °C in the simulations leads, as predicted earlier [7,27,28], to a sharp downward discontinuity in g(H\textsubscript{2}), which is not observed experimentally (Figure 1). To obtain acceptable fits of our calculated yields to the experimental data above 150 °C, we were therefore led, in order to counterbalance the influence of the rate constant for the self-reaction of $e^{-}_{\text{aq}}$, to adjust the
temperature dependence of certain parameters that are involved in the physicochemical stage of the radiolysis, i.e., the electron thermalization distance \( r_{th} \), the dissociative electron attachment (DEA), and the branching ratios of the different excited water molecule decay channels. This was really our only option because the parameters involved in the nonhomogeneous chemical stage, namely the rate constants of the various spur reactions and their temperature dependences, are set by the data recommended by Elliot and Bartels [8].

3.2 Temperature dependence of the thermalization distance of subexcitation electrons, DEA, and branching ratios of the excited water molecule decay channels

The values of \( r_{th} \) (for a definition of our average electron thermalization distance \( r_{th} \), see [7,9,10,12]) were obtained from comparing our computed time-dependent \( e^-_{aq} \) yield data to recent picosecond (\( \sim 60 \) ps to 6 ns) and conventional nanosecond (using methyl viologen MV\(^{2+}\) scavenging of electrons) pulse radiolysis measurements of the decay kinetics of \( e^-_{aq} \) at several different temperatures between 25 and 350 °C [32] (see Figure 2, at 300 °C, for the sake of illustration). Interestingly, fitting the kinetic traces was critically dependent on the selected value of \( r_{th} \). Using this best fitting procedure over the temperature range studied, \( r_{th} \) is found to remain relatively unchanged below \( \sim 100-150 \) °C (and equal to the \( r_{th} \) value at 25 °C), but to decrease sharply at higher temperatures (Figure 3). Noteworthy, \( r_{th}/r_{th}(25 \) °C) at 300 °C is equal to \( \sim 0.4 \), a value that is very close to that we adopted (while using a totally different approach based on best fits of our calculated ‘escape’ yields with experiment) in our previous studies on the radiolysis of water at high temperatures [7,13,33]. Moreover, the observed decrease of \( r_{th} \) above 100-150 °C is consistent with our previous work [7]. Physically, it indicates that there is an increase in the scattering cross sections of subexcitation electrons (those electrons are known to be very sensitive to the structural order of the surrounding medium, owing to their non-negligible delocalized character; in various media, their scattering cross sections have been
shown to increase rapidly when the degree of order diminishes [34]) that accounts for a
decrease in the degree of structural order of water molecules due to an increasing breaking
of hydrogen bonds with temperature. This also suggests that the effect resulting from this
electron scattering mechanism prevails over that originating from a change in the initial
spatial distribution of electrons in spurs due to the decrease in the density (p) of pressurized
water. Note that this latter effect led Swiatla-Wojcik and Buxton [27], as well as LaVerne
and Pimblott [28], to assume an increase in $r_{th}$ at elevated temperature.

The observation of a marked discontinuity of $r_{th}$ around ~100-150 °C is clearly a
novel finding. This peculiar behavior should reflect some change in the structural
characteristics of water at these temperatures. More precisely, it tends to suggest that liquid
water undergoes a rapid alteration in its local structural order or, equivalently, in its
hydrogen bonding network, near 100-150 °C. Such a result is obviously of critical
importance in our understanding of the radiation chemistry of water at high temperatures
and in turn also in its modeling. It could, for example, shed new light on the mechanism by
which the rate constant for the self-reaction of $e^{-}_{aq}$ drops at temperatures above 150 °C.
Quite remarkably, certain indications exist in the literature from molecular dynamics and
Monte-Carlo computer simulations as to the presence of such a loss of order in the
molecular structure of water around 100-150 °C. For example, Svisshchev et al. [35]
showed that at and above 200 °C the interstitial coordination in water disappears from the
spatial structure, indicating the loss of continuous H-bond network beyond the first H-bond
neighbors and the weakening of the correlations between water molecules. Kalinichev and
Bass [36] also found that the average number of H-bonds per water molecule falls below
the percolation threshold for the continuous 3D network of hydrogen bonds at the
temperatures above 100-200 °C. Although these calculations seem very supportive of our
proposal on the significance of the change in $r_{th}$ around 100-150 °C, work is planned to
further investigate water’s molecular geometry and the change in the topology of
intermolecular hydrogen bonding in this particular range of temperatures.
Building on our findings on $r_{th}$ and in the absence of other detailed experimental information, we incorporated in our modeling calculations a dependence on temperature of the DEA and of the branching ratios of the different decay channels for excited water molecules having the same functional characteristics as those of $r_{th}$ (Figure 4). We believe that this is a reasonable approach since these parameters should all be affected consistently by any change (diminution) in hydrogen bonding at elevated temperatures. Such a procedure also seems to be justified by the agreement we have obtained between model and experiment. For example, as illustrated in Figure 4a, the DEA was taken constant up to $\sim 100 \, ^\circ C$ (and equal to its value at 25 °C), and then increased rapidly up to $\sim 200-250 \, ^\circ C$ to finally follow a linear variation with temperature above $\sim 250 \, ^\circ C$. We also assumed that the values of these parameters at 350 °C were equal to those observed in water vapor (noting that a depleted hydrogen bonding in the liquid with increasing temperature is consistent with a change in those parameters towards their observed gas-phase values [27]). Thus, the maximum value of the DEA cross section, adjusted to $\sim 2.85 \times 10^{-18} \, \text{cm}^2$ at $\sim 8.7 \, \text{eV}$ in order to reproduce the prompt (apparently) ‘nonscavengeable’ yield of H$_2$ observed at room temperature [12], was set equal to its corresponding gas-phase value of $\sim 6.7 \times 10^{-18} \, \text{cm}^2$ [37] at 350 °C. As for the branching ratios associated with the various channels through which the excited water molecules decay, they remain largely unknown in the liquid phase.

Similarly, as shown in Figure 4b, a temperature dependence incorporating a discontinuity around 100-150 °C was included in the modeling for the decomposition of the different excited states of water, both electronic and vibrational. The contributions of these channels at 350 °C were also assumed to be equal to those reported for the gas phase [10,12].

3.3 Temperature dependence of the g-values for $e^-_{aq}$, $'OH$, $H^-$, $H_2O_2$, and $H_2$

The g-values of the various radiolytic products, calculated at the end of spur expansion (the lifetime, $\tau_s$, of the spur and its temperature dependence have been determined recently [33,38]; calculations show that $\tau_s$ decreases by about an order of magnitude over the 25-350 °C temperature range, going from $\sim 4.2 \times 10^{-7} \, \text{s}$ at 25 °C to $\sim 5.7$
times 10^{-8} s at 350 °C) from our Monte-Carlo simulations, are compared with experimental data in Figure 5a-e. As can be seen, a very good overall and simultaneous agreement is found between all calculated and experimental yields up to 350 °C. In particular, the sharp downward discontinuity predicted for g(H_2) at 150 °C (Figure 1) no longer appears (Figure 5e).

With the exception of g(H_2), all calculated g-values are consistent with the general observation that when the temperature is increased, the yields of 'free radicals' g(e^{-}_{aq}), g(\cdot OH), and g(\cdot H) continuously increase while the 'molecular' yield g(H_2O_2) decreases. Although H_2 is a molecular product, g(H_2) was observed to continue to increase with temperature, particularly above 200 °C. This anomalous increase in g(H_2) is briefly discussed below. The general trend of having yields of free radicals that increase with temperature can readily be explained from the fact that many important recombination reactions in the spur are not diffusion-controlled and therefore have rate constants that increase less with temperature than do the diffusion of the individual species out of the spur [7,20,29]. In other words, as the temperature increases, diffusion of the radical species out of the spur increases more rapidly than recombination, and one should have less molecular recombination product. This conclusion, of course long been known, was recently corroborated by picosecond pulse radiolysis experiments [32,48] on the decay kinetics of the hydrated electron in liquid water up to 350 °C and also in supercritical water.

### 3.4 Temperature dependence of g(H_2) above 200 °C: On the importance of the reaction $H^+ + H_2O \rightarrow H_2 + \cdot OH$

As mentioned above, g(H_2) is observed to continue to increase with temperature, particularly above 200 °C [5,29,31,43]. In an attempt to quantitatively explain this anomalous increase in H_2 yield, an additional channel for H_2 formation was postulated by Swiatla-Wojcik and Buxton (henceforth referred to as SWB) [44]. Using calculations based on an extended spur diffusion-kinetic model, these authors suggested that the reaction of hydrogen atoms with water:
\[ \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + \cdot \text{OH} , \]  

(1)

which can normally be neglected at room temperature, could become important at elevated temperatures. It is noteworthy that Sunaryo et al. [49], as early as 1995, had already emphasized the possible role of this reaction in the radiolysis of water at high temperatures. Based on a rate constant of $0.086 \, \text{M}^{-1} \, \text{s}^{-1}$ at 25 °C estimated from thermodynamic data, and literature values of $g(\text{H}_2)$ as a function of temperature, SWB calculated a corresponding activation energy of $\sim 66.3 \, \text{kJ/mol}$ over the temperature range 20-300 °C. More specifically, they inferred that a reaction rate constant of $\sim 3.2 \times 10^4 \, \text{M}^{-1} \, \text{s}^{-1}$ was required to explain the temperature dependence of $g(\text{H}_2)$ at 300 °C [44]. This value, however, was disputed by Bartels [50] on the basis of thermodynamic considerations. In his comment, this latter pointed out that this reaction could not be as fast as suggested by SWB and that the correct number for its rate constant was probably an order of magnitude lower. He suggested a value of $\sim 2.2 \times 10^3 \, \text{M}^{-1} \, \text{s}^{-1}$ at 300 °C as a best estimate [8,50]. In reply to this comment, Swiatla-Wojcik and Buxton [51] re-analyzed Bartels’ thermodynamic estimate and showed, in agreement with his results, that the rate constant of reaction (1) at room temperature was actually three orders of magnitude smaller than originally estimated. However, SWB found $1.75 \times 10^4 \, \text{M}^{-1} \, \text{s}^{-1}$ for the rate constant at 300 °C, a value somewhat lower than their original estimate. Most interestingly, Bartels [47] recently submitted a second comment in which he corrected several errors in his original calculations. Although he reached nearly identical results, he nevertheless concluded that an upper limit of $\sim 10^4 \, \text{M}^{-1} \, \text{s}^{-1}$ for the rate constant of reaction (1) at 300 °C appeared very reasonable. This latter result, as well as the revised estimate of SWB, turns out to be consistent with a most recent experimental estimate of this rate constant by Ghandi and coworkers [45] who inferred a value of about $10^4 \, \text{M}^{-1} \, \text{s}^{-1}$ from muon spin resonance spectroscopy measurements. Based on those above results, we adopted in our simulations this latter value for the rate constant of reaction (1).
Without going into all the details regarding the formation of H₂, which have already been discussed at length elsewhere, we show in Figure 5e the overall variation of g(H₂) as a function of temperature as obtained by our Monte-Carlo simulations, when incorporating reaction (1) and without incorporating this reaction. According to our simulations, it appears that reaction (1) is needed to reproduce the unexplained increase in the H₂ yield above 200 °C. Moreover, in view of the good agreement obtained between simulated and experimental g(H₂) results, our calculations tend to validate the value obtained independently by Swiatla-Wojcik and Buxton [46], Bartels [47], and Ghandi and coworkers [45], namely $\sim 10^4 \text{ M}^{-1} \text{s}^{-1}$ at 300 °C, that we used in this work for the rate constant of reaction (1).

4. Conclusion

In this work, we re-examined our Monte-Carlo simulation code of the low-LET radiolysis of liquid water at high temperatures in an attempt to reconcile our computed g-values of the various radiolytic products with newly measured or recently re-assessed experimental data up to 350 °C. Contrary to previous work, the inclusion in the simulations of the abrupt drop observed in the rate constant for the self-reaction of the hydrated electron above 150 °C led us to re-evaluate the temperature dependence of certain parameters intervening in the physicochemical stage of the radiolysis. In particular, the electron thermalization distance, determined by comparing our calculated time-dependent $e^-_{aq}$ yield data to recent picosecond pulse radiolysis measurements of the decay kinetics of $e^-_{aq}$ at different temperatures, was shown to exhibit a discontinuity at $\sim 100-150$ °C. Such a behavior suggested that liquid water might undergo a rapid alteration in its local structural order or, equivalently, in its hydrogen bonding network, near these temperatures, a result apparently supported by molecular dynamics and Monte-Carlo computer simulations. Building on these findings on $r_{th}$, similar functional forms were consistently attributed to the dependence on temperature of the dissociative electron attachment and the
decomposition of water excited states. Incorporating all this information in our simulations, a very good overall and simultaneous agreement was obtained between all calculated and experimental yields up to 350 °C. Finally, the importance of the chemical reaction of hydrogen atoms with water in contributing to the yet unexplained increase in the primary yield of H₂ above 200 °C was also pointed out. According to our calculations, a good agreement between simulated and experimental g(H₂) results was obtained with a rate constant of $10^4 \text{M}^{-1}\text{s}^{-1}$ at 300 °C.

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References


Figure 1: Influence of the bimolecular self-reaction of $e^-_{aq}$ on the primary yield of $H_2$ in the low-LET radiolysis of liquid water. The solid line shows our Monte-Carlo simulation results of $g(H_2)$ as a function of temperature, when the abrupt drop in the value of the rate constant for the self-reaction of $e^-_{aq}$ above 150 °C is incorporated in the calculations. As can be seen, $g(H_2)$ shows a marked inflection at $\sim 150$ °C which is not observed experimentally. Symbols, representing experimental data, are from [5] (■, □), [29] (▲), [30] (○), and [31] (▼).
Figure 2: Comparison of the experimental fast decay kinetics of $e^-_{aq}$ in water (H$_2$O) at 300 °C and 25 MPa, with our Monte-Carlo simulation results. The value of $r_{th}$ was obtained from a best fitting of the kinetic traces. The red line and the solid circles represent the experimental data obtained by direct picosecond pulse radiolysis (~60 ps to 6 ns, ~15 Gy/pulse) and by conventional nanosecond pulse radiolysis using $e^-_{aq}$ scavenging by MV$^{2+}$, respectively [32].
Figure 3: Temperature dependence of $r_{th}$ over the range 25-350 °C (solid line). The average electron thermalization distance at 25°C calculated from our simulations is $r_{th}(25 \, ^\circ C) \sim 11.3$ nm [12]. The dashed line corresponds to the temperature dependence of $r_{th}$ that we adopted in our previous studies on the radiolysis of water at high temperatures [7,13,33].
Figure 4: Temperature dependence of (a) the dissociative electron attachment (DEA) cross section and (b) the branching ratios for the different competing mechanisms in the fate of vibrationally excited water molecules (H$_2$O$^*$)$_{vib}$ (formed by recombination of a subexcitation electron with its water parent cation) and directly excited electronic states of water molecules. Values at 25 °C are from [12]. Values at 350 °C were assumed to be equal to those observed in water vapor [10,12] (see text).
FIG. 5

300-MeV protons
(LET ~ 0.3 keV/μm)
Liquid water, 25°C

(a) $g(e^-)$ (molec./100 eV)

(b) $g(\text{OH}^-)$ (molec./100 eV)

(c) $g(\text{H}^1)$ (molec./100 eV)

(d) $g(\text{H}_2\text{O}_2)$ (molec./100 eV)

(e) $g(\text{H}^1)$ (molec./100 eV)
Figure 5: Variation of the primary free-radical and molecular yields (in molec./100 eV) for the radiolysis of liquid water as a function of temperature over the range 25-350 °C: (a) \( g(\text{e}^-_{\text{aq}}) \), (b) \( g(\cdot \text{OH}) \), (c) \( g(\cdot \text{H}) \), (d) \( g(\text{H}_2\text{O}_2) \), and (e) \( g(\text{H}_2) \). Simulated results are shown as solid lines. Experimental data are from: [5] (■,□), [8] (- - -, recommended temperature dependence for the \( g \)-value), [29] (▲), [30] (○), [31] (▼), [39] (▲), [40-42] (●), and [43] (△). Note that the \( g \)-values reported for \( \text{e}^-_{\text{aq}} \) and \( \cdot \text{OH} \) are slightly elevated (as compared to the true "escape" yields) as a consequence of too high solute scavenging capacities (the reciprocal of the scavenging capacity gives a measure of the time scale over which the scavenging is occurring) used in the experiments [8,40-42]. This explains the difference that we observe between our simulated \( g(\text{e}^-_{\text{aq}}) \) and \( g(\cdot \text{OH}) \) values and the corresponding experimental data, these yields being simply not compared at the same time. Note also that our simulations incorporate the reaction \( \cdot \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \cdot \text{OH} \) suggested by Swiatl-Wojcik and Buxton [44] to account for the unexplained increase in the yield of \( \text{H}_2 \) at high temperature. The rate constant for this reaction was taken here equal to \( 10^4 \text{ M}^{-1} \text{s}^{-1} \) at 300 °C [45-47]. The dotted line shown for \( g(\text{H}_2) \) above 200 °C represents our simulated results calculated without incorporating this reaction in the simulations.
TEMPERATURE DEPENDENCE OF THE FRICKE DOSIMETER AND SPUR EXPANSION TIME IN THE LOW-LET HIGH-TEMPERATURE RADIOLYSIS OF WATER UP TO 350 °C: A MONTE-CARLO SIMULATION STUDY


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Foreword:

In this work, I updated our Monte-Carlo programs for the simulations of the Fricke dosimeter and also for the simulations of the radiolysis of aqueous 0.4 M H₂SO₄ solutions. In particular, I incorporated the temperature dependence of certain parameters intervening in the physicochemical stage of the radiolysis and also the best recommended values of the reaction rate constants reported by Elliot and Bartels (2009). I performed all the calculations of the lifetime of the spur. Finally, I wrote the first draft of the article.
ABSTRACT – Monte-Carlo simulations of the radiolysis of the ferrous sulfate (Fricke) dosimeter with low-linear energy transfer (LET) radiation (such as $^{60}$Co γ-rays or fast electrons) have been performed as a function of temperature from 25 to 350 °C. The predicted yields of Fe$^{2+}$ oxidation are found to increase with increasing temperature up to ~100-150 °C, and then tend to remain essentially constant at higher temperatures, in very good agreement with experiment. By using a simple method based on the direct application of the stoichiometric relationship that exists between the ferric ion yields so obtained $G(\text{Fe}^{3+})$ and the sum \{3 \left[ g(e^-_{aq} + H^+) + g(\text{HO}_2^+) \right] + g(\text{OH}) + 2 g(\text{H}_2\text{O}_2) \},$ where $g(e^-_{aq} + H^+), g(\text{HO}_2^+), g(\text{OH}),$ and $g(\text{H}_2\text{O}_2)$ are the primary radical and molecular yields of the radiolysis of deaerated 0.4 M $\text{H}_2\text{SO}_4$ aqueous solutions, the lifetime ($\tau_s$) of the spur and its temperature dependence have been determined. In the spirit of the spur model, $\tau_s$ is an important indicator for overlapping spurs, giving the time required for the changeover from nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution. The calculations show that $\tau_s$ decreases by about an order of magnitude over the 25-350 °C temperature range, going from ~4.2 x 10$^{-7}$ s at 25 °C to ~5.7 x 10$^{-8}$ s at 350 °C. This decrease in $\tau_s$ with increasing temperature mainly originates from the quicker diffusion of the individual species involved. Moreover, the observed dependence of $G(\text{Fe}^{3+})$ on temperature largely reflects the influence of temperature upon the primary free-radical product yields of the radiolysis, especially the yield of H$^+$ atoms. Above ~200-250 °C, the more and more pronounced intervention of the reaction of H$^+$ atoms with water also contributes to the variation of $G(\text{Fe}^{3+})$, which may decrease or increase slightly, depending on the choice made for the rate constant of this reaction. All calculations reported herein use the radiolysis database of Elliot (Atomic Energy of Canada Limited) and Bartels (University of Notre Dame) that contains all the best currently available information on the rate constants, reaction mechanisms, and g-values in the range 20 to 350 °C.
Keywords – Liquid water; aqueous 0.4 M H₂SO₄ solution; Fricke dosimeter; radiolysis; temperature; radical and molecular yields; kinetics of formation and yield of Fe³⁺ ions; spur expansion; duration of nonhomogeneity; Monte-Carlo simulations.

I. Introduction

The radiation chemistry of liquid water is of considerable importance, not only for the intrinsic scientific interest it generates, but as well, because of its relevance to a number of practical applications. It is particularly important in radiation biology where living cells are composed of about 70-85% water by weight, and also in a number of domains of nuclear science and technology, such as in water-cooled nuclear power reactors where a quantitative understanding of the yields and activities of decomposition products of water is needed in order to mitigate the effects of water radiolysis and thus limit unwanted corrosion and degradation of materials by oxidizing species. A good summary of the present status of aqueous radiation chemistry is given in refs. 1-7.

The radiolysis of pure, deaerated liquid water by low-LET (linear energy transfer or energy loss per unit track length, -dE/dx), sparsely ionizing radiation (such as ⁶⁰Co γ-rays, fast electrons, or high-energy protons), at room temperature, is generally well understood. Briefly, it leads to the formation of the free radicals and molecular products \( \text{e}^-_{\text{aq}} \) (the "hydrated" electron), \( \text{OH}^- \), \( \text{H}_3\text{O}^+ \), \( \text{H}^+ \), \( \cdot \text{OH} \), \( \text{H}_2 \), \( \text{H}_2\text{O}_2 \), \( \text{HO}_2^-/\text{O}_2^- \) \( (pK_a = 4.8 \text{ at } 25 \degree C) \), etc.

Under usual irradiation conditions (i.e., at modest dose rates), these species are generated nonhomogeneously on subpicosecond time scales in small, spatially well-separated regions of dense ionization and excitation events, called "spurs", along the track of the incident radiation. Owing to diffusion from their initial positions, the radiolytic products then either react within the spurs as they develop in time or escape into the bulk solution. The so-called "primary" radical and molecular yields (or "escape" yields) \( g(\text{e}^-_{\text{aq}}) \), \( g(\text{H}^+) \), \( g(\cdot \text{OH}) \), \( g(\text{H}_2) \), \( g(\text{H}_2\text{O}_2) \), etc., represent the numbers of species of each kind formed or destroyed per
100 eV of absorbed energy that remain after spur expansion. At 25 °C, the lifetime of a spur is generally taken to be \( \sim 10^{-7} - 10^{-6} \) s. By this time, the species that have escaped from spur reactions become homogeneously distributed throughout the bulk of the solution and available to react with dissolved solutes (if any) present (in moderate concentrations) at the time of irradiation.

At elevated temperatures, however, the time at which the homogeneous chemistry takes over within the solution is not well determined, even if one can expect the changeover from (nonhomogeneous) spur kinetics to homogeneous kinetics to occur faster than at ambient temperature. In fact, our earlier Monte-Carlo simulations already indicated that the time at which the nonhomogeneous chemical stage is completed diminishes with increasing temperature. Such a trend was also observed in recent measurements of the fast spur decay kinetics of \( e_{aq}^- \) using pulse radiolysis in the picosecond/nanosecond time range at elevated temperatures. The present study is precisely an attempt to quantitatively assess the temperature dependence of the spur expansion, more specifically the “spur expansion” time or yet the duration of nonhomoogeneity (nonhomogeneous to homogeneous conversion time) – called \( \tau_s \) thereafter – from ambient up to 350 °C. The approach adopted here employs Monte-Carlo simulations of the radiolysis of the ferrous sulfate (Fricke) dosimeter, as described below.

II. The Fricke dosimeter

One of the most studied systems in radiation chemistry is the air-saturated (~2.5 \times 10^4 M O_2) solution of 1-10 mM ferrous sulfate in aqueous 0.4 M H_2SO_4, which is referred to as the “Fricke dosimeter” after Hugo Fricke who first published accounts of its properties in 1927-1929. Of all aqueous systems studied, the Fricke dosimeter is certainly the best understood, and the most widely used, liquid chemical dosimeter. Much has already been published on its underlying reaction mechanism and response in a wide variety of scenarios.
including LET and temperature effects.\textsuperscript{15,17} The chemistry of this system is based upon the oxidation of ferrous ions to ferric ions by the species H', \(^{1} \text{HO}_{2}^{*}\), \(^{1} \text{OH}\), and \(^{1} \text{H}_{2} \text{O}_{2}\)\textsuperscript{18} that are formed in the water of the irradiated solution under aerated conditions.\textsuperscript{1,15,19-21} From this mechanism, the yield of \(^{3+} \text{Fe}\) ions in an irradiated Fricke dosimeter can readily be expressed in terms of the escape yields (i.e., at \(\tau_{s}\)) of the radical and molecular products of the radiolysis of air-free 0.4 \(M\) \(\text{H}_{2} \text{SO}_{4}\) aqueous solution by the following stoichiometric equation:\textsuperscript{1,19,21}

\[
G(\text{Fe}^{3+}) = 3 \left[ g(e^{-}_{\text{aq}} + H^{+}) + g(\text{HO}_{2}^{*}) \right] + g(\text{OH}) + 2 \ g(\text{H}_{2} \text{O}_{2}) ,
\]

where \(g(e^{-}_{\text{aq}} + H^{+})\) represents the sum of the primary yields of the reducing radicals \(e^{-}_{\text{aq}}\) and \(H^{+}\).

III. Procedure used to estimate the "spur expansion" time \(\tau_{s}\)

A simple procedure, based on the use of eqn. (1) (i.e., on the well-established reaction mechanism of the Fricke dosimeter), has been implemented to determine \(\tau_{s}\) and its dependence on temperature from ambient up to 350 °C. This procedure involves the following three steps: (i) a direct Monte-Carlo simulation of the radiolytic oxidation of \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\) in the aerated Fricke dosimeter is first conducted in order to determine \(G(\text{Fe}^{3+})\) as a function of temperature; (ii) Monte-Carlo simulations of the radiolysis of air-free 0.4 \(M\) \(\text{H}_{2} \text{SO}_{4}\) aqueous solutions are next performed to determine, for the 25-350 °C temperature range studied, the yields of the species \(H^{+}\), \(\text{HO}_{2}^{*}\), \(\text{OH}\), and \(\text{H}_{2} \text{O}_{2}\) that are involved in eqn. (1) as a function of time during the nonhomogeneous chemical stage (i.e., during spur expansion);\textsuperscript{22} and (iii) the lifetime of the spur \(\tau_{s}\) and its temperature dependence are then readily obtained by identifying, at each considered temperature, the coordinates of the intersection of the curve showing the \textit{directly} simulated ferric ion yields and the
corresponding yield values calculated using eqn. (1) at different selected times. These various steps are described in more detail below.

IV. Monte-Carlo simulations

Monte-Carlo simulation methods are used to model the complex sequence of events that are generated in liquid water following absorption of ionization radiation. Such a procedure is particularly well-suited to account for the stochastic nature of the phenomena. The detailed description and implementation of our Monte-Carlo code IONLYS-IRT that simulates the radiolysis of air-free aqueous 0.4 $M$ H$_2$SO$_4$ solutions (pH $\sim$ 0.46) and the radiation-induced oxidation of ferrous sulfate solutions in the (aerated) Fricke dosimeter at both ambient and elevated temperatures have been given previously.$^{7,11,21,23}$ In brief, the IONLYS simulation program covers the early “physical” and “physicochemical” stages of radiation action up to $\sim 10^{-12}$ s. It models, event by event, all the basic physical interactions (energy deposition) and the subsequent establishment of thermal equilibrium in the system (conversion of the physical products created locally after completion of the physical stage into the various initial radical and molecular products of the radiolysis, distributed in a highly nonhomogeneous track structure). The complex spatial distribution of reactants at the end of the physicochemical stage, which is provided as an output of the IONLYS program, is then used directly as the starting point for the subsequent “nonhomogeneous chemical” stage (from $\sim 10^{-12}$ to $\sim 10^{-7}$-$10^{-6}$ s at 25 °C). This third stage, during which the individual reactive species diffuse randomly at rates determined by their diffusion coefficients and react with one another or, competitively, with any added solutes present at the time of irradiation (and for which the relevant reaction rates are known) until all spur processes are complete (at $\tau_s$), is covered by our IRT program. This IRT program can obviously also be used efficiently to describe the “homogeneous” chemical stage that takes place at longer times, as is the case here for the simulation of the Fricke dosimeter in which
ferric ions are produced at a wide variety of times. This program employs the "independent reaction times" (IRT) method, a computer efficient stochastic simulation technique that is used to simulate reaction times without following the trajectories of the diffusing species.\textsuperscript{24,25} Its implementation has been described in detail.\textsuperscript{26} The ability of this program to give accurate time-dependent chemical yields under different irradiation conditions has been well validated by comparison with full random flights (or "step-by-step") Monte-Carlo simulations, which do follow the reactant trajectories in detail.\textsuperscript{27,28}

The effects of the background concentration of H\textsuperscript{+} in aqueous 0.4 M sulfuric acid solutions were added to the IRT program as pseudo first-order reactions. We also supplemented the reaction scheme for the radiolysis of pure deaerated liquid water\textsuperscript{6,7,26,29} to include the reactions that account for the species (HSO\textsubscript{4}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, SO\textsubscript{4}\textsuperscript{2-}, and S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}) present in irradiated aqueous H\textsubscript{2}SO\textsubscript{4} solutions.\textsuperscript{7,21,30} In addition, we introduced the effect of ionic strength of the solutions on all reactions between ions.\textsuperscript{7,21,31} Over the 25-350 °C temperature range studied, the correction to the reaction rate constants was made using the following equation\textsuperscript{32,33}

\[
\log\left(\frac{k}{k_0}\right) = 3.64 \times 10^6 \frac{Z_a Z_b}{(\varepsilon T)^{3/2}} \left(\frac{I^{1/2}}{1 + I^{1/2}}\right) \tag{2}
\]

where \(k\) is the rate constant at ionic strength \(I\), \(k_0\) is the rate constant in the limit of zero ionic strength (i.e., at infinite dilution of ions), \(Z_a\) and \(Z_b\) are the algebraic numbers of charges on the reactants (positive for cations and negative for anions), \(T\) is the absolute temperature (in K), \(\varepsilon\) is the dielectric constant of the medium (for water, \(\varepsilon = 78.5\) at 25 °C and 13.0 at 350 °C), and \(I\) (in M) is defined as:\textsuperscript{34}

\[
I = \frac{1}{2} \sum_i Z_i^2 C_i \tag{3}
\]

where \(Z_i\) is the charge number of the \(i_{th}\) ion and \(C_i\) is its molar concentration (the sum extends over all ionic species present in the solution). According to eqn. (2), the rate
constants will increase, decrease, or remain the same with increasing ionic strength, depending on whether the ions have the same sign, opposite signs, or whether one species is uncharged. Finally, in our simulations the "direct" action of ionizing radiation on the sulfuric acid anions (mainly the hydrogen sulfate ion $\text{HSO}_4^-$) was neglected, which is a reasonably good approximation in the sulfuric acid concentration studied.\(^{35}\)

To stochastically model the chemistry of the Fricke dosimeter, we added to the IRT program the reactions of $\text{Fe}^{2+}$ ions with the oxidizing species $\text{HO}_2^*$, $'\text{OH}$, and $\text{H}_2\text{O}_2$ that are formed in the water of the irradiated solutions under aerated conditions.\(^{7,21,36}\) Under normal irradiation conditions, the radical concentrations are low compared with the background concentrations of $\text{Fe}^{2+}$ ions and $\text{O}_2$ in solution, and those reactions were treated in the IRT program as pseudo first-order. The values of the rate constants at 25 °C of the individual reactions taking place in the radiolytic oxidation of $\text{Fe}^{2+}$ ions to $\text{Fe}^{3+}$ have previously been determined.\(^{7,21,29,37-39}\) The most rapid reaction of $\text{Fe}^{2+}$ ions is with $'\text{OH}$ radicals ($k = 3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) while the slowest component of the kinetics of $\text{Fe}^{3+}$ formation is due to the reaction of $\text{Fe}^{2+}$ with hydrogen peroxide ($k = 52 \text{ M}^{-1} \text{ s}^{-1}$). For example, in the case of 5 mM $\text{FeSO}_4$ solutions considered in this work, the (Fenton-type) reaction\(^{40}\)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + '\text{OH} + \text{OH}^- \quad (4)$$

takes several seconds to go to completion,\(^{21}\) which significantly increases the computer time usually needed for modeling the radiolysis of liquid water. The remaining intermediate stage is due to the reaction of $\text{Fe}^{2+}$ with hydroperoxyl radicals ($k = 7.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). In the simulations reported here, the time evolution of $G(\text{Fe}^{3+})$ was followed until $\sim$50-200 s.

As for the calculations of $G(\text{Fe}^{3+})$ as a function of temperature from ambient up to 350°C, we used an extended version of our IONLYS-IRT code which was developed previously to include the effects of high temperature on the low-LET radiolysis of liquid
The important parameters are the yields of the primary products of water radiolysis and the rate constants of their inter-reactions. In this version of IONLYS-IRT, we used the radiolysis database, including rate constants, diffusion coefficients, reaction mechanisms, and g-values, recently compiled by Elliot and Bartels. This new database provides a recommendation for the best values to use in high-temperature modeling of water radiolysis up to 350 °C. In addition, the inclusion in the simulations of the rapid drop observed in the rate of the self-reaction of $e_{aq}^{-}$ above 150 °C (contrary to previous work) led us to re-evaluate the temperature dependence of some parameters involved in the early physicochemical stage of the radiolysis, namely, the electron thermalization distance ($r_{th}$), the dissociative electron attachment (DEA), and the branching ratios of the different excited water molecule decomposition channels. The details of this re-evaluation are published elsewhere but we briefly summarize them here. In essence, the values of $r_{th}$ were obtained from comparing our simulated time-dependent $e_{aq}^{-}$ yield data to recent picosecond (~60 ps to 6 ns) and conventional nanosecond (using $e_{aq}^{-}$ scavenging by methyl viologen MV$^{2+}$) pulse radiolysis measurements of the decay kinetics of $e_{aq}^{-}$ at several different temperatures between 25 and 350 °C. Using this best fitting procedure, $r_{th}$ – defined as the length of the vector (|Rf - Ri|) from the point of departure (Ri) to the final (Rf) position of the electron after thermalization – was found to remain essentially unchanged up to ~100-150°C (and equal to its value at 25 °C), but to decrease sharply at higher temperatures with $r_{th}/r_{th}(25 °C) = 0.29$ at 350°C. Physically, this decrease in $r_{th}$ above 100-150 °C was interpreted as indicating an increase in the scattering cross-sections of subexcitation electrons ($e_{sub}^{-}$) that accounts for a loss of structural order of water molecules due to an increasing breaking of hydrogen bonds with temperature. Building on these findings on $r_{th}$, we also incorporated in our modeling calculations a dependence on temperature of the dissociative attachment of subexcitation electrons and of the branching ratios of the different decay channels for excited water molecules (as $r_{th}$, these other physicochemical
parameters are sensitive to the local structural order of water). This dependence was in a functional form similar to that of \( r_{th} \), i.e., taken constant up to \(-100\text{-}150 \, ^\circ\text{C}\) and then followed by a marked discontinuity around these temperatures. In the absence of other detailed experimental information, the values of these latter parameters at 350 \( ^\circ\text{C}\) were assumed to be equal to those observed in water vapor,\(^{41}\) a procedure that has already been used previously.\(^{45}\)

The temperature dependences of the rate constants for the ferrous ion reactions with 'OH, \( \text{HO}_2^- \), and \( \text{H}_2\text{O}_2 \) were scaled from their values at 25 \( ^\circ\text{C} \) using simple Arrhenius equations with activation energies of 9.2, 42, and 42 kJ/mol, respectively.\(^{37,40,46,47}\) Finally, as there are no experimental data available on the temperature dependences of the diffusion coefficients of the \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions, the procedure adopted here was to scale the 25 \( ^\circ\text{C} \) values (0.719 \( \times \) 10\(^{-9} \) and 0.604 \( \times \) 10\(^{-9} \) m\(^2\) s\(^{-1}\), respectively)\(^{18}\) according to the self-diffusion in liquid water.\(^{11}\)

All Monte-Carlo simulations reported here were performed along the liquid-vapor coexistence curve, the density of the pressurized water decreasing from 1 g/cm\(^3\) (1 bar or 0.1 MPa) at 25 \( ^\circ\text{C} \) to 0.575 g/cm\(^3\) (16.5 MPa) at 350 \( ^\circ\text{C} \).\(^{49}\) For this temperature range, calculations show that \( g \)-values vary only little with the applied pressure (density). Finally, to reproduce the effects of fast electron or \( ^{60}\text{Co} \) \( \gamma \)-ray radiolysis, we used short (typically, \(~150 \mu\text{m} \)) segments of 300-MeV proton tracks, over which the average LET value obtained in the simulations was nearly constant and equal to \(~0.3 \text{ keV}/\mu\text{m} \) at 25 \( ^\circ\text{C} \).\(^{50}\) Such model calculations thus gave “track segment” yields at a well-defined LET.\(^4\) The number of proton histories (usually \(~150 \)) was chosen so as to ensure only small statistical fluctuations in the computed averages of chemical yields, while keeping acceptable computer time limits.
V. Results and discussion

Figure 1 shows the time evolution of $G(\text{Fe}^{3+})$ as obtained from our simulations of the radiolysis of the Fricke dosimeter by 300-MeV incident protons at different temperatures in the range 25-350 °C. As we can see from this figure, $G(\text{Fe}^{3+})$ is time dependent as a result of the differences in the lifetimes of the reactions occurring in the oxidation of ferrous sulfate by radiation. All reactions take place faster at higher temperature. The kinetics of $\text{Fe}^{3+}$ formation at 350°C is several orders of magnitude faster than at room temperature. Also, an interesting feature shown in this figure is the increase of $G(\text{Fe}^{3+})$ with temperature up to ~100-150 °C, followed by stabilization to a value essentially constant at higher temperatures. The influence of the irradiation temperature on the Fricke yield is further illustrated in Fig. 2 over the range 25-350 °C. As can be seen, a very good agreement is obtained between our computed $\text{Fe}^{3+}$ yields and the available experimental data. Interestingly, the predicted yield of $\text{Fe}^{3+}$ increases from ~15.4 to 16.7 molec./100 eV on going from 25 to 150 °C, which corresponds to a temperature coefficient of ~1.0% per degree over this range of temperature.

In Fig. 3, we show the sensitivity of our simulated Fricke yield results on variations in the value of the rate constant for the oxidation of water by the hydrogen atom:

$$H^* + H_2O \rightarrow H_2 + \cdot OH,$$

which was recently suggested by Swiatla-Wojcik and Buxton (hereafter referred to as SWB) to quantitatively explain the anomalous increase of the primary yield of $H_2$ in the low-LET radiolysis of water above ~200-250 °C. Using deterministic diffusion-kinetic calculations, SWB inferred that a reaction rate constant of $3.2 \times 10^4 M^{-1} s^{-1}$ was required to account for the observed additional yield of $H_2$ at 300 °C. This rate constant value, however, was disputed by Bartels on the basis of thermodynamic arguments. This latter argued that reaction (5) could not be as fast as suggested and proposed that a better estimate
of this number was rather $-2.2 \times 10^3 \, M^1 \, s^{-1}$ at 300 °C. In reply to these comments, Swiatla-Wojcik and Buxton\textsuperscript{58} re-analyzed Bartels's thermodynamic estimate to eventually lead to a revised value of $1.75 \times 10^4 \, M^1 \, s^{-1}$ for the rate constant at 300 °C. According to our own most recent Monte-Carlo simulations of the radiolysis of water at high temperatures,\textsuperscript{41} it appears that reaction (5) is actually needed if we want to reproduce the unexplained increase in the H$_2$ yield above $-200$ °C. Moreover, calculations\textsuperscript{41} also show that a good agreement between simulated and experimental $g$(H$_2$) results is obtained with the rate constant of $-10^4 \, M^1 \, s^{-1}$ at 300 °C, a value recently inferred by Ghandi and coworkers\textsuperscript{59} from muon spin resonance spectroscopy experiments and also very close to that re-estimated by SWB.\textsuperscript{58} Thus, all computations presented in this study were carried out by incorporating reaction (5) and using, unless otherwise specified, Ghandi et al.'s reported rate constant value. As we can see from Fig. 3, using SWB's rate constant\textsuperscript{56} for reaction (5) leads to values of $G$(Fe$^{3+}$) that decrease slightly above $-200$-250 °C. On the contrary, if we adopt the rate constant given by Bartels, the $G$(Fe$^{3+}$) values so obtained increase slightly at elevated temperatures. The choice of Ghandi et al.'s rate constant for reaction (5), in turn, leads to values of $G$(Fe$^{3+}$) which are essentially insensitive to temperature above $-150$ °C. For the sake of reference, we also calculated $G$(Fe$^{3+}$) in complete absence of reaction (5). The results, shown in Fig. 3, indicate an increase in $G$(Fe$^{3+}$) above $-200$-250 °C which is slightly higher than that found when using the reaction rate constant value proposed by Bartels. Unfortunately, there are no experimental data currently available in the literature in this range of temperatures with which to compare the above results. It thus appears difficult at present to conclude on the basis of this study only, on the importance of the role of reaction (5) in the low-LET radiolysis of water at high temperatures or, equivalently, on the rate constant that is indeed associated with this reaction.
As mentioned above, a simple three-step procedure, based on the use of eqn. (1) of the Fricke dosimeter, was employed to determine the "spur expansion" time \( \tau_s \) as a function of temperature from 25 to 350 °C. This procedure, illustrated in Fig. 4, can be described as follows (see also Sect. III).

(i) Monte-Carlo simulations of the radiolytic oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) in the aerated Fricke dosimeter irradiated by 300-MeV incident protons are first performed in order to directly determine \( G(\text{Fe}^{3+}) \) as a function of temperature. These \( G(\text{Fe}^{3+}) \) calculations, already presented in Figs. 1-3, are shown as the thick solid line in Fig. 4. Note that, in this figure, the computed values of \( G(\text{Fe}^{3+}) \) are shown in their raw form, unlike in Figs. 1-3 where these data have been smoothed.

(ii) Monte-Carlo simulations of the radiolysis of deaerated 0.4 \( \text{M} \) H\(_2\)SO\(_4\) aqueous solutions (pH ~ 0.46) are next carried out in the same irradiation conditions to determine, for temperatures in the range 25-350 °C, the yields of the species (H\(^+\), HO\(_2\), \('\text{OH}, and \text{H}_2\text{O}_2\) that are involved in eqn. (1) at different selected times during the period of nonhomogeneous chemistry following irradiation (i.e., during spur expansion). Using these yield values, the right-hand side of eqn. (1) – which is of course not equal in general to the Fricke yield \( G(\text{Fe}^{3+}) \) and which we will thus call here "\( \Gamma \)" for the sake of convenience\(^{22} \) – can then be calculated at each selected time between \(~10^{-8}\) and \(~10^{-6}\) s as a function of temperature. The various calculated curves of "\( \Gamma \)" vs. temperature, parameterized by time, thus obtained are shown in Fig. 4.

(iii) Finally, for the range of temperature studied, the times \( \tau_s \) at which spur reactions are complete are obtained from the data displayed in Fig. 4 by simply identifying the intersections of the \( G(\text{Fe}^{3+})\)-vs.-temperature curve directly obtained from the simulations in (i) with each of the "\( \Gamma \)" curves vs. temperature calculated from the right-hand side of eqn. (1) at different times in (ii). The lifetime of the spur and its temperature dependence are then simply obtained from the coordinates of all those intersections (at these particular
points, $G(\text{Fe}^{3+}) = \text{"I"}$). The corresponding values of $\tau_s$ are shown in Fig. 5 as a function of temperature.

The above procedure is particularly useful because it offers, to our knowledge for the first time, a quantitative estimate of the time required to observe the transition from nonhomogeneity to homogeneity in the distribution of the reactive species$^{60}$ formed in $^{60}$Co-$\gamma$-irradiated water as the temperature is raised from 25 up to 350 °C. In the spirit of the spur model,$^{8,9} \tau_s$ is an important indicator for overlapping spurs and the establishment of homogeneity following irradiation. In this regard, $\tau_s$ is well-known to be dependent on factors such that the quality of the radiation (LET) and the rate of energy deposition (i.e., the dose rate). Here, we demonstrate that $\tau_s$ also strongly depends upon the irradiation temperature. Indeed, as can be seen from Fig. 5, $\tau_s$ is found to decrease over the temperature range studied by about an order of magnitude, from $\sim4.2 \times 10^{-7}$ s at 25 °C to $\sim5.7 \times 10^{-8}$ s at 350 °C.$^{51}$ This decrease in $\tau_s$ with increasing temperature, which essentially originates from the quicker diffusion of the individual species involved in spur reactions, was already identified in our earlier Monte-Carlo simulations of the radiolysis of water at high temperatures.$^{11,12}$ Experimentally, such a trend was also clearly observed recently, especially in the $e^-_{\text{aq}}$ decay measurements of Baldacchino et al.$^{13}$ using pulse radiolysis in the picosecond/nanosecond time range from room temperature up to 350 °C. These authors observed that with increasing temperature the decay of $e^-_{\text{aq}}$ became less and less pronounced. At 350 °C, they reported an almost flat signal from $\sim100$ ps to 2.75 ns, suggesting an efficient escape of hydrated electrons from spur reactions. Similar conclusions were obtained by Muroya et al.$^{14}$ who first reported the kinetics of the decay of $e^-_{\text{aq}}$ in supercritical water (D$_2$O) at 400 °C, and most recently in H$_2$O at several different temperatures between 25 and 350 °C (see Sect. IV),$^{41}$ using picosecond time-resolved experiments in the range $\sim60$ ps to 6 ns.
Closer examination of the data presented in Fig. 5 shows that the variation of \( \tau_s \) with temperature can be well represented by the empirical functional equation

\[
\tau_s = A t^n,
\]

where \( n \) is the slope of the straight line in the log-log plot of \( \tau_s \) against temperature shown in the inset of Fig. 5. A fit of eqn. (6) to the data using a least-squares method gives \( n \approx 0.775 \pm 0.015 \). In other words, our calculations predict that \( \tau_s \) is roughly inversely proportional to the temperature power \( 3/4 \) over the 25-350 °C temperature range studied.

Before closing, it is worth saying a few additional words on the (stoichiometric) relationship that exists between \( G(\text{Fe}^{3+}) \) and the various primary radical and molecular yields of the radiolysis of a deaerated aqueous 0.4 M \( \text{H}_2\text{SO}_4 \) solution [see eqn. (1)]. In fact, to better assess the relative importance of these yields in the production of \( \text{Fe}^{3+} \) ions in the Fricke dosimeter, we present in Fig. 6 the results of our Monte-Carlo simulations showing the variations of the g-values for \( \text{H}^+ \) (considering the conversion of \( \text{e}^-_{\text{aq}} \) to \( \text{H}^+ \) in the spurs in acidic solution\textsuperscript{18}), \( \cdot\text{OH}, \text{H}_2\text{O}_2, \text{H}_2, \) and \( \text{HO}_2^- \) (calculated at the end of spur expansion, i.e., at \( \tau_s \)) as a function of temperature over the range 25-350 °C. As in neutral water\textsuperscript{6,41} it is seen that, with the exception of \( g(\text{H}_2) \), the primary yields of free-radical products increase with increasing temperature while the molecular yield \( g(\text{H}_2\text{O}_2) \) decreases. This general trend of having yields of free radicals that increase with temperature is explained from the fact that most important radical recombination reactions in the spur are not diffusion-controlled and therefore have rate constants that increase less with temperature than do the diffusion of the individual species out of the spur.\textsuperscript{11,33,63} In other words, as the temperature increases, diffusion of the radical species out of spurs increases more rapidly than recombination, and one should anticipate less molecular recombination product. As one can see from Fig. 6, our computed results generally agree very well with experimental yields reported in the literature.\textsuperscript{1,44,51,62,64} They are also in good accord with recent diffusion-kinetic model
calculated results in irradiated acidic water (data not shown here).\(^6\) Of particular note is the remarkable agreement found between our calculated g-values for 'OH and H' and those measured by Katsumura et al.\(^5\) up to 250 °C. For example, these authors concluded that g(H') "seems to maintain an almost constant value" over their investigated range of temperatures. Such a result is very well reproduced by our calculations, which show that, indeed, g(H') varies little between 25 and 350 °C. Turning to the effect of temperature on the Fricke yield shown in Figs. 2 and 3, one can now better understand (or rather visualize), in light of the results shown in Fig. 6, why G(Fe\(^{3+}\)) increases with increasing temperature up to ~100-150 °C and why it is relatively temperature independent at higher temperatures. Clearly, G(Fe\(^{3+}\)) is highly sensitive to the primary free-radical yields, especially H' atoms (via formation of HO\(_2^*\)) and also, but to a lesser degree (in fact, by a factor of ~3) hydroxyl radicals. Below ~100-150 °C, the increase in G(Fe\(^{3+}\)) is due primarily to the combined action of g(H') and g('OH), which both increases, the contribution of H\(_2\)O\(_2\) to the oxidation of Fe\(^{2+}\) ions to Fe\(^{3+}\) being only relatively inefficient in this temperature range. On the contrary, at higher temperatures, the combined reductions of g(H') and g(H\(_2\)O\(_2\)) more or less counterbalance the increase in g('OH) with the net result that the observed Fricke yield appears as relatively independent of temperature.

VI. Conclusion

In this work, we have presented a simple procedure, based on the well-established reaction mechanism of the Fricke dosimeter, to estimate the temperature dependence of the lifetime of the spur (\(\tau_s\)) in the low-LET radiolysis of water under ordinary irradiation conditions. This procedure uses Monte-Carlo simulations of the radiolysis of the ferrous sulfate (Fricke) dosimeter and of deaerated 0.4 M H\(_2\)SO\(_4\) aqueous solutions at different selected times during spur expansion. \(\tau_s\) is found to vary approximately as \(t^n\) with \(n \approx 0.775 \pm 0.015\) over the range 25 to 350 °C, going from \(-4.2 \times 10^{-7}\) s at 25 °C to \(-5.7 \times 10^{-8}\)
s at 350 °C. To our knowledge, this is the first time that such a quantitative assessment of the time required for the changeover from spur kinetics to homogeneous kinetics is performed in the low-LET radiolysis of water as a function of temperature up to 350 °C. Moreover, our calculated $G(\text{Fe}^{3+})$ values compare very well with the available experimental data and are also in good accord with those predicted theoretically by other authors. This good overall agreement between calculated and experimental yield values gives, in turn, good support to the validity and consistency of the assumptions employed in this study.

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Figure 1: Time evolution of $G(\text{Fe}^{3+})$ (in molec./100 eV) for 300-MeV incident protons (LET ~ 0.3 keV/μm at 25 °C) in air-saturated solutions of 5 mM FeSO$_4$ in aqueous 0.4 $M$ H$_2$SO$_4$ at different temperatures in the range 25-350 °C. The different lines correspond to our theoretical simulations at 25 °C (solid line), 50 °C (dotted line), 100 °C (dashed line), 200 °C (dash-dot line), and 350 °C (dash-dot-dot line) (see text). The arrow on the right of the figure shows the accepted value (15.6 molec./100 eV) of the yield of the Fricke dosimeter for $^{60}$Co γ-rays and fast electrons at room temperature (see, for example, refs. 1, 15, 19, 21, and 50).
Figure 2: Yield of Fe\(^{3+}\) ions (at ~50 s) (in molec./100 eV) in aerated Fricke (5 mM FeSO\(_4\) in aqueous 0.4 M H\(_2\)SO\(_4\)) solutions as a function of temperature, for 300-MeV irradiating protons (LET ~ 0.3 keV/\(\mu\)m at 25 °C). The solid line shows the values of \(G(\text{Fe}^{3+})\) obtained from our Monte-Carlo simulations in the range 25-350 °C (see text). The dotted line represents the \(G\)-values for the Fricke dosimeter predicted by Běgusová and Pimblott (ref. 38) from stochastic IRT simulations employing simulated electron track structures. Experiment: (□) ref. 44, (▲) ref. 51, (●) ref. 52, (○) ref. 53, and (▼) ref. 54.
Figure 3: Sensitivity of our Monte-Carlo simulations of the low-LET radiolysis of aerated Fricke (5 mM FeSO₄ in aqueous 0.4 M H₂SO₄) solutions to the value of the rate constant for the reaction of H atom with water. Simulated Fe³⁺ ion yields (in molec./100 eV) are obtained at ~50 s following ionization, over the studied range 25-350 °C (see text). Symbols, representing experimental data, are the same as in Fig. 2. The solid line (which is the same as that shown in Fig. 2) shows our computed results of $G(\text{Fe}^{3+})$ obtained with the reaction rate of $10^4 \text{ M}^1 \text{s}^{-1}$ at 300 °C recently estimated by Ghandi and coworkers (ref. 59). Note that this rate
was shown to best account for the observed $\text{H}_2$ formation above $\sim 200$-$250 \, ^\circ\text{C}$ (ref. 41). The dash-dot line represents our $G(\text{Fe}^{3+})$ values computed with the rate constant proposed by Bartels (refs. 6 and 57) ($2.2 \times 10^3 \, M^{-1} \, s^{-1}$ at $300 \, ^\circ\text{C}$), while the dash-dot-dot line shows our simulated results of $G(\text{Fe}^{3+})$ obtained with the rate constant suggested by Swiatla-Wojcik and Buxton (ref. 56) ($3.2 \times 10^4 \, M^{-1} \, s^{-1}$ at $300 \, ^\circ\text{C}$). Finally, the dashed line represents our simulated results of $G(\text{Fe}^{3+})$ calculated without incorporating reaction (5) in the simulations.
Figure 4: Yield of Fe$^{3+}$ ions (in molec./100 eV) in aerated Fricke (5 mM FeSO$_4$ in aqueous 0.4 M H$_2$SO$_4$) solutions as a function of temperature, for 300-MeV incident protons. The thick solid line shows the (raw) values of $G(\text{Fe}^{3+})$ obtained directly (at ~50 s) from our Monte-Carlo simulations (it is the same as the solid line shown in Figs. 2 and 3 after smoothing of the data). All the other curves (in different colors) show the "T" values calculated at different times between ~10$^{-6}$ and 10$^{-8}$ s from the right-hand side of eqn. (1) using the radical and molecular product yields obtained at each selected time from our Monte-Carlo simulations of the radiolysis of deaerated 0.4 M H$_2$SO$_4$ aqueous solutions. The time $\tau_s$ at which spur reactions are complete and its temperature dependence are obtained by simply identifying the coordinates of the intersections of the thick solid curve with all the other, time-parameterized curves (see text).
Figure 5: Time of spur expansion $\tau_s$ as a function of temperature for low-LET irradiations of water. The solid line indicates the time required to observe, at a given temperature, the transition from nonhomogeneity to homogeneity in the distribution of the reactive species. $\tau_s$ markedly diminishes with increasing temperature, approaching a value of $\sim 5.7 \times 10^{-8}$ s at 350 °C. The inset shows a log-log plot of $\tau_s$ against temperature, the solid circles representing the coordinates of the intersections of the curve showing the *directly* simulated Fricke yields and those representing the "I" yields calculated from the right-hand side of eqn. (1) at different times (see Fig. 4). The straight line was obtained from a least-squares fit of eqn. (6) to the data (see text).
Figure 6: Variations of the primary free-radical and molecular yields (in molec./100 eV), calculated at the end of spur expansion (i.e., at $t_s$) (see Fig. 5), of the radiolysis of deaerated $0.4 \, M \, H_2SO_4$ aqueous solutions as a function of temperature over the range 25-350 °C. The different lines represent the results of our Monte-Carlo simulations performed with 300-MeV incident protons (LET ~ 0.3 keV/µm at 25 °C) for $g(H')$ (solid line), $g('OH)$ (dashed line), $g(H_2O_2)$ (dash-dot line), $g(H_2)$ (dotted line), and $g(HO_2^*)$ (dash-dot-dot line) (see text). Note that our simulations incorporate reaction (5) with a rate constant of $10^4 \, M^1 \, s^{-1}$ at 300 °C (ref. 59). Note also that the yield indicated "H" in the figure actually represent the sum "e$^-_{aq} + H^+". Experimental data: (o) (ref. 1), (+) (ref. 44), (□,■,-----) (ref. 51), and (V) (ref. 62).
References


10. Throughout this paper, radiation chemical yields are quoted in units of molecules per 100 eV (abbreviated as "molec./100 eV"), as g(X) for primary yields and G(X) for experimentally measured yields. For conversion into SI units (mol/J), 1 molec./100 eV ≈ 0.10364 μmol/J (see ref. 2).


18. At the acid concentration of 0.4 M H$_2$SO$_4$, the H$^+$ ions very rapidly scavenge most, if not all, of the e$^-_{aq}$ radicals in spurs to form H$^*$ atoms (see, for example, C. Ferradini and J.-P. Jay-Gerin, *Res. Chem. Intermed.*, 2000, **26**, 549). In the presence of oxygen the H$^*$ atoms react with oxygen to form additional HO$_2^*$.


22. It should be stressed here that eqn. (1) applies only if the radical and molecular yields intervening on the right-hand side of the equation are the “primary” yields, i.e., those taken specifically at the time corresponding to the end of spur expansion $\tau_s$. 

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32. R. E. Weston, Jr. and H. A. Schwarz, Chemical Kinetics, Prentice-Hall, Englewood Cliffs, New Jersey, 1972. The function $f(I) = I^{1/2}/(1 + I^{1/2})$ that appears in eqn. (2), is derived from the Debye-Hückel theory. It is known that this theory is limited to the low concentration regime and, more specifically, below about 0.1 $M$ in concentration.
Above this value of $I$ the theory begins to show deviations. However, if one judges from Fig. 6.2 of the book of Weston and Schwarz, these deviations remain relatively limited even for the ion concentration range considered in Fricke solutions. There are other theories that work for higher ionic strengths, but they are based on experimentally determined coefficients that depend on types of ions present in the solution. There are no extensive tables of these coefficients, so their use is rather limited. Overall, the use of eqn. (2) is a reasonable compromise especially as we have shown that taking into account the ionic strength in the rate constants actually had only little impact on the values of calculated yields.


35. In fact, in 0.4 M H$_2$SO$_4$, only ~3.5% of the total energy expended in the solution is initially taken up by HSO$_4^-$ ions rather than by H$_2$O (assuming that the energy absorbed by each component is proportional to its electron fraction).

36. For solutions of 0.4 M in H$_2$SO$_4$ there is a small amount of 'OH radicals that react with HSO$_4^-$ to form the sulfate radical SO$_4^{2-}$ according to 'OH + HSO$_4^-$ $\rightarrow$ H$_2$O + SO$_4^{2-}$ ($k = 1.5 \times 10^5$ M$^{-1}$ s$^{-1}$) (see, for example, refs. 21, 23 and 30). However, the overall ferric ion yield remains the same as given by eqn. (1) since the sulfate radical reacts with Fe$^{2+}$ in the same way as 'OH: SO$_4^{2-}$ + Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ + SO$_4^{2-}$ ($k = 9.9 \times 10^8$ M$^{-1}$ s$^{-1}$); see P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, 17, 1027; see also ref. 20.


40. Note that thermal decomposition of H₂O₂ is not taken into account in the simulations. However, this process may not necessarily be negligible at temperatures above 150°C; see, for example, A. J. Elliot, M. P. Chenier, D. C. Ouellette and V. T. Koslowsky, *J. Phys. Chem.*, 1996, **100**, 9014; J. Takagi and K. Ishigure, *Nucl. Sci. Eng.*, 1985, **89**, 177; see also refs. 6 and 38.


44. C. J. Hochanadel and J. A. Ghormley, *Radiat. Res.*, 1962, **16**, 653. These authors also reached a similar conclusion, pointing out that, at higher temperature, "subexcitation electrons are thermalized more rapidly".


50. Since the density of (pressurized) water decreases with increasing temperature (see ref. 49), this influences somewhat the particle’s LET (the energy depositions become further apart when the temperature increases). For example, for 300-MeV irradiating protons, our computed average LET value at 350°C is ~0.19 keV/μm. This decrease in the LET with increasing temperature, however, has no particular effect on the Fricke yield values, which are known to remain nearly constant for LETs lower than ~0.3 keV/μm. See, for example, N. V. Klassen, K. R. Shortt, J. Seuntjens and C. K. Ross, *Phys. Med. Biol.*, 1999, 44, 1609; see also ref. 21.


55. This value compares well with that (~0.85% per degree) predicted by Běgusová and Pimblott (ref. 38) from their stochastic IRT simulations of the γ-radiolysis of the aerated Fricke solution over this same 25-150°C temperature range (see Fig. 2).


59. K. Ghadi, C. D. Alcorn, G. Legate, P. W. Percival and J.-C. Brodovitch, in *Proceedings of the 2nd Canada-China Joint Workshop on Supercritical Water-
60. Homogeneity means that there are no statistical fluctuations in the number densities for all very small regions of the volume being examined. See, for example, G. A. Kenney and D. C. Walker, *J. Chem. Phys.*, 1969, 50, 4074.


V. DISCUSSION

V.1. Radiolysis of water at high temperature

Radiolysis of water at high temperature becomes important when the water-cooled nuclear power reactors came into use. In operational reactor it is necessary to select conditions such that the radiolytic decomposition of the water is suppressed. And this is achieved most effectively when the radiation chemistry of water at high temperature is understood, one needs to know:

1) The primary yields of oxidizing and reducing species which formed during radiolysis.
2) The rate constants for the reaction taking place in spurs and tracks that result in these primary yields.

As a result of the limitation of both parameters above, the chemical yields for some of radiolytic products, and the temperature dependence of some reaction rate constants at high temperature are unknown. Attempts have been made to estimate high temperature g-values on the basis of those measured at lower temperatures. Such extrapolation, however, may produce rather crude or even wrong value. In that situation the numerical modeling presents a complementary method for estimation of the g-values in experimentally inaccessible regions.

In the present study, we have re-examined our Monte-Carlo simulations in an attempt to reconcile our computed g-values of the various radiolytic products (e^-aq, 'OH, H', H_2O_2, and H_2) with re-assessed experimental data up to 350 °C. Some parameters in the physicochemical stage have been adjusted in an attempt to counterbalance the effect of the abrupt drop in the rate constant for the self-reaction of hydrated electron above 150 °C.

The initial yields of each radiolytic species as a function of temperature are shown in Figure V.1. As a first approximation, we can assume that the initial yields are independent of temperature. Hence, the variation of those radiolytic yields with temperature mostly results from the various chemical reactions that contribute to their formation or decay.
**Figure V.1** Temperature dependence of the initial yields of $e^{-}_{aq}$, 'OH, H', H$_2$O$_2$, and H$_2$ obtained from our Monte-Carlo simulations of the low-LET radiolysis of water at 10$^{-13}$ s.

**V.2 Contributions of the various reactions to the radiolytic yields**

The variations of the yields of the various species with temperature mainly result from those reactions involved in their formation or decay that occur during the time interval of nonhomogeneous spur chemistry. To gain further insight into the effects of temperature in the radiolysis of water, it is of interest to examine the unfolding of the various reactions that contribute to the formation or decay of each species in the radiation track. This can readily be done with our Monte-Carlo simulations. The importance of these reactions can be quantified by the yield variation that they cause, expressed as a cumulative $\Delta g$-value. Figures V.2 - V.6 show the effect of increasing temperature on the main spur reactions that are involved in the formation and decay of $e^{-}_{aq}$, 'OH, H', H$_2$O$_2$, and H$_2$ as they expand by diffusion in the time interval $\sim$10$^{-12}$-10$^{-6}$ s.
V.2.1 Production and decay of hydrated electrons

The hydrated electron, $e_{aq}$, is probably the most studied of the transient chemical species produced in the radiolysis of water. The temperature dependence of the hydrated electron yield has been measured in the fast electron pulse radiolysis of water (SHIRAISHI et al. 1989; ELLIOT et al., 1993; LIN et al. 2004), and its scavenged yield with a number of solutes (KENT and SIMS, 1992b; JHA et al. 1972; JANIK et al. 2007).

As the temperature increases, our result shows that the yield of $e_{aq}$ increases up to the maximum at about 250 °C, then decreases at higher temperature. The three main spur reactions which are involved in the decay of $e_{aq}$ are listed below.

\begin{align*}
  e_{aq}^- + H^+ &\rightarrow H^+ \quad (16) \\
  e_{aq}^- + OH &\rightarrow OH^- \quad (42) \\
  e_{aq}^- + H^+ &\rightarrow H_2 + OH^- \quad (43) \\
  e_{aq}^- + e_{aq}^- &\rightarrow H_2 + 2 OH^- \quad (44)
\end{align*}

The contribution of each spur reactions have been shown in Figure V.2. As for reaction (16), the temperature dependence for the reaction of $e_{aq}^-$ with proton has been confirmed recently by STANISKY et al. (2009). Its rate constant increases as a function of temperature in Arrhenius plot. This is lead to consume more hydrated electron at higher temperature. The contribution of the reaction (42) to the decay of $e_{aq}^-$ becomes less and less important as the temperature increases. This is due to the fact that the rate constant for this reaction increases much less steeply with temperature than the diffusion coefficient of the individual species (ELLIOT and OUELLETTE, 1994; ELLIOT et al., 1996). As a consequence, more hydrated electrons are available as the temperature increases. In other word, more hydrated electrons can react in other spur reactions or more hydrated electrons can escape in to the bulk. The decay of hydrated electrons by reaction (43) is quite small and almost constant for all the temperature range.
Figure V.2 Contribution of the main spur reactions that are involved in the formation and decay of $e^{-}_{aq}$, as a function of temperature. Calculated from our Monte-Carlo simulations of the low-LET radiolysis of liquid water at elevated temperature (25-350 °C).

Of particular significance, the measured temperature dependence of the rate constant of the bimolecular decay of hydrated electron (reaction 44) has been emphasized recently to be regarded as independent of pH by Bartels and coworkers. As we have observed, the contribution on the hydrated electron yield as a function of temperature increases up to 150 °C, and then decrease sharply at higher temperatures. In fact, most of the computer modelers of the radiolysis of water at high temperatures have employed an extrapolation procedure at temperatures above 150 °C by assuming that this reaction is diffusion controlled above 150 °C. This assumption was justified mainly by the good agreement obtained between modeling and experiment. Consequently, the incorporation of the drop in the reaction rate constant of the self reaction of $e^{-}_{aq}$ in the simulations leads to the number...
of available hydrated electrons and importantly it also leads to a sharp downward discontinuity in the H₂ yield, which is not observed experimentally. Additional channels for the formation of H₂ are needed, in order to reproduce the yield of H₂ at high temperature.

V.2.2 Production and decay of 'OH radicals

Overall, from Figure 5 in article No. 1, the yield of hydroxyl radical ('OH) increases almost linearly with temperature. Our calculated g('OH) is slightly lower than the experimental data as a consequence of too high solute scavenging capacities (the reciprocal of the scavenging capacity gives a measure of the time scale over which the scavenging is occurring) used in the experiment (LIN et al., 2004, 2005; ELLIOT and BARTELS, 2009; LIN and KATSUMURA, 2010). This explains the difference that we observed between our simulated g('OH) values and the corresponding experimental data, these yields being simply not compared at the same time. The cumulative yield variations Δg('OH) of the main reactions that contribute to the formation and decay of 'OH, calculated from our Monte-Carlo simulations in neutral water at elevated temperature, are illustrated in Figure V.3.

From the figure, it is seen that, in neutral water, 'OH is produced mainly by the back reaction of H₂O₂:

\[
\text{H}_2\text{O}_2 \, + \, e^{-}_{\text{aq}} \to \text{OH}^- \, + \, '\text{OH}
\]

(45)

As for its decay, it is dominated by the three reactions (46), (47), and (48) listed below:

\[
'\text{OH} \, + \, e^{-}_{\text{aq}} \to \text{OH}^- 
\]

(46)

\[
'\text{OH} \, + \, '\text{OH} \to \text{H}_2\text{O}_2 
\]

(47)

\[
'\text{OH} \, + \, \text{H}^+ \to \text{H}_2\text{O} 
\]

(48)

\[
'\text{OH} \, + \, \text{OH}^- \to \text{O}^- \, + \, \text{H}_2\text{O} 
\]

(49)

Reaction (47) is the main reaction that consumes hydroxyl radicals.
Figure V.3 Contribution of the main spur reactions that are involved in the formation and decay of 'OH, as a function of temperature. Calculated from our Monte-Carlo simulations of the low-LET radiolysis of liquid water at elevated temperature (25-350 °C).

There is clear evidence that, at elevated temperatures, all those decay reactions of hydroxyl radicals become partially diffusion controlled with rate constant varying less with temperature than the diffusion coefficients of the individual species. As a result, the decay of the 'OH radicals is reduced as the temperature increases, that is, more 'OH radicals can escape the spur: the 'OH yield increases with temperature, which is what we observed.

V.2.3 Production and decay of H' atoms

The H' atom is one of the minor radical species in the radiolysis of water. It is relatively small, but is important for fundamental considerations. H' atoms are mainly
formed by the decay of excited states of water on the sub-picosecond time scale, and also by the reactions of hydrated electrons during the kinetic evolution of the ion track:

$$e^{-}_{aq} + H^+ \rightarrow H'$$ \hspace{1cm} (16)

The competition between H' atom loss by combination reactions (43, 50, and 51) and its formation by reaction (16) makes the prediction of H' atom kinetics very difficult. They behave like hydrated electrons in some systems and like 'OH radicals in others, which makes it difficult to find selective scavengers.

$$e^{-}_{aq} + H' \rightarrow H_2 + OH^-$$ \hspace{1cm} (43)

$$H' + H' \rightarrow H_2$$ \hspace{1cm} (50)

$$H' + 'OH \rightarrow H_2O$$ \hspace{1cm} (51)

As we can see from Figure 5 (article no 1), the temperature dependence of g(H') is in agreement with the values reported by ELLIOT et al. (1993) and also with the experimental data of LIN et al. (2004, 2005) and LIN and KATSUMURA (2010), but slightly lower than the recommended values given by ELLIOT and BARTELS (2009). These differences may be due to the uncertainty that exists on the measurement of the hydrogen atom yields as we discussed above.

Figure V.4 illustrates the temperature dependence of the cumulative yield variations \(\Delta g(H')\) of the main reactions that are involved in the formation and decay of H', calculated from our Monte-Carlo simulations in neutral water over the temperature range 25-350 °C.

At high temperatures, the yield of H' radicals mainly originates from the intraspur reaction (16). It clearly appears that reaction (16), which rapidly converts e^{-}_{aq} into hydrogen atoms, largely dominates all of the H' decay reactions. The decay of H' radicals is mostly due to reactions (43) and (51). Only a small amount of H' radicals is consumed by reaction (50).
Figure V.4 Contribution of the main spur reactions that are involved in the formation and decay of H\textsuperscript{+}, as a function of temperature. Calculated from our Monte-Carlo simulations of the low-LET radiolysis of liquid water at elevated temperature (25-350 °C).

V.2.4 Production and decay of H\textsubscript{2}O\textsubscript{2}

Hydrogen peroxide is one of the main oxidizing species in the radiolysis of water. An important practical application for examining is its role in nuclear power reactors. H\textsubscript{2}O\textsubscript{2} formed in the radiolysis of water is found to be the main corrosion product, and it is involved in the oxidation damage in almost every domain of nuclear technology. To complete our understanding of the kinetic is important for many aspects of fundamental and applied radiation effects (ALLEN, 1961; DRAGANIĆ and DRAGANIĆ, 1971; BUXTON, 1987). A major problem in the assessment of H\textsubscript{2}O\textsubscript{2} damage in the steady-state operation of BWRs is that it undergoes thermal decomposition at high temperature. It is also very
difficult to measure radiation chemical yields directly in the harsh environments of reactor cores.

![Graph showing the contribution of main spur reactions in the formation and decay of H₂O₂ as a function of temperature.](image)

**Figure V.5** Contribution of the main spur reactions that are involved in the formation and decay of H₂O₂, as a function of temperature. Calculated from our Monte-Carlo simulations of the low-LET radiolysis of liquid water at elevated temperature (25-350 °C).

As we can see from Figure V.5, irradiation of water at high temperatures leads to a decrease in H₂O₂ yields due to the fact that, as the temperature is raised, diffusion of free radical species out of spurs/tracks increase more rapidly than recombination, and one should have less molecular recombination products. These results are in good agreement with experiment. The three main reactions involved in the formation and decay of H₂O₂ are listed below.

\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (52)
\]

\[
\text{H}^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 \quad (53)
\]
\[ \text{H}_2\text{O}_2 + e^{-}_{\text{aq}} \rightarrow \cdot \text{OH} + \text{OH}^{-} \]  

(54)

In the whole temperature range, it is usually assumed that the primary mechanism to form \( \text{H}_2\text{O}_2 \) is the fast combination reaction of \( \cdot \text{OH} \) radicals (52) which are produced in the decomposition of water. Only small amount of \( \text{H}_2\text{O}_2 \) are formed by reaction (53). However the contribution of reaction (54) to the removal of \( \text{H}_2\text{O}_2 \) decreases with increasing temperature. The important of these reactions are quantified in Figure V.5. There is clear evidence that the combination reaction of \( \cdot \text{OH} \) radicals is the major source of primary hydrogen peroxide. Moreover, the contribution of this reaction decreases in magnitude almost linearly with increasing temperature. The decay of \( \text{H}_2\text{O}_2 \) is dominated by reaction (54).

V.2.5 Production and decay of \( \text{H}_2 \)

One very important practical application of the radiolysis of water at high temperature is the use of molecular hydrogen dissolved in the cooling water of pressurized water reactors (PWRs) and boiling water reactors (BWRs) to mitigate corrosion. Hydrogen is known to reduce the concentration of oxidizing species such as \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) and lower the electrochemical corrosion potential (ECP) of metal in the reactor’s internal components, which is associated with cracking. The beneficial effect of molecular hydrogen has been known for many years and justification for its use has been based on the mechanism proposed by ALLEN et al. (1952).

The yield of \( \text{H}_2 \) increases slightly with temperature. To gain further insight into the effects of temperature on the molecular hydrogen yield, Figures V.6 shows the effect of increasing temperature on the main spur reactions that are involved in the formation and decay of \( \text{H}_2 \).
Figure V.6  Contribution of the main spur reactions that are involved in the formation and decay of H₂, as a function of temperature. Calculated from our Monte-Carlo simulations of the low-LET radiolysis of liquid water at elevated temperature (25-350 °C).

Figure V.6 shows that, in neutral water, the two main processes which result in significant production of H₂ are reaction (43) and (44), only small contribution to the H₂ formation come from reaction (49). At temperature higher than 150 °C, the H₂ contribution from reaction (44) is much reduced since its rate constant decreases sharply (ELLIOT and BARTELS, 2009). The main contribution at temperature higher than 150 °C mainly comes from the reaction (43).

\[ e^-_{aq} + H^+ + H_2O \rightarrow H_2 + OH^- \]  \hspace{1cm} (43)
\[ e^-_{aq} + e^-_{aq} + 2 H_2O \rightarrow H_2 + 2 OH^- \]  \hspace{1cm} (44)
\[ H^+ + H^+ \rightarrow H_2 \]  \hspace{1cm} (49)
According to the previous feature, at high temperature, many diffusion controlled reactions turn to be partially diffusion controlled reactions. The amount of H₂ diffusing out of the spur decreases. In contrary, the experiments have been observed that H₂ yield slightly increases with temperature. It might be considered that the H₂ is not only produced in the nonhomogeneous chemical stage but also can be produced at earlier time by several possibilities in the physicochemical stage such as DEA processes, the dissociation of excited water molecules or even the recombination of subexcitation electrons with germinate water cations as discussed in section III (article No. 1). Furthermore, by including all the H₂ contribution which produce in the physicochemical stage, there is still some H₂ missing at high temperature (>200 °C).

To quantitatively reproduce the experimental data of H₂ yield, an additional channel for H₂ formation such as the reaction (55) of hydrogen atoms with water is required at high temperature (above 200 °C).

\[ \text{H}^* + \text{H}_2\text{O} \rightarrow \text{H}_2 + \cdot \text{OH} \quad (55) \]

Reaction (55) is an interesting choice because its effect, which can be completely neglected at room temperature, could play an important role at high temperatures. Details of this study will be discussed in the next section.

V.3 On the importance of the reaction H* + H₂O → H₂ + \cdot OH as a possible source of molecular hydrogen in the low-LET radiolysis of water above 200 °C

A key challenge in controlling the water chemistry of water-moderated nuclear reactors is the ability to understand and mitigate the effects of water radiolysis (see, for example: LIN, 1996; McCRACKEN et al., 1998; KATSUMURA, 2004; GUZONAS et al., 2009). In fact, under the operating conditions (high temperature and pressure) of existing reactors, the radiolytic formation of oxidizing species, both radical and stable species such as \'OH, O₂⁻ (or HO₂⁻ depending on the pH), H₂O₂, and O₂ (the latter two being of greatest concern), may lead, unless mitigating steps are taken, to corrosion and degradation of components in the reactor circuits, as well as to the release and transport of corrosion

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products (radioactive and inactive) with the development of deposits on in-core and piping surfaces. In current reactor designs, one commonly used remedial measure is to add excess molecular hydrogen to the coolant in sufficient concentrations to chemically suppress the net radiolytic decomposition of the water. In the presence of a surplus of dissolved H₂ in the system, the corrosive H₂O₂ and O₂ gas production can be efficiently reduced through a short chain reaction, whereby H₂ initially reacts with 'OH radicals to produce H atoms, the latter then reacting with H₂O₂ to reproduce 'OH radicals and water. The decrease in H₂O₂ concentration occurs finally because the overall rate of reactions which destroy H₂O₂ is faster than that of reactions which produce H₂O₂ including its radiolytic formation. Note that in the absence of added H₂, H₂O₂ normally reacts with 'OH radicals to give HO₂⁻ (or O₂⁻), a precursor of O₂.

In such a context of industrial applicability, it is of prime importance to clearly identify and quantify all sources of in situ radiolytic H₂ production (or consumption). This information is obviously essential to the development of comprehensive simulation models of the coolant's radiation chemistry capable of predicting as realistically as possible the true value of the so-called "critical hydrogen concentration", defined as the minimum concentration of added H₂ required in the reactor coolant to suppress the production of oxidants by water radiolysis. In close connection with these remarks, it has been experimentally reported that, although H₂ is a molecular product, the primary molecular hydrogen yield, g(H₂), in deaerated neutral water irradiated by low-LET radiation (X- or γ-rays, fast electrons) increases with increasing temperature, particularly above 200 °C. It is worth noting that, with the exception of g(H₂), all g-values are consistent with the general (and expected) observation that when the temperature is increased, the yields of free radicals g(eₐq), g("OH), and g(H') continuously increase while the yield of the other molecular recombination product, hydrogen peroxide g(H₂O₂), decreases (ELLIOT and BARTELS, 2009; SANGUANMITH et al., 2011). The exact mechanism responsible for this anomalous increase in g(H₂) is still unknown. However, SWIATLA-WOJCIK and BUXTON (2005, 2010) (henceforth referred to as SWB) suggested that the reaction of hydrogen atoms with water

\[ H^\prime + H_2O \rightarrow H_2 + \cdot \text{OH}, \quad (55) \]
which can normally be neglected at room temperature, could quantitatively explain the temperature dependence of H₂ yield at high temperatures. Quite remarkably, several other authors, including ISHIGURE et al. (1987), SHIRAISHI et al. (1994), and especially SUNARYO et al. (1995a), had already discussed in the past the possible importance of this reaction in the high temperature γ-radiolysis of water, although no measurement of its rate constant had been reported. Using deterministic diffusion-kinetic modeling calculations, SWB calculated an activation energy of ~66.3 kJ/mol over the range 20-300 °C and inferred that a rate constant \( k_{55} \approx 3.2 \times 10^4 \, M^{-1} \, s^{-1} \) was required to account for the additional yield of H₂ observed at 300 °C. Given its potential applications in a better understanding of the reactions occurring in water-cooled nuclear reactors (SIMS, 2006; SIMS et al., 2010), this reaction has received a great deal of attention recently. In particular, the rate constant proposed by SWB was disputed by BARTELS (2009) on the basis of thermodynamic considerations. The latter pointed out that this reaction could not be as fast as required by SWB and suggested that a best estimate for its rate constant was \( 2.2 \times 10^3 \, M^{-1} \, s^{-1} \) at 300 °C.

In reply to these comments, SWIATLA-WOJCIK and BUXTON (2010) re-analyzed Bartels’ thermodynamic estimate and showed that an upper limit for \( k_{55} \) at 300 °C was actually \( 1.79 \times 10^4 \, M^{-1} \, s^{-1} \), thereby confirming the high value they had previously predicted. Finally, GHANDI and coworkers (2010) have recently investigated the reaction of H* atoms with superheated water (H₂O and D₂O) at temperatures up to 450 °C using muon spin spectroscopy experiments with muonium as an analogue of a hydrogen atom. From these experiments, these authors were able to infer a rate constant of \( \sim 10^4 \, M^{-1} \, s^{-1} \) at 300 °C for reaction (55), a value that actually lies between those suggested by SWB and Bartels. Notwithstanding these recent developments, the values for \( k_{55} \) reported thus far, which span a range of more than one order of magnitude \((8.14 \times 10^2 \) to \( 3.2 \times 10^4 \, M^{-1} \, s^{-1} \) at ~300°C) (BURNS and MARSH, 1981; ISHIGURE et al., 1987, 1995; SWIATLA-WOJCIK and BUXTON, 2005, 2010; BARTELS, 2009; ELLIOT and BARTELS, 2009; GHANDI et al., 2010), remain largely uncertain, thereby making it difficult to obtain a clear conclusion as to the real contribution of reaction (55).

In the work reported here, we carry out Monte-Carlo simulations of the radiolysis of high-temperature water including reaction (55) to examine the effect of changing the value
of the rate constant of this reaction on the simulated temperature dependence of \( g(H_2) \). The aim of this sensitivity analysis is to provide insight as to the impact of this reaction on the radiolysis and as a source of \( H_2 \) formation at high temperature.

**V.3.1 Sensitivity of \( H^+ + H_2O \rightarrow H_2 + \cdot OH \) to the production of \( H_2 \) as a function of temperature**

Systematic measurements of the \( g \)-values of \( H_2 \) formed in the low-LET radiolysis of liquid water have been reported as a function of temperature by several laboratories (KENT and SIMS, 1992b; ELLIOT et al., 1993; SUNARYO et al., 1995b; JANIK et al., 2007; ELLIOT and BARTELS, 2009).

![Figure V.7](image)

**Figure V.7** Rate constants used in the present sensitivity study for the reaction (55) of hydrogen atoms with water as a function of reciprocal absolute temperature: SWIATLA-WOJCIK and BUXTON (1995) \( 3.2 \times 10^4 \ M^{-1} \ s^{-1} \) at 300 °C; dot line), BARTELS (2009) (see also ELLIOT and BARTELS, 2009) \( 2.2 \times 10^3 \ M^{-1} \ s^{-1} \) at 300 °C; dash-dot line), and GHANDI et al. (2010) \( 10^4 \ M^{-1} \ s^{-1} \) at 300 °C; solid line).
The results of the temperature dependence of our primary H$_2$ yields, computed at the end of spur expansion (GUZONAS et al., 2010) from our Monte-Carlo simulations incorporating reaction (55) and using different reported rate constants for that reaction (see Figure V.7) (SWIATLA-WOJCIK and BUXTON, 2005; BARTELS, 2009; ELLIOT and BARTELS, 2009; GHANDI et al., 2010), are compared with available experimental data in Figure V.8.

**Figure V.8** Primary yield of H$_2$ versus temperature over the range 25-350 °C. Calculations include reaction (55) of hydrogen atoms with water. For the sake of comparison, the dash line represents our simulated results of g(H$_2$) calculated without reaction (55). The dot line shows our simulated results of g(H$_2$) calculated with the rate constant of reaction (55) given by SWIATLA-WOJCIK and BUXTON (2005) ($3.2 \times 10^4$ M$^{-1}$s$^{-1}$ at 300 °C; see Figure V.7), while the dash-dot line represents our g(H$_2$) values computed with the rate constant predicted by BARTELS (2009) (see also ELLIOT and BARTELS, 2009) ($2.2 \times 10^3$ M$^{-1}$s$^{-1}$ at 300 °C; see Figure V.7). The solid line shows our simulated results of g(H$_2$) obtained with the rate constant inferred by GHANDI et al. (2010) from muon spin spectroscopy experiments ($10^4$ M$^{-1}$s$^{-1}$ at 300 °C; see Figure V.7). Symbols, representing experimental data, are from: (☉) SPINKS and WOODS (1990), (■, □) JANIK et al. (2007), (▲) ELLIOT et al. (1993), and (▲) SUNARYO et al. (1995b).
As can be seen from Figure V.8, up to ~200 °C, the increase of \( g(\text{H}_2) \) with temperature is well reproduced by our calculated \( g \)-values (SANGUANMITH et al., 2011a) whatever the value of \( k_{55} \) considered. In other words, we can thus conclude, as it was in fact expected, that the contribution of reaction (55) to \( \text{H}_2 \) formation is totally negligible in this temperature range. However, above 200 °C, very different functional dependences for \( g(\text{H}_2) \) with temperature can be obtained depending on the choice of the value of the rate constant assigned to reaction (55). Indeed, Figure V.8 shows that if reaction (55) is not included in the simulations the resulting calculated yields increase much less with increasing temperature than what is observed experimentally. If Bartels’ rate constant \( k_{55} = 2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \) at 300 °C (Figure V.7) (BARTELS, 2009; ELLIOT and BARTELS, 2009) is now used in the calculations, the simulated \( g(\text{H}_2) \) values are slightly increased compared to those obtained in the absence of reaction (55), but remain well below the experimental measurements. If, instead, we choose the rate constant of \( 3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \) at 300 °C as predicted by SWB (Figure V.7) (SWIATLA-WOJCIK and BUXTON, 2005), we obtain too high values for \( g(\text{H}_2) \) (Figure V.8).

According to our simulations, it appears that reaction (55) is needed to quantitatively account for the increase in the \( \text{H}_2 \) yield observed above 200 °C. Such a result underlining the importance of reaction (55) in the radiolysis of water at high temperatures is consistent with the current models of reactor coolant’s radiolysis chemistry, which predict that the only significant/sensitive rate constants are those for this reaction and its reverse reaction (SIMS et al., 2010). Figure V.8 also shows that the best agreement between simulated and experimental \( g(\text{H}_2) \) results is obtained with the rate constant \( k_{55} = 10^4 \text{ M}^{-1} \text{ s}^{-1} \) at 300 °C recently inferred by GHANDI and coworkers (2010) from muon spin spectroscopy experiments (see Figure V.7).

V.3.2 \( \text{H}_2 \) formation in high-temperature water radiolysis

A variety of precursors and mechanisms, both physicochemical and chemical, have been proposed for the formation of the observed yield of \( \text{H}_2 \) in the \( \gamma \)-radiolysis of water (see, for example: SWIATLA-WOJCIK and BUXTON, 1995; COBUT et al., 1996; PASTINA et al., 1999; HERVÉ DU PENHOAT et al., 2000). Without going into all the details
regarding the possible sources of H₂, which have already been discussed at length elsewhere, these mainly include:

- **at early time** (i.e., during the physicochemical stage), the DEA to a water molecule ($e^-_{\text{sub}} + H_2O \rightarrow H_2O^-\text{ which may decompose by giving } H^- \text{ followed by } H^- + H_2O \rightarrow H_2 + OH$) and the dissociation of excited water molecules [$H_2O* \rightarrow H_2 + O(1D)$, where $O(1D)$ is an atomic oxygen in its singlet $^1D$ state] formed directly in an initial act or by geminate recombination of a subexcitation electron with the water cation (MEESUNGNOEN and JAY-GERIN, 2010), and

- **during the time of spur expansion** (i.e., in the nonhomogeneous chemical stage) the three following chemical reactions:

\[
\begin{align*}
\text{(43)} & \quad e^-_{\text{aq}} + H^- + H_2O \rightarrow H_2 + 'OH' \\
\text{(44)} & \quad e^-_{\text{aq}} + e^-_{\text{aq}} + 2 H_2O \rightarrow H_2 + 2OH^- \\
\text{(49)} & \quad H^- + H^- \rightarrow H_2
\end{align*}
\]

plus of course reaction (55) above.

To better visualize the relative importance of reaction (55) in the overall H₂ production, we compare in Figure V.9 its contribution, expressed as a cumulative $\Delta g$-value, with those of the DEA, the dissociation of excited water molecules, and the reactions (43), (44), and (49) that occur during spur expansion. Our calculations, which are performed here with the rate constant $k_{55} = 10^4 M^{-1} s^{-1}$ at 300 °C (GHANDI et al., 2010), clearly show that reaction (55) is mostly responsible for the increase in $g(H_2)$ with temperature above ~200°C ($\Delta g(H_2) \approx 0.17 \text{ molec./100 eV at 350 °C}$), while its contribution at lower temperatures can be regarded as nonexistent. Besides these results, it is worth noting the sharp drop of the cumulative yield variation $\Delta g(H_2)$ due to reaction (44) above 150°C. This abrupt decrease directly reflects the (yet unexplained) sharp downward discontinuity that has been observed in the rate constant of reaction (44) (CHRISTENSEN and SEHESTED, 1986; ELLIOT, 1994; MARIN et al., 2007) and whose consequences for the temperature dependence of $g(H_2)$ have been discussed in some detail recently (SANGUANMITH et al., 2011a). As can also be seen from Figure V.9, the contribution of the DEA to H₂ formation, which amounts to $\Delta g(H_2) \approx 0.28 \text{ molec./100 eV at 350 °C}$, is a factor of almost 2 larger than that
due to the dissociative electron-cation geminate recombination \([\Delta g(H_2) \sim 0.16 \text{ molec./100 eV at 350 °C}]\), suggesting that dissociative electron attachment of subexcitation electrons is the dominant (physicochemical) mechanism for producing \(H_2\) at early times, in good agreement with previous reports (COBUT et al., 1998; SWIATLA-WOJCIK and BUXTON, 2001; JANIK et al., 2007).

Figure V.9 Temperature dependence of \(g(H_2)\) and the cumulative \(\Delta g(H_2)\) values corresponding to the various physicochemical processes (DEA and dissociation of excited water molecules formed either directly or by electron-cation geminate recombination) and the spur reactions (43)-(44), (49), and (55) that are involved in the formation of \(H_2\) over the range 25-350 °C, calculated from our Monte-Carlo simulations using the rate constant \(k_{55} = 10^4 \text{ M}^{-1} \text{ s}^{-1}\) at 300 °C (GHANDI et al., 2010). It is worth noting that the contributions of the various spur reactions involved in the decay of \(H_2\) are negligibly small under the present conditions.
Finally, we should note the continuous decrease of $\Delta g(H_2)$ resulting from reaction (43) for temperatures above 200°C as a consequence of the increasing competition that takes place between this reaction and reactions (55) and (49) as the temperature increases. In fact, if at room temperature the contribution of reaction (43) to $H_2$ production largely predominates over that of reaction (49) [$\Delta g(H_2) = 0.11$ versus $0.01$ molec./100 eV], it is only slightly greater than the latter at 350 °C [$\Delta g(H_2) = 0.09$ versus $0.07$ molec./100 eV] (see Figure V.9).

V.4 Simple method to calculate the lifetime of spur and its temperature dependence in the low-LET radiolysis of water

The radiolysis of pure, deaerated liquid water by low-LET ("linear energy transfer" or energy loss per unit track length, $-dE/dx$), sparsely ionizing radiation (such as $^{60}$Co γ-rays, fast electrons, or high-energy protons), leads to the formation of radical and molecular species, namely, $e^{-}_{aq}$ (the "hydrated electron"), $\cdot OH$, $H_3O^+$, $H^+$, $\cdot OH$, $H_2$, $H_2O_2$, $HO_2^-/O_2^-$ (p$K_a$ = 4.8 at 25 °C), etc. Under usual irradiation conditions (i.e., at modest dose rates), these species are generated non-homogeneously on sub-picosecond time scales in small, spatially well-separated regions of dense ionization and excitation events, called "spurs", along the track of the incident radiation (MAGEE, 1953). Owing to diffusion from their initial positions, the radiolytic products then either react within the spurs as they develop in time or escape into the bulk solution. At ambient temperature and pressure, the lifetime of a spur is generally taken to be $10^{-7}-10^{-6}$ s. By this time, the species that have escaped from spur reactions become homogeneously distributed throughout the bulk of the solution and the track of the radiation no longer exists. The radical and molecular products are then available to react with dissolved solutes (if any) present (in moderate concentrations) at the time of irradiation (MEESUNGNOEN and JAY-GERIN, 2005a).

At elevated temperatures, however, the time ($\tau_s$) at which the homogeneous chemistry takes over within the solution is not well determined, even if one can expect the changeover from nonhomogeneous spur kinetics to homogeneous kinetics to occur faster than at ambient temperature (HERVÉ DU PENHOAT et al., 2000; MEESUNGNOEN et al..
In a recent work (SANGUANMITH et al., 2011b), we used a simple procedure, based on Monte-Carlo simulations of the ferrous sulfate (Fricke) dosimeter, to estimate the temperature dependence of \( \tau_s \) in the low-LET radiolysis of water from 25 to 350 °C. The calculations, carried out with air-saturated solutions of 5 mM FeSO\(_4\) in aqueous 0.4 \( M \) H\(_2\)SO\(_4\), showed that \( \tau_s \) decreased by about an order of magnitude over the 25-350 °C temperature range, going from \( \sim 4.2 \times 10^{-7} \) s at 25 °C to \( \sim 5.7 \times 10^{-8} \) s at 350 °C.

However, shortly after the publication of this work, we discovered that \( \tau_s \) was in fact sensitive to the concentration of Fe\(^{2+}\) ions used in the calculations (between 1 and 10 mM, which is the normal range of Fe\(^{2+}\) ion concentrations in the Fricke dosimeter). This is well illustrated in Figure V.10 where \( \tau_s \), calculated by using the same procedure as described above, is displayed for three different concentrations of Fe\(^{2+}\), namely, 1, 5, and 10 mM.

![Spur lifetime \( \tau_s \) as a function of temperature in the low-LET radiolysis of liquid water, calculated as an application of the radiolysis of the aerated Fricke dosimeter for three different concentrations of Fe\(^{2+}\) ions, namely, 1, 5, and 10 mM.](image)

**Figure V.10** The spur lifetime \( \tau_s \) as a function of temperature in the low-LET radiolysis of liquid water, calculated as an application of the radiolysis of the aerated Fricke dosimeter for three different concentrations of Fe\(^{2+}\) ions, namely, 1, 5, and 10 mM.
We quickly realized that this sensitivity to the concentration of FeSO₄ was due, to a large extent, from the fact that some H⁺ atoms could directly be scavenged by Fe²⁺ (and more so that the concentration of Fe²⁺ is higher) instead of reacting with O₂. Indeed, as shown in the reaction scheme below, in the case H⁺ reacts with Fe²⁺, according to reaction (32), only one Fe³⁺ ion will be produced, whereas if H⁺ reacts with oxygen to form HO₂⁻ according to reaction (30) three Fe³⁺ ions will be formed by the reaction sequence (31)-(34). This effect was not included in our original calculations.

\[
\begin{align*}
    \text{Fe}^{2+} + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2 \quad (56) \\
    \text{H}^+ + \text{O}_2 & \rightarrow \text{HO}_2^- \quad (30) \\
    \text{Fe}^{2+} + \text{HO}_2^- & \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad (32) \\
    \text{HO}_2^- + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \quad (33) \\
    \text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH} \quad (34) \\
    \text{Fe}^{2+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} \quad (31)
\end{align*}
\]

To take reaction (56) explicitly into account in the above procedure for calculating \( \tau_s \), the following stoichiometric equation:

\[
G(\text{Fe}^{3+}) = 3 (\{g(\text{H}^+)_{\text{H}^+ + \text{O}_2} + g(\text{HO}_2^-)\} + g(\text{H}^+)_{\text{H}^+ + \text{Fe}^{2+}} + g(\cdot\text{OH}) + 2 g(\text{H}_2\text{O}_2)) \quad (57)
\]

should thus be used instead of Eq. (18). Here, \( g(\text{H}^+)_{\text{H}^+ + \text{Fe}^{2+}} \) represents the number of H⁺ atoms surviving spur expansion that will react with Fe²⁺ ions only. Similarly, \( g(\text{H}^+)_{\text{H}^+ + \text{O}_2} \) denotes the number of H⁺ atoms escaping spur reactions that will react only with O₂. Obviously, \( g(\text{H}^+)_{\text{H}^+ + \text{Fe}^{2+}} + g(\text{H}^+)_{\text{H}^+ + \text{O}_2} = g(\text{H}^+) \).

After making appropriate corrections according to Eq. (57), we then determined \( \tau_s \) for the same three concentrations of Fe²⁺ ions (i.e., 1, 5, and 10 mM) and found that the resulting values of \( \tau_s \), especially above 100 °C, were indeed nearly independent of the Fe²⁺ concentration considered (see Figure V.11). These values are in fact close to those obtained previously for 5 mM before corrections (SANGUANMIT et al, 2011b).
To avoid this kind of difficulty, we then developed an alternative method of calculating the lifetime of the spur and its temperature dependence, which is independent of the presence of any scavengers or pH of the solution, and based primarily on the value of the LET of the studied radiation and the random (Brownian) motion of the various diffusing species (TORQUATO, 1991) formed in the radiolysis of water. This approach allowed us to obtain a “mean” lifetime of the spur, $\bar{\tau}_s$, by simply averaging all individual $\tau_s$ values corresponding to each of the (main) radiolytic species $e^{-aq}$, $H^+$, $OH^-$, $H_2$, $H_2O_2$, $H^+$, and $OH^-$. For a three-dimensional random walk, the spur lifetime corresponding to a given species can be defined by (FREEMAN, 1982)

$$ r^2 = 6 \, D \tau_s $$

(58)
where \( r \) is the root-mean-square displacement of the species in time \( \tau_s \) and \( D \) is its diffusion coefficient in the medium. There are, unfortunately, no experimental data available on the temperature dependences of \( D \) for the various considered species in water, except for the hydrated electron (HERVÉ DU PENHOAT et al., 2000). The diffusion coefficients for \( \text{H}^+ \), \( \cdot \text{OH} \), \( \text{H}_2 \), and \( \text{H}_2\text{O}_2 \) have been obtained by scaling the 25 \(^\circ\text{C} \) values according to the temperature dependence for the self-diffusion of water (HERVÉ DU PENHOAT et al., 2000; ELLIOT and BARTELS, 2009). The diffusion coefficients for the proton and hydroxide ion were obtained from polynomial fits to experimental data, as reported by Elliot and Bartels (PELLIOT and BARTELS, 2009). The radius \( r \) of the (spherical) spur at time \( \tau_s \) (i.e., when the spurs on expanding by diffusion will touch each other) can simply be calculated from the LET of the considered radiation and the average energy being lost in a spur.

At 25 \(^\circ\text{C} \), LET \( \sim 0.3 \text{ keV/\mu m} \)

The average energy loss in a spur is about 47 eV

\[
\begin{align*}
300 \text{ eV} & \approx 6 \text{ interactions} \\
47 \text{ eV} & \approx \frac{2000 \text{ Å}}{2}
\end{align*}
\]

Distance between two spurs \( = \frac{1 \text{ \mu m}}{5} \approx 2000 \rightarrow \bar{r} = \frac{2000}{2} \text{ Å} \)

Calculate spur lifetime for each species \( r^2 = 6D\tau_s \)

\( (e^-_{aq}, \text{H}^+, \cdot \text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}^+, \cdot \text{OH}) \)

The average spur lifetime \( \bar{\tau}_s = \frac{\sum (\tau_{s,i}) G_i}{\sum G_i} \)
For example, at 25 °C, the LET corresponding to 300-MeV incident protons is ~0.3 keV/μm and the average energy deposit in each spur is ~47 eV (as calculated from our IONLYS program). In other words, there will be, for a track length of ~1 μm, 6 interactions (spurs), the distance between two adjacent spurs being about 2000 Å and r ~ 1000 Å. \( \tau_s \), which is the time required for a given species to diffuse a distance \( r \), was then directly inferred from Eq. (58). This calculation was repeated at different temperatures between 25 and 350 °C. It should be recalled here that the LET is a function of temperature, decreasing with increasing temperature. This is due to the fact that the density of water is decreasing with increasing temperature (from 1 g/cm\(^3\) at room temperature to 0.575 g/cm\(^3\) at 350 °C) (LINSTROM and MALLARD, 2005), and this influences the particle's scattering mean free path (MFP) which is related to the scattering cross section through the simple relation \( \text{MFP} = 1/(\sigma N) \), where \( \sigma \) is the total cross section and \( N \) is the number of scatterers per unit volume (HERVÉ DU PENHOAT et al., 2000).

As different radiolytic species have different primary yields, the "average" spur lifetime \( \bar{\tau}_s \) is obtained by summing over all the individual \( \tau_{s,i} \) values corresponding to each of the species present in the spurs after appropriate weighting is made according to their respective yields \( G_i \):

\[
\bar{\tau}_s = \frac{\sum_{i} (\tau_{s,i}) G_i}{\sum_{i} G_i}
\]

The values of \( \bar{\tau}_s \) so determined are shown in Figure V.12. They are found to decrease from ~3.0 \( \times \) 10\(^{-7}\) s at 25 °C to ~5.8 \( \times \) 10\(^{-8}\) s at 350 °C, in very good agreement with those obtained using the previous procedure based on the application of the radiolysis of the Fricke dosimeter (but after corrections were taken into account) at 5 mM FeSO\(_4\).
Figure V.12 Comparison between the lifetimes of spur obtained by different methods. The solid line illustrates the spur lifetime, obtained from Eq. (59). The dash and dot lines represent the spur lifetimes obtained by using the procedure based on the radiolysis of the Fricke dosimeter (5 mM FeSO₄) before and after corrections were taken into account, respectively.
VI. CONCLUSION

In this work, Monte-Carlo simulations were used to investigate the effect of temperature on the primary yields (g-values) of the radical and molecular products of the radiolysis of pure deaerated liquid water over the range 25-350 °C. To reproduce the effects of $^{60}$Co $\gamma$-radiolysis, the initial energy deposition was approximated by considering short segments (~150 μm) of 300-MeV proton tracks, corresponding to an average LET obtained in the simulations of ~0.3 keV/μm.

Bartels and coworkers have emphasized that the anomalous drop observed above 150 °C in the temperature behavior of the rate constant of the bimolecular decay of $e^{-}_{aq}$ in alkaline solutions should be regarded as independent of pH. Consequently, the incorporation of this drop in the simulations leads to a sharp downward discontinuity in $g(H_2)$ at ~150 °C, which is not observed experimentally. To obtain the best global fit of our calculated yields to the experimental data, it has thus been necessary to adjust the temperature dependence of certain parameters intervening in the physicochemical stage of the radiolysis, namely, the electron thermalization distance ($r_{th}$), the dissociative electron attachment (DEA), and the branching ratios of the different excited water molecules decay channels. The values of these parameters have been obtained by comparing our computed time-dependent $e^{-}_{aq}$ yield data to recent picosecond and conventional nanosecond pulse radiolysis measurements of the decay kinetics of $e^{-}_{aq}$ at several different temperatures.

The independent reaction time (IRT) approximation was subsequently used to simulate the nonhomogeneous chemical evolution of the various reactive species formed in the tracks at the end of the physicochemical stage (~$10^{-12}$ s). Our g-values for the reducing ($e^{-}_{aq}, H^-, H_2$) and oxidizing (‘OH, H$_2$O$_2$) radiolytic species, calculated at the time of the end of spur expansion, suggest an increase in $g(e^{-}_{aq}), g(\cdot OH), g(H^-),$ and $g(H_2)$ and a decrease in $g(H_2O_2)$ with increasing temperature, in very good agreement with experiment.
The spur expansion time ($\tau_s$), which gives the time required for the changeover from nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution, has next been determined by using a procedure based on the direct application of the ferrous sulfate (Fricke) dosimeter. The calculations, which employed Monte-Carlo simulations of the radiolysis of the aerated Fricke solution ($0.4 \, M \, H_2SO_4, 5 \, mM \, FeSO_4, 0.25 \, mM \, O_2$), showed that $\tau_s$ decreases as a function of temperature from $-4.2 \times 10^{-7}$ s at 25 °C to $-5.7 \times 10^{-8}$ s at 350 °C. To ensure that the values of $\tau_s$ thus calculated were not tainted by uncertainty due to the effect of pH and/or the effect of scavengers used, a simple model was put forward to calculate $\tau_s$ while avoiding the constraints imposed by the use of the Fricke solution. This model was based on the initial energy deposition in spurs, followed by the random diffusion of the species formed. The values of $\tau_s$ obtained by this model after appropriate averaging over the different species present in the spurs were found to decrease from $-4.4 \times 10^{-7}$ to $-5.8 \times 10^{-8}$ s over the temperature range 25 to 350 °C, in very good agreement with our previous calculations.

Remarkably, we sought to quantify the actual contribution of the reaction $H^+ + H_2O \rightarrow H_2 + \cdot OH$, a reaction that has been proposed to explain the abnormal increase in the primary yield of $H_2$ in $\gamma$-irradiated water at high temperatures and for which a controversy currently exists in the literature. To investigate this problem, we used Monte-Carlo simulations of the radiolysis of high-temperature water over the range from ambient up to 350 °C, and performed a sensitivity analysis to examine the effect of its rate constant on the $H_2$ yield as a function of temperature. Comparing our calculated $g(H_2)$ with experimental data, it was shown that the oxidation reaction of water by $H^+$ atoms can actually be considered as a source of molecular hydrogen at high temperature. Judging from our simulations, this reaction seems to be needed to quantitatively account for the increase in the primary $H_2$ yield observed above 200 °C. Moreover, the best agreement between simulated and experimental results was obtained with a rate constant of $10^4 \, M^{-1} \, s^{-1}$ at 300 °C, a value that has recently been inferred from muon spin spectroscopy experiments.

After adjusting all these parameters as mentioned above, our results of the various yields were found to agree very well with most of the available experimental data over the
whole temperature range considered. This good overall and simultaneous agreement between all experimental and calculated yield values demonstrates, in turn, that Monte-Carlo simulation methods offer a most promising and efficient avenue to study quantitatively temperature effects in the radiolysis of water.
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APPENDIX 1 – ARTICLE No.3

FAST NEUTRON RADIOLYSIS OF THE FERROUS SULFATE (FRICKE) DOSIMETER: MONTE-CARLO SIMULATIONS

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Foreword:

Since the availability, in August 2009, of Elliot and Bartels’ AECL report, which provides all the recommended reaction rate constants for the modeling of high-temperature water radiolysis, I used this material to update our IRT simulation program. By using this updated version, I repeated all the simulations of the fast neutron radiolysis of the Fricke dosimeter, including the dependence of the yield of ferric ions $G(\text{Fe}^{3+})$ on fast neutron energy (0.5-10 MeV) and the effect of temperature on the $G(\text{Fe}^{3+})$ values from 25 to 300 °C.
Abstract

Monte-Carlo calculations are used to simulate the stochastic effects of fast neutron-induced chemical changes in the radiolysis of the ferrous sulfate (Fricke) dosimeter. To study the dependence of the yield of ferric ions, \( G(\text{Fe}^{3+}) \), on fast neutron energy, we have simulated, at 25 °C, the oxidation of ferrous ions in aerated aqueous 0.4 \( M \) \( \text{H}_2\text{SO}_4 \) (pH 0.46) solutions when subjected to \( \sim 0.5-10 \) MeV incident neutrons, as a function of time up to \( \sim 200 \) s. The radiation effects due to fast neutrons are estimated on the basis of track segment (or “escape”) yields calculated for the first four elastically scattered recoil protons with appropriate weighting according to the energy deposited by each of these protons. Our results show that the radiolysis of dilute aqueous solutions by fast neutrons produces smaller radical yields and larger molecular yields (relative to the corresponding yields for the radiolysis of water by \( ^{60}\text{Co} \) \( \gamma \)-rays or fast electrons) due to the high LET associated to fast neutrons. The effect of recoil ions of oxygen, which is also taken into account in the calculations, is shown to decrease \( G(\text{Fe}^{3+}) \) by about 10%. Our calculated values of \( G(\text{Fe}^{3+}) \) are found to increase slightly with increasing neutron energy over the energy range covered in this study, in reasonably good agreement with experimental data.

We have also simulated the effect of temperature on the \( G(\text{Fe}^{3+}) \) values in the fast neutron radiolysis of the Fricke dosimeter from 25 to 300 °C. Our results show an increase of \( G(\text{Fe}^{3+}) \) with increasing temperature, which is readily explained by an increase in the yields of free radicals. For 0.8-MeV incident neutrons (the only case for which experimental data are available in the literature), there is a \( \sim 29\% \) increase in \( G(\text{Fe}^{3+}) \) on going from 25 to 300 °C. Although these results compare relatively well with experiment, more experimental data, in particular for different incident neutron energies, would be needed to test more critically our \( \text{Fe}^{3+} \) ion yield results at elevated temperatures.
Key words: liquid water, aerated sulfuric acid aqueous solutions, radiolysis, fast neutrons, recoil ions (protons and oxygen ions), linear energy transfer (LET), free-radical and molecular yields, Fricke (ferrous sulfate) dosimeter, kinetics of formation and yield of Fe$^{3+}$ ions, temperature, Monte-Carlo simulations.
I. Introduction

Radiation chemistry of liquid water is of considerable importance, on the one hand, for the intrinsic scientific interest it generates, but as well, because of its relevance to a number of practical applications, particularly in radiation biology (where living cells are composed of about 70%-85% water by weight). It is also of importance in nuclear technology, such as in water-cooled nuclear power reactors (where water, used both as moderator and as a heat transport medium, is circulating around the reactor core at temperatures of 250-310 °C) where, in order to mitigate the effects of water radiolysis and thus minimize corrosion (that occurs through the radiolytic production of oxidizing species, such as 'OH, H₂O₂, O₂, etc.), the yields and activities of decomposition products of water must be well understood. In fact, the radiolysis of water and aqueous solutions has been the subject of numerous experimental and theoretical investigations for almost a century (more is known about the radiation chemistry of water than any other liquid). A good summary of the present status of aqueous radiation chemistry is given in refs. 1-3.

Stochastic simulation methods employing Monte-Carlo techniques have been used with success to model the complete evolution of physical and chemical events generated by the interaction of ionizing radiation with pure liquid water. These simulation methods have permitted detailed studies of the relationship between track structure and radiation-induced chemical change. In particular, the primary interactions and the fast kinetics of reactive radicals and ions as a function of the linear energy transfer (LET) of the ionizing radiation, pH, and temperature can be efficiently modeled. Such a modeling can also be done in a nuclear reactor, where the cooling water undergoes radiolytic decomposition induced by gamma, fast electron, and neutron radiation in the core. As experiments at high temperatures and pressures and in mixed radiation fields are difficult to perform, computer simulations in this latter case are a particularly important route of investigation.
In the present study, Monte-Carlo calculations are used to predict the ferric ion yields from the action of fast (~0.5-10 MeV) neutrons in the ferrous sulfate (Fricke) dosimeter (4) as a function of the incident neutron energy, and to examine their temperature dependence for the range 25-300 °C.

1.1 Radiolysis of liquid water and aqueous solutions

1.1.1 The radiolysis of water

A thorough understanding of the radiolysis of water involves knowledge of the early deposition of the energy of the incident ionizing radiation (mainly through ionization, electronic excitation, and dissociation of the water molecules), and the subsequent physicochemical and nonhomogeneous chemical evolution of the system (5, 6) to times, at room temperature, on the order of ~10\(^{-7}\)-10\(^{-6}\) s, after which the remaining radiolytic products are usually regarded as homogeneously distributed in the bulk of the solution. Briefly, the radiolysis of pure deaerated liquid water by low-LET radiation (such as \(^{60}\)Co \(\gamma\)-rays, hard X-rays, fast electrons, or high-energy protons) mainly leads to the formation of the radicals and molecular products \(e^-_{\text{aq}}\) (hydrated electron), \(H^+\) (hydrogen atom), \(H_2\) (molecular hydrogen), \(^\cdot\)OH (hydroxyl radical), \(H_2O_2\) (hydrogen peroxide), \(HO_2^-/O_2^-\) (hydroperoxyl/superoxide anion radicals, \(pK_a = 4.8\)), \(H^+\), \(OH^-\), etc. (for a review, see ref. 7). Under ordinary irradiation conditions, these species are generated nonhomogeneously on subpicosecond time scales in small, spatially isolated regions of dense ionization and excitation events, commonly referred to as "spurs" (8), along the track of the radiation. Owing to diffusion from their initial positions, the radiolytic products then either react within the spurs as they expand or escape into the bulk solution. The so-called primary radical and molecular yields (long-time or escape yields) \(G_{e^-_{\text{aq}}}, G_{H^+}, G_{H_2}, G_{\cdot\text{OH}}, G_{H_2O_2}\), etc., represent the numbers of species of each kind formed or destroyed per 100 eV of absorbed energy that remain after spur expansion and become available to react with added solutes at moderate concentrations.
For low-LET radiation, the radiolysis of pure deaerated liquid water can be described by the following global equation, written for an absorbed energy of 100 eV (2) (the symbol $\rightarrow$ is used to distinguish reactions brought about by the absorption of ionizing radiation):

$$G_{-\text{H}_2\text{O}} \text{H}_2\text{O} \rightarrow G_{\text{e}^-_{\text{aq}}} \text{e}^-_{\text{aq}} + G_{\text{H}^+} \text{H}^+ + G_{\text{H}_2} \text{H}_2 + G_{\text{H}_2^+} \text{H}_2^+ + G_{\text{OH}^-} \text{OH}^-$$

$$+ G_{\cdot\text{OH}^-} \cdot\text{OH} + G_{\text{H}_2\text{O}_2} \text{H}_2\text{O}_2 + G_{\text{HO}_2^-}/\text{O}_2^- \cdot\text{HO}_2^-/\text{O}_2^- + \ldots, \quad (1)$$

where the coefficients $G_x$ are the primary radical and molecular yields of the various radiolytic species $X$, and $G_{-\text{H}_2\text{O}}$ denotes the corresponding yield for net water decomposition. For $^{60}\text{Co}$ $\gamma$-rays (photon energies of 1.17 and 1.33 MeV) or fast electrons of the same energies, at neutral pH and 25 °C (average LET ~ 0.3 keV/µm), the most recently reported values of the primary yields are (3) (in units of molecules per 100 eV):$^8$

$$G_{\text{e}^-_{\text{aq}}} = 2.50 \quad G_{\text{H}^+} = 0.56 \quad G_{\text{H}_2} = 0.45$$

$$G_{\cdot\text{OH}^-} = 2.50 \quad G_{\text{H}_2\text{O}_2} = 0.70. \quad (2)$$

These primary yield values, including the contribution of $\text{HO}_2^-/\text{O}_2^-$,$^9$ are linked by the following relationships:

$$G_{\text{e}^-_{\text{aq}}} + G_{\text{OH}^-} = G_{\text{H}^+}$$

$$G_{\text{e}^-_{\text{aq}}} + G_{\text{H}^+} + 2 G_{\text{H}_2} = G_{\cdot\text{OH}^-} + 2 G_{\text{H}_2\text{O}_2} + 3 G_{\text{HO}_2^-}/\text{O}_2^- - \ldots, \quad (3)$$

expressing the charge conservation and material balance of Eq. (1).

---

$^8$ These units for $G$-values (abbreviated as "molec./100 eV") are used throughout in this work. For conversion into SI units (mol J$^{-1}$): 1 molec./100 eV $\approx 1.0364 \times 10^{-7}$ mol J$^{-1}$.

$^9$ Note that, for low-LET radiolysis, $\text{HO}_2^-/\text{O}_2^-$ is a minor radiolytic product because its very small yield of $\approx 0.02$ molec./100 eV (9) accounts for less than 1% of the other primary radiolytic species.
Within the lifetime of a spur, the yields of the radical and molecular species produced by the irradiation vary with time, and also depend on the radiation type (or LET) and the added solute (scavenger) concentration. One of the main goals in the study of the radiation chemistry of water is the determination of those yields and their time dependences, under different irradiation conditions.

I.1.2 Time scale of events and formation of primary radical and molecular products in neutral water radiolysis

The overall process of producing chemical changes by ionizing radiation can be conveniently divided into three, more or less clearly delineated, consecutive, temporal stages (5, 6) that are briefly described below.

(i) The “physical stage” consists of the phenomena by which energy is transferred from the incident high-energy radiation (for example, γ-rays from \(^{60}\)Co or X-ray photons, or charged particles, such as fast electrons, protons or heavy ions generated by a particle accelerator, or neutron radiation, or high-energy α-particles from suitable radioactive nuclides) to the water. It lasts not more than \(\sim 10^{-16}\) s. The result of this energy absorption is the production, along the path of the radiation, of a large number of ionized and electronically excited water molecules (denoted \(H_2O^{*+}\) and \(H_2O^{*\text{elec}}\), respectively):\(^{10}\)

\[
H_2O \rightarrow H_2O^{*+} + e^- \quad (4)
\]

\[
H_2O \rightarrow H_2O^{*\text{elec}} \quad (5)
\]

Generally, the electron ejected in the ionization event has sufficient energy to ionize or excite one or more other water molecules in the vicinity, and this leads, as mentioned above, to the formation of track entities, or spurs, that contain the products of the events. For low-LET radiation, the spurs are separated by large

\(^{10}\) Note that \(H_2O^{*\text{elec}}\) represents here the many excited states, including the so-called superexcitation states (10) and the collective electronic oscillations of the “plasmon” type (11).
distances relative to their diameter and the track can be viewed, at this stage, as a random succession of nonoverlapping spherical spurs.

(ii) The "physicochemical stage" consists of the processes that lead to the establishment of thermal equilibrium in the system. The duration of this stage is of the order of $10^{-12}$ s for aqueous solutions. During this stage, the ions and excited-state water molecules dissipate their excess energy by bond rupture, luminescence, energy transfer to neighboring molecules, etc.

The ionized water molecules are unstable. They are allowed to undergo a random walk during their very short lifetime ($\sim 10^{-14}$ s) (12) via a sequence of electron transfers (about 20, one the average, over a few molecular diameters; see ref. 13) from neighboring water molecules to the $\text{H}_2\text{O}^+$ hole (i.e., electron-loss center) (14). These short-lived $\text{H}_2\text{O}^+$ radical cations subsequently decompose to form $'\text{OH}$ radicals by transferring a proton to an adjacent $\text{H}_2\text{O}$ molecule:

$$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + '\text{OH}, \quad (6)$$

where $\text{H}_3\text{O}^+$ (or equivalently, $\text{H}^+_{\text{aq}}$) represents the hydrated hydrogen ion.

The energetic secondary electrons lose kinetic energy by a sequence of interactions with the medium until they attain thermal energies ($\sim 0.025$ eV at 25 °C) after $\sim 4 \times 10^{-14}$ s (15). In the course of their thermalization, the slowing-down ("dry") electrons can be recaptured by their parent ions due to the Coulomb attraction of the latter which tends to draw them back together to undergo electron-cation "geminate" recombination:

$$\text{e}^- + \text{H}_2\text{O}^{++} \rightarrow \text{H}_2\text{O}^{+\ast}_{\text{vib}} \quad (7)$$

As the electron is recaptured, the parent ion is transformed into a (vibrationally) excited neutral molecule.

The electron released in the ionization event can cause further ionization and excitation to occur if it has sufficient kinetic energy. Eventually, its energy falls below the first electronic excitation threshold of water ($\sim 7.3$ eV; see ref. 16),
forming the so-called "subexcitation electron" (17). This latter loses the rest of its energy relatively slowly by exciting vibrational and rotational modes of water molecules. Once it is thermalized ($e^{-}\text{th}$), it can be localized or "trapped" (then forming the so-called "wet" electron whose exact physicochemical nature is still the subject of investigation) ($e^{-}\text{tr}$) in a pre-existing potential energy well of appropriate depth in the liquid before it reaches a fully relaxed, hydrated state ($e^{-}\text{aq}$) as the dipoles of the surrounding molecules orient under the influence of the negative charge of the electron. In liquid water at 25 °C, thermalization, trapping, and hydration can then follow in quick succession (less than $\sim 10^{-12}$ s; e.g., see refs. 18, 19):

$$e^- \rightarrow e^{-}\text{th} \rightarrow e^{-}\text{tr} \rightarrow e^{-}\text{aq}$$  \hspace{1cm} (8)

In the course of its thermalization, the ejected electron can also temporarily be captured resonantly by a water molecule to form a transient molecular anion. This anion then undergoes dissociation mainly into $H^-$ and $'OH$ according to

$$e^- + H_2O \rightarrow H_2O^- \rightarrow H^- + 'OH$$  \hspace{1cm} (9)

followed by the reaction of the hydride anion with another water molecule through a fast proton transfer reaction:

$$H^- + H_2O \rightarrow H_2 + OH^-$$  \hspace{1cm} (10)

Reaction (9) corresponds to the so-called dissociative electron attachment (or DEA) process, which has been observed in amorphous solid water at $\sim 20$ K for electron energies between $\sim 5$ and 12 eV (20). DEA to water was suggested to be responsible, at least in part, for the yield of "nonscavengeable" molecular hydrogen in the radiolysis of liquid water at early times (13, 21). This proposed mechanism for the production of $H_2$ has received strong support from recent experiments that have shown that the previously accepted nonscavengeable yield of $H_2$ is due to precursors of $e^-\text{aq}$ and it can be lowered with appropriate (dry electron) scavengers at high concentration (22).
Excited molecules may be produced directly in an initial act [reaction (5)] or by neutralization of an ion [reaction (7)]. We have little knowledge about the decay channels for excited water molecules in the liquid phase and the branching ratios associated with each of them. Fortunately, the contribution of the water excited states to the primary radical and molecular products in water radiolysis is of relatively minor importance in comparison with that of the ionization processes, so that the lack of information about their decomposition has only limited consequences. Consequently, the competing deexcitation mechanisms of H₂O⁺ are generally assumed to be essentially the same as those reported for an isolated water molecule,¹¹ namely (e.g., see refs. 13, 23, 24):

\[
\begin{align*}
\text{H}_2\text{O}^+ & \rightarrow \text{H}^+ + \cdot\text{OH} \\
\text{H}_2\text{O}^+ & \rightarrow \text{H}_2 + \text{O}(^1D) \\
\text{H}_2\text{O}^+ & \rightarrow 2\text{H}^+ + \text{O}(^3P) \\
\text{H}_2\text{O}^+ & \rightarrow \text{H}_2\text{O} + \text{release of thermal energy}
\end{align*}
\]

(11a) (11b) (11c) (11d)

where O(¹D) and O(³P) represent oxygen atoms produced in their singlet ¹D excited state and triplet ³P ground state, respectively. The dissociation of H₂O⁺ via reaction (11a) is generally considered as the main source of the "initial" (i.e., at the end of the physicochemical stage, prior to spur/track expansion) yield of H⁺ atoms. As for the different branching ratios (or decay probabilities) associated with reactions (11a-d), they are chosen in order to consistently match the observed picosecond G-values of the various spur species (24, 25). It should be recalled here that the O(¹D) atoms produced in reaction (11b) react very efficiently with water to form H₂O₂ or possibly also 2'OH (26). In contrast, ground-state oxygen atoms O(³P) in aqueous solution are rather inert to water but react with most additives (27).

¹¹ Note that the same decay processes have been reported to occur for the electronically and vibrationally excited H₂O molecules in the gas phase.
(iii) The "nonhomogeneous chemical stage" consists of the period after $\sim 10^{-12}$ s, during which the radiolytic species generated previously in a nonhomogeneous track structure ($e_{aq}^-, \cdot OH, H^+, H_2O^+, H_2, OH^-, \cdot O', ...$) undergo chemical reactions as they diffuse away from the site where they were originally produced. These species react together to form molecular or secondary radical products, or with dissolved solutes (if any) present at the time of irradiation, until all spur/track reactions are complete. Table 1 gives the principal reactions that are likely to occur while the spurs expand. The time for completion of spur processes is generally taken to be $\sim 10^{-7}-10^{-6}$ s. By this time, the spatially nonhomogeneous distribution of reactive species has relaxed. Beyond a few microseconds, the reactions which occur in the bulk solution can usually be described with conventional homogeneous chemistry methods (e.g., see ref. 28).

1.1.3 The effect of pH

Although the standard Fricke dosimeter (dilute aqueous solution of ferrous ions in 0.4 M sulfuric acid) was developed as early as 1927 (see below), the great majority of radiolysis experiments concerning acidic aqueous solutions were conducted only from the 1950's. The acid most often utilized is $H_2SO_4$ in 0.4 M aqueous solutions (pH ~ 0.46). One of the reasons having originally dictated this choice comes from the fact that the dominant anion $HSO_4^-$ was then considered as not intervening, under these conditions, in the course of the radiolysis (2, 4). As for the radical and molecular yields, the values obtained from the study of a large number of systems, both inorganic (such as $Fe^{2+}, Ce^{IV}, Ti^+, and V^V$) and organic (e.g., formic acid, oxalic acid, and other organic compounds), in sulfuric acid medium present a remarkable agreement (29). For all chosen solutes within certain limits of concentrations, the generally adopted primary yields (expressed in units of molec./100 eV) of radicals and molecular products obtained in the $^{60}Co \gamma$-irradiation of 0.4 M $H_2SO_4$ aqueous solutions at 25 °C are (30, 31):

$$G_{e_{aq}^-} + G_{H^+} = 3.70 \quad G_{H_2} = 0.40 \quad G_{\cdot OH} = 2.90 \quad G_{H_2O_2} = 0.80. \quad (12)$$
It is interesting to note that a few other acids like HCl, HClO₄ (perchloric acid), and (COOH)₂ (oxalic acid) were also employed in radical and molecular yield determinations at low pH. A comparison of the results obtained shows that the primary yield values given in Eq. (12) are generally similar for solutions of the same pH.

Above pH 4 up to strongly alkaline solutions, the primary yields of radicals and molecular products in the γ-radiolysis of (air-free) water are essentially constant and independent of pH (32). In acid solutions with pH < 4, the yield of the reducing free radicals eaq and H⁺, represented by the sum \( G_{e_{aq}+H^+} = G_{e_{aq}} + G_{H^+} \), increases as the proportion of H⁺ increases through the reaction:

\[
e_{aq} + H^+ \rightarrow H^+ , \quad k_{13} \approx 1.12 \times 10^{10} M^{-1} s^{-1} \text{ (taking into account ionic strength effects; see below)}
\]  

competing with other reactions of e⁻aq in the spurs. At the acid concentration of 0.4 M H₂SO₄, the H⁺ ions very rapidly scavenge most, if not all, of the e⁻aq radicals in spurs to form H⁺ atoms (32-34). An increase in acidity below pH 4 also leads to slight increases in the primary yields of oxidizing products G⁻OH and GH₂O₂, while there is a slight decrease in GH₂ (e.g., see ref. 29).

At high acidities (pH < 1), a certain proportion of the OH radicals react with hydrogen sulfate anions HSO₄⁻ to form the sulfate radical \( SO_4^{2-} \) according to

\[
\cdot OH + HSO_4^- \rightarrow H_2O + SO_4^{2-}
\]

with a rate constant taken to be \( k_{14} = 1.5 \times 10^5 M^{-1} s^{-1} \) (35, 36). As a result of reaction (14), G⁻OH reaches a weakly pronounced maximum around pH 1 and then diminishes steeply as the pH is reduced below 1. This has been well reproduced by Autsavapromporn et al. (36) who used Monte-Carlo simulations to investigate the influence of acidity on the primary yields of chemical species produced in the radiolysis of deaerated aqueous sulfuric acid solutions over the range from neutral solution to 0.4 M H₂SO₄.
The values of the radical and molecular yields given here for the radiolysis of aqueous solutions at low pH mainly concern low-LET radiation (\(\gamma\)-rays or fast electrons, LET \(\sim 0.3\) keV/\(\mu\)m). In contrast, fast neutrons, particles of interest to us in this work, constitute high-LET radiation because they are stopped by collisions with atomic nuclei, which become recoil protons and oxygen ions, losing their energy in dense tracks (e.g., see ref. 37). In acid water, very little work has been done with fast-neutron radiation. In fact, the only experimental data available in the literature are those of Katsumura and coworkers (38, 39), who determined the primary yields of water decomposition products in 0.4 \(M\) \(\text{H}_2\text{SO}_4\) aqueous solutions irradiated with 0.8-MeV neutrons as a function of temperature up to 275 °C. At room temperature, these G-values are (38):

\[
G_{e^-_{\text{aq}}+\text{H}^+} = 1.25 \quad G_{\text{H}_2} = 0.99 \quad G_{\cdot\text{OH}} = 0.68 \quad G_{\text{H}_2\text{O}_2} = 1.27.
\]  

(15)

As we can see, the yields of free radicals are decreased and the molecular product yields increased compared with those for \(\gamma\)-radiolysis [given in Eq. (12)], reflecting the high-LET character of fast neutrons.

1.1.4 The influence of LET

A great many experimental and theoretical studies have shown that the yields in the radiolysis of water are strong functions of the quality of the incident radiation, a measure of which is its LET (e.g., see refs. 3, 18, 24, 37, 40-48). Let us briefly consider the changing phenomena in tracks as LET increases.

At the lowest LET (e.g., for sparsely ionizing radiation such as fast electrons), tracks are clearly separated initially into spurs that develop independently in time (see above). If the spurs are taken as spherical beads, then the low-LET track would look like a “string of beads” (49). Even the adjacent spurs are so far apart that there is practically no overlapping among reactants. In this case, the predominant effect is radical production. As LET increases, the mean separation distance between the spurs decreases, and the isolated “spur” structure changes to a situation in which the spurs are not initially overlapping but they will overlap...
shortly thereafter (due to diffusion of the reactive species) before the expansion of the track is complete. As LET continues to increase, the spurs are merged initially to form a dense continuous cylindrical track. This permits more radicals to be formed in close proximity with correspondingly greater probability of reacting with one another to produce molecular products or to recombine to water. Densely ionizing radiations therefore tend to produce high yields of molecular products, at the expense of free-radical yields. Various examples of the primary radical and molecular yields in 0.4 \( M \) \( \text{H}_2\text{SO}_4 \) aqueous solutions, obtained with radiations of increasing LET up to \( \sim 4000 \text{ keV/\mu m} \) (radiolysis with fission fragments from dissolved \( ^{252}\text{Cf} \)) are given in Table 2.

There are two exceptions to this rule: (i) the primary yield of \( \text{HO}_2^+ \) (or its basic form \( \text{O}_2^- \) at neutral pH) radicals, which are the most abundant radicals produced at high LET, increases with increasing LET, a behavior that is akin to the molecular yields, and (ii) the primary yield of \( \text{H}_2\text{O}_2 \) rises with increasing LET to a maximum, after which it falls. The origin of these two exceptions has received much attention recently. It has been hypothesized (61) and then demonstrated using Monte-Carlo track simulations that multiple ionization (MI) of water molecules (and especially the mechanism of double ionization) is responsible for the formation of \( \text{HO}_2^+ \) at high LET (24, 47, 62, 63) and for the maximum of \( G_{\text{H}_2\text{O}_2} \) as a function of LET (24, 47, 64). Moreover, Meesungnoen and Jay-Gerin (65) have shown that this mechanism of MI could also be at the origin of the substantial production in situ of molecular oxygen observed in heavy-ion tracks (for radiation of low LET, \( \text{O}_2 \) is not a radiolytic product), a result of particular significance in radiobiology and of practical relevance in radiotherapy.

The exact structure of a particle track is determined by a number of particle characteristics including its charge, energy, LET, and other parameters. These characteristics are responsible not only for the detailed geometry of the track (commonly referred to as the track structure), but also for the subsequent chemistry that occurs in it. At high LET, tracks can be visualized as a cylinder; this
cylinder has a "core" of high ionization density, due to the passage of the incident particle, and is surrounded by a region (called the "penumbra") of less dense ionizations arising from comparatively low-LET secondary electrons (or "δ-rays") that are ejected at various angles (depending upon their energies) to the track axis (66). Based on the quantum mechanical theory of stopping power (-dE/dx) of Bethe (67), one can readily observe that LET does not uniquely characterize product yields in the heavy ion radiolysis of water (for a review, see ref. 3). This irradiating-ion dependence of the yields at a given LET is explained by the differences in the

12 It is worth recalling here that Bethe's theory is the gold standard for describing the LET (customarily called "stopping power" in the domain of radiation physics) for fast charged particles over a broad energy range. For kinetic energies of ions that are small compared to their rest-mass energy, the nonrelativistic (uncorrected) Bethe stopping power formula (67-70) is given by (in SI units):

\[
\frac{-dE}{dx} = \left( \frac{1}{4\pi\varepsilon_0} \right)^2 \frac{4\pi Z^2 e^4}{m_0 V^2} N \ln \left( \frac{2m_0 V^2}{I} \right),
\]

(16)

where Ze is the charge on the incident ion, V is the ion velocity, m_0 is the rest mass of an electron, \(\varepsilon_0\) is the permittivity of vacuum, N is the number of electrons per cubic meter of the absorbing medium, and I is the mean of all the ionization and excitation potentials of the bound electrons in the absorber. In most cases, I is determined by fitting the theory to experimental results related to the stopping power. For liquid water, I = 79.7 ± 0.5 eV (71). Based on the first-order Born approximation in the electromagnetic interaction between the incident particle and the atomic electrons, the Bethe formula (16) has a wide range of validity except for slow, highly charged heavy particles such as fission fragments. For an accurate assessment of the LET at energies in the Bragg peak region and below, a number of corrections (shell corrections, higher-order Born terms proportional to \(Z^3\) and \(Z^4\), and effects due to charge exchange) must be made to this formula (e.g. see refs. 69, 70).
microscopic track structure due to the spatial distributions of the ejected secondary electrons (e.g., see ref. 72). Nevertheless, the LET still remains nowadays the most commonly used parameter to describe the observed yields because it gives a general, although not an exact, representation of the concentration of reactive species in the particle track.

1.1.5 The influence of temperature

An obvious reason for understanding the radiation chemistry of liquid water at high temperatures is the technologically important application of such knowledge to the design and chemistry control of water-cooled nuclear power reactors, which currently operate with temperatures in the range ~250-330 °C and ~7-15 MPa pressure. The aqueous radiolysis products generated in these reactors must be assessed since they can induce deleterious corrosion, hydriding, and stress corrosion cracking processes both in the core and in the associated piping components (e.g., see refs. 37, 73-82). However, direct measurement of the chemistry in reactor cores is extremely difficult. The extreme conditions of high temperature, pressure, and mixed neutron/gamma radiation fields are, of course, not compatible with normal chemical instrumentation. For these reasons, theoretical calculations and chemical models have been used, with some simplifying assumptions, to simulate and predict the detailed radiation chemistry of the water in the core and the consequences for materials (83).

Of basic interest is knowledge of the effect of temperature on the primary yields of the radiolysis products $e^{-}_{aq}$, $H^+$, $^{•}OH$, $H_2$, and $H_2O_2$, as well as on the rate constants of their reactions. Experimental determinations using low-LET radiation at temperatures from ambient up to ~350 °C (15, 76, 77, 83-97) have shown that $G_{e^{-}_{aq}}$, $G_{H^+}$, $G_{^{•}OH}$, and $G_{H_2}$ continuously increase, while $G_{H_2O_2}$ decreases, with increasing temperature. Based on a compilation and critical review of the radiolysis data available in 2008, Elliot and Bartels (97) have recommended the following equations for the temperature dependences of the primary radical and molecular radiolysis yields (in molec./100 eV) in the range 20-350 °C:
\[ G_{e^-_{aq}} = 2.641 + 4.162 \times 10^{-3} t + 9.093 \times 10^{-6} t^2 - 4.717 \times 10^{-8} t^3 \]
\[ G_{OH} = 2.531 + 1.134 \times 10^{-2} t - 1.269 \times 10^{-5} t^2 + 3.513 \times 10^{-8} t^3 \]
\[ G_{H_2} = 0.419 + 8.721 \times 10^{-4} t - 4.971 \times 10^{-6} t^2 + 1.503 \times 10^{-8} t^3 \]
\[ G_H = 0.556 + 2.198 \times 10^{-3} t - 1.184 \times 10^{-5} t^2 + 5.223 \times 10^{-8} t^3 \]
\[ G_{H_2O_2} = 0.752 - 1.620 \times 10^{-3} t , \]

where \( t \) is the temperature in °C.\(^{13}\)

These observed temperature dependences of the \( G \)-values have been reproduced satisfactorily by deterministic diffusion-kinetic modeling of spur processes (23, 103-106) and Monte-Carlo track simulations (15, 92, 107, 108). That the yields of free radicals increase with temperature is a matter that can readily be explained from the fact that many important reactions are not diffusion controlled and therefore have rate constants that increase less steeply with temperature than do the diffusion coefficients of the individual species (e.g., see refs. 87, 92). In other words, as the temperature is raised, diffusion of free radical species out of spurs/tracks increases more rapidly than recombination, and one should have less molecular recombination products (83, 86). One difficulty,  

\(^{13}\) In the past few years, measurements of the yields for \( e^-_{aq}, H^+ \) atom, \( H_2 \), and \( 'OH \) radical production in low-LET radiolysis of water have been extended up to \( \sim 400 \) °C, i.e., beyond the thermodynamic critical point of water (\( t_c = 373.95 \) °C, \( P_c = 22.06 \) MPa or \( 217.7 \) atm). Very peculiar, and even sometimes contradictory, behaviors have been observed thus far in going from the subcritical to the supercritical regime (83, 94-96, 98-100). Note here that supercritical water is of particular interest nowadays because of its possible use as the heat transport medium in the next-generation ("Generation IV") technologies of nuclear reactors aimed at supplying future worldwide needs for electricity, hydrogen, and other products (101, 102). However, this range of elevated temperatures (and pressures) is beyond the scope of the present study.
however, appears in explaining the experimentally observed monotonic increase of
$G_{H_2}$ at high temperature (83, 85, 86, 97). In fact, although the above model
calculations have found an increase of $G_{H_2}$ up to ~150-200 °C as resulting from the
bimolecular recombination of two $e^-_{aq}$ (23, 92), the computed $G_{H_2}$ tends to
decrease at higher temperatures (92, 104). The fact that the experimental $G_{H_2}$
values continue to increase with temperature (even though the yield of the other
molecular recombination product, $H_2O_2$, decreases) raises interesting questions
such as, for example, the need to postulate an additional channel for $H_2$ formation
in the early-time physicochemical stage of the radiolysis, which for some reason
becomes more probable at high temperature (83, 109, 110).

Rate constants are sensitive functions of temperature and for this reason are
important parameters in predictive modeling of high temperature water chemistry.
What is generally known is the temperature dependence of the observed reaction
rate constant ($k_{obs}$), from which it is possible to extract information on the
temperature dependences of the “activation” and “diffusion” processes that are
involved in the reaction. For reactions whose rates are nearly diffusion-controlled at
room temperature, $k_{obs}$ is best described by the Noyes equation:

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{k_{act}},$$

(17)

where $k_{diff}$ is the rate constant for a truly diffusion-controlled reaction and $k_{act}$ is the
rate constant that would be measured if diffusion had no influence on the reaction
rate (111). A number of reactions pertinent to the radiation chemistry of water have
been found to be best described by Eq. (17) (e.g., see ref. 76). The Arrhenius
equation is used to evaluate $k_{act}$ empirically:

$$k_{act} = A \exp(-E_{act}/RT),$$

(18)
where $E_{\text{act}}$ is the activation energy of the process, $A$ is referred to as the pre-exponential factor, $R$ is the gas constant and $T$ is the absolute temperature (in Kelvin). $k_{\text{diff}}$ is given by the Smoluchowski equation (e.g., see refs. 23, 76, 92, 112):

$$k_{\text{diff}} = 4\pi \beta N_{\text{Av}} (D_A + D_B) a_{A,B}, \quad (19)$$

where $N_{\text{Av}}$ is Avogadro's number, $(D_A + D_B)$ is the sum of diffusion coefficients for both reacting species, $\beta$ is a spin statistical factor for radical-radical reactions, and $a_{A,B}$ is the encounter (or reaction) distance. When the reactants are ions, Eq. (19) is multiplied by the Debye factor (113):

$$f_D = \frac{\delta}{e^\delta - 1}. \quad (20)$$

where $\delta$ is given by

$$\delta = \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 \varepsilon(T) a_{A,B} k_B T}, \quad (21)$$

where $Z_A$ and $Z_B$ are the charges on the ions, $e$ is the electron charge, $\varepsilon_0$ is the permittivity of free space, $\varepsilon(T)$ is the dielectric constant of the medium, and $k_B$ is Boltzmann's constant.$^{14}$

---

$^{14}$ In the case of a reaction between identical species, the term $4\pi$ in Eq. (19) is replaced by $2\pi$ in order to avoid counting twice every pair of reactants. For reactions between ions, both $k_{\text{diff}}$ and $k_{\text{act}}$ must be corrected for the effect of ionic strength (see Sect. III). In evaluating the reaction between two radicals, the electron spin of the radical has to be taken into account; the statistical spin factor $\beta$ introduced in Eq. (19) accounts for the fact that only those random encounters that produce a singlet electronic state will contribute to the reaction rate. For free radicals, such a singlet state is reactive whereas the complementary triplet state is not. The value of $\beta$ is actually set by the spin relaxation time of the radicals involved. For most radicals, the spin-lattice relaxation time is much longer than the
More and more reactions – many of them involving the hydrated electron (e.g., see refs. 78, 97, 116) – have been found to exhibit negative Arrhenius activation energies at elevated temperatures (i.e., the rate of reaction actually decreases gradually with temperature above a certain temperature). As an example, we can cite here the bimolecular recombination of two $\text{e}^-_{\text{aq}}$ (76, 79, 97, 117, 118), an important contributor to $G_{\text{H}_2}$ in water radiolysis and a fascinating reaction from the point of view of fundamental chemical physics. Basically, $k_{\text{obs}}$ shows Arrhenius behavior up to 150 °C with an activation energy of 20 kJ/mol, and then rapidly decreases above this temperature. The mechanistic details of the apparent peculiarity of this reaction have been discussed by several authors (79, 117-120).

Very little information is available for the temperature dependence of fast neutron $G$-values. At the University of Tokyo, experiments on 0.4 $M$ $\text{H}_2\text{SO}_4$ solutions at temperatures up to 250 °C were carried out in the “YAYOI” source reactor where 95% of the radiation energy came from fast neutrons (38, 121). In these experiments, the average energy and LET of the fast neutrons were calculated to be ~0.8 MeV and ~60 keV/μm, respectively (38, 39). The $G$-values of water decomposition products were determined by using a combination of the aerated and deaerated Fricke dosimeter and the ceric sulfate dosimeter. The data reported by these authors (38, 39) indicated that the $G$-value for free-radical species increased significantly with temperature whereas the yield of the molecular species decreased. Elliot and coworkers (77, 87) used another approach to estimate the temperature dependence of $G$-values for fast neutron radiolysis. In water, most of the fast-neutron energy is deposited through ionization of the water by recoil protons, which are formed from the elastic scattering of the neutrons. The initial energy of these protons varies from the maximum energy of the fast neutrons down to zero; the actual distribution of the proton energies can easily be calculated encounter time (i.e., there are no triplet-singlet transitions during the encounter), so that $\beta$ of 0.25 is appropriate (76, 112, 114, 115).
(see Sect. II). For example, for an incident 2-MeV neutron,\textsuperscript{15} it can be shown that the most significant contribution to the radiolysis comes from the first four collisions that generate recoil protons, having LET values of \( \sim 23, 43, 71, \) and \( 80 \text{ keV/\mu m} \), respectively. The radiation chemical yields corresponding to these four values of LET (assuming that LET can be used as a unifying parameter to connect yields) can be estimated experimentally (using different high-energy ion beam radiolysis results, as shown in Figs. 1 and 2 of Elliot et al. (87). The fast-neutron yields are then the sum of these yields after appropriate weighting has been made according to the fraction of total energy deposited by each of these protons. Using this procedure, Elliot and coworkers (77, 87) estimated the \( G \)-values of primary species for a 2-MeV fission neutron at 25, 250, and 300 °C (see Table 3). Finally, let us mention the work of Sunaryo et al. (88, 89, 122) who reported experimental \( G \)-values for the decomposition products of neutral water up to 250 °C for \( \sim 0.8\text{-MeV} \) fast neutrons from the YAYOI reactor (see also refs. 90, 91).\textsuperscript{16} Their data, also shown in Table 3, are qualitatively similar to those of Elliot et al. (87) except for \( G_{\text{H}_2\text{O}_2} \), which they report as being much larger and always increasing with temperature. Possible physical and chemical reasons for these differences have been discussed by McCracken et al. (37).

\section*{1.2 The ferrous sulfate, or Fricke, chemical dosimeter}

In chemical dosimetry, radiation dose is determined from the chemical change produced in an appropriate medium. Any well-characterized quantitative chemical reaction may serve as the basis for a dosimeter. One of the most studied systems in radiation chemistry is the air-saturated (~2.5 \( \times \) 10\textsuperscript{-4} \( M \) \text{O}_2) solution of 1-10 mM

\textsuperscript{15} The 2-MeV neutron was chosen by Elliot et al. (77, 87) because the in-reactor fission-neutron flux peaks at this energy (74).

\textsuperscript{16} To our knowledge, these are the only data that have been obtained using reactor radiation.
ferrous sulfate in aqueous 0.4 M H₂SO₄, which is referred to as the “Fricke dosimeter” after Hugo Fricke who first published accounts of its properties in 1927-1929 (123). Of all aqueous systems studied, the Fricke dosimeter is the best understood, and the most widely used, liquid chemical dosimeter. It is straightforward to prepare and it provides an easy quantification of the energy deposited by ionizing radiation. The chemistry of this system is based upon the oxidation of ferrous ions to ferric ions by the oxidizing species 'OH, HO₂*, ¹⁷ and H₂O₂ that are produced in the radiolytic decomposition of water (4, 7, 40, 124). From this mechanism, the yield of Fe³⁺ ions in an irradiated Fricke dosimeter can be expressed in terms of the escape yields of the radical and molecular products of the radiolysis of the solution by the following stoichiometric equation (7):

\[
G(\text{Fe}^{3+}) = 3 (G_{\text{aq}^-\text{H}^+} + G_{\text{HO}_2}) + G_{\text{OH}} + 2 G_{\text{H}_2\text{O}_2} \tag{22}
\]

This relationship, which has been confirmed by experiment, shows that the production of Fe³⁺ ions is highly sensitive to factors that alter the free-radical yields, especially the yield of H⁺ atoms. In particular \( G(\text{Fe}^{3+}) \) depends on the type of the radiation used. Data by a number of different authors have shown that \( G(\text{Fe}^{3+}) \) steadily decreases with increasing LET, this dependence reflecting the lower yields of radicals that escape the high-LET track as compared with low-LET radiolysis (e.g., see ref. 36). Representative values of \( G(\text{Fe}^{3+}) \) for several types of radiation, including fast neutrons, are collected in Table 4.

The part played by sulfuric acid and its anions is generally ignored when the ferrous sulfate system is described, although with the standard dosimeter solution (0.4 M H₂SO₄) a certain proportion of the hydroxyl radicals react with HSO₄⁻ ions to form the sulfate radical SO₄⁻² [see reaction (14)]. However, this does not affect the overall ferric ion yield \( G(\text{Fe}^{3+}) \), which remains the same as given by Eq. (22), since

¹⁷ The radiation-induced reducing radicals \( e^-_{\text{aq}} \) and H⁺ are rapidly transformed into HO₂⁺ at low pH and in the presence of oxygen (see Sect. III).
SO₄²⁻ (or, equivalently, its protonated form HSO₄⁻, although no pKₐ value has been determined) is stoichiometrically equivalent to 'OH, oxidizing one ferrous ion to a ferric ion (138):

\[
\text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad k_{23} = 2.79 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \quad \text{(taking into account ionic strength effects; see below)}
\]

or dimerizing to a product (S₂O₈²⁻) that, like H₂O₂, oxidizes two ferrous ions (7).¹⁸

The usual range of the Fricke dosimeter is from ~30 to 400 Gy. The upper limit is set by oxygen depletion [when oxygen is completely consumed, G(Fe³⁺) decreases to ~8.2 molec./100 eV for fast electrons or ⁶⁰Co γ radiation; e.g., see ref. 4] and the lower limit by the analytical method. By suitable modifications of the composition of the system or of its analysis, it is possible to extend the useful range beyond these limits. Higher doses can be measured by means of the “super” Fricke dosimeter, which consists of 10 mM Fe²⁺ in 0.4 M H₂SO₄ and is saturated with pure oxygen (~1.25 x 10⁻³ M O₂). This system can then be used up to 2000 Gy.

The Fricke dosimeter is widely accepted in radiation-chemical work because of the accuracy, reproducibility, and linearity of its response as a function of dose (with care, Fricke dosimetry is capable of 0.1% precision for ⁶⁰Co γ-rays, high-energy X-rays or fast electrons) (127). It has been accurately standardized by calorimetry, ionization measurements, and other physical methods, and is nowadays used not only for absolute dose measurements but also as a standard against which most other systems are calibrated (e.g., see refs. 7, 128).

**1.3 Objectives**

This study addresses the effect of fast neutrons on the chemistry and the yield of Fe²⁺ oxidation in the Fricke dosimeter. Following a procedure already employed by other authors (e.g., see refs. 77, 105, 139, 140), the neutron G-values reported

¹⁸ Contrary to HSO₄⁻, the sulfate ion SO₄²⁻ has been reported to be unreactive toward 'OH.
here are calculated from the weighted G-values for the recoil charged particles
(mainly protons, or deuterons for the case of heavy water, and to a smaller extent,
oxygen nuclei) released by neutron interactions in the FeSO₄ medium. Monte-
Carlo computer simulations are used (i) to model the physicochemical
development, the nonhomogeneous chemical kinetics, and the diffusion of the
reactive species induced by these recoil ions in radiolysis, and (ii) to determine the
corresponding ferric-ion yields. As is well-known, the combined application of
stochastic track structure simulation and track chemistry modeling has proven to
offer an efficient approach (i) to understand the underlying reaction mechanisms
and pathways by which radiolytic species are formed at the molecular level
following irradiation and (ii) to place on a quantitative basis the effects of the
various parameters that can influence the radiation chemical data (for a review,
see ref. 141). The present work focuses, in particular, on the temperature
dependence of the oxidation of Fe²⁺ to Fe³⁺ in the fast neutron radiolysis of the
Fricke solution (e.g., see refs. 92, 142).

More specifically, the main objectives of this work are:

(i) To study the oxidation of ferrous ions in the Fricke dosimeter subjected to
fast (~0.5-10 MeV) neutron irradiation, and to calculate the time profiles of the
chemical yield of ferric ions G(Fe³⁺).

(ii) To investigate the dependence of G(Fe³⁺) on the energy of incident
neutrons over the range of temperature from ambient up to ~300 °C.

(iii) To compare the simulation results with experimental data currently
available in the literature in order to validate the assumptions employed in the
calculations.
II. NEUTRON INTERACTIONS IN WATER
II.1 Types of interactions and slowing down of fast neutrons

II.1.1 Types of interactions

The neutron (n) is a radioactive particle of charge zero and mass slightly greater (by ~1.293 MeV) than that of a proton (p). Like the proton, it is a spin one-half fermion. Together with the proton, the neutron is a constituent particle of all atomic nuclei (except, obviously, $^1$H) (recall here that protons and neutrons attract each other with a short range but very strong force, called the nuclear force; in nuclei, they are referred to as nucleons). While neutrons can be stable when bound inside nuclei, free (or isolated) neutrons are unstable and undergo $\beta$-decay, disintegrating into a proton, an electron (with a maximum kinetic energy of 782 keV), and an antineutrino with a characteristic half-life of $10.61 \pm 0.16$ min (143). Even though it is not a chemical element, the free neutron is often included in tables of nuclides. It is then considered to have an atomic number of zero and a mass number of one.

Neutrons can be generated from a variety of nuclear reactions over a very wide range of energies. We cannot accelerate neutrons as we can for charged particles, but we can start with high-energy neutrons and reduce their energy through collisions with atoms of various materials. This process of slowing is called "moderating" the neutrons.

The interaction of the neutron depends very much on its kinetic energy. In this respect, it is customary to class the possible neutron kinetic energies into four ranges to facilitate discussion about the different possible interactions of neutrons with matter. Some commonly used energy ranges and the names applied are: slow neutrons ($0 \leq E_n < 1$ keV),\(^{19}\) intermediate neutrons ($1$ keV $\leq E_n < 500$ keV), fast

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\(^{19}\) The "slow" neutron category listed here includes several other well-known groups, such as "thermal" and "cold" neutrons. Thermal neutrons are in thermal equilibrium with the medium in which they are diffusing; they possess a Maxwell-
neutrons ($500 \text{ keV} \leq E_n < 10 \text{ MeV}$), and high-energy neutrons ($E_n \geq 10 \text{ MeV}$) (144). These categories are useful since dominant interactions can usually be identified in the regions given.

Because neutrons carry no charge, their interaction with atomic electrons is exceedingly small, and direct ionization by neutrons in passing through matter is a completely negligible effect. The interaction of neutrons with matter is confined to nuclear effects and may be one of two major types: "scattering" or "absorption". These include elastic and inelastic scattering, nuclear reactions, and capture processes (for reviews of the characteristics of the different types of neutron interactions, see refs. 145, 146). When a neutron is scattered by an atomic nucleus, its energy and direction change but the nucleus is left with the same number of protons and neutrons it had before the interaction. The nucleus will have some recoil velocity and it may be left in an excited state, which will lead to the eventual release of radiation. In "elastic" scattering, indicated by $(n,n)$, the energy of the incident neutron is shared between the recoiling neutron and nucleus. "Inelastic" scattering, referred to $(n,n)$, is similar to elastic scattering except that the nucleus

Boltzmann velocity distribution determined by the absolute temperature of the medium. At 20 °C, thermal neutrons have a most probable energy of 0.025 eV. Cold neutrons have energies considerably less than 0.025 eV, often as low as 0.001 eV.

Note that a simple notation for nuclear reactions is used to give a concise indication of an interaction of interest and to distinguish between scattering and absorption reactions. If a neutron $n$ impinges on a target nucleus $T$, a resultant nucleus $R$ is formed and an outgoing particle $g$ is released; this interaction is shown as $T(n,g)R$. To denote a type of interaction without regard for the initial and final nuclei involved, only the portion written in parentheses is shown. The symbols $n$, $p$, $d$, $\alpha$, $e^-$, and $\gamma$, are used in this notation to represent neutron, proton, deuteron, $\alpha$-particle, electron, and gamma ray, respectively.
undergoes an internal rearrangement into an excited state from which it eventually releases radiation (most reactions are accompanied by the emission of a nuclear deexcitation γ-ray); in this case, part of the original kinetic energy of the incoming neutron is used to place the nucleus into an excited state. Obviously, if all the excited states of the nucleus are too high in energy to be reached with the energy available from the incoming neutron, inelastic scattering is impossible. In particular, the hydrogen nucleus does not have internal excitation states, so only elastic scattering events can occur in that case. When a neutron is absorbed or captured by a nucleus, a wide range of radiation can be emitted or fission can be induced. The compound nucleus may rearrange its internal structure and release one or more γ-rays. Charged particles may also be emitted, the more common ones being protons, deuterons, and α-particles. The nucleus may also promptly reemit excess neutrons (note that the reemission of one neutron is indistinguishable from a scattering event). Finally, there may be a fission event in which, after the neutron is captured, the nucleus fragments into several parts with creation of fission products (nuclei of intermediate atomic weight).

II.1.2 Slowing down of fast neutrons

II.1.2.1 Hydrogen-containing substances as the most effective media for neutron moderation

For "fast" neutrons (i.e., those with kinetic energies below about 10 MeV) which will concern us in this work, most slowing down is accomplished through a process of many successive "billiard-ball" elastic collisions with atomic nuclei, following the simple laws of conservation of energy and momentum of classical particle physics. In elastic scattering, the total kinetic energy of the neutron and nucleus is unchanged by the interaction. During the interaction, a fraction of the

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21 In this energy range, fast neutrons can be considered as non-relativistic particles, since their mass is much larger than their kinetic energy; the description of neutron elastic collision can thus be performed using non-relativistic mechanics.
neutron's kinetic energy is transferred to the nucleus. For a neutron of kinetic energy \( E_n \), encountering a nucleus of mass number \( A \), the energy \( E_r \) transferred to the struck nucleus (assumed to be initially at rest) is given by (e.g., see refs. 144-148):

\[
E_r = E_n \frac{4A}{n(1+A)^2} \cos^2 \theta_r ,
\]

(24)

where \( \theta_r \) is the recoil-nucleus angle with respect to the original direction of travel of the neutron (in the laboratory system of coordinates). According to Eq. (24), \( E_r \) ranges from zero up to a maximum:

\[
(E_r)_{\text{max}} = E_n \frac{4A}{n(1+A)^2} ,
\]

(25)

If all energy transfers between zero and \( (E_r)_{\text{max}} \) are equally probable (i.e., if the elastic scattering angular distribution is spherically symmetric in the centre-of-mass system, which is certainly a good assumption at the energies considered here), the average recoil energy imparted to the struck nucleus after a collision is

\[
\overline{E_r} = E_n \frac{2A}{(1+A)^2} ,
\]

(26)

which leads to (by energy conservation)

\[
\overline{E_n} = E_n \left[ 1 - \frac{2A}{(1+A)^2} \right]
\]

(27)

for the average energy of the outgoing neutron (quantities with bars over them denote mean values). Clearly, Eqs. (26) and (27) show that the lighter the nucleus with which a neutron collides, the greater the fraction of the neutron's kinetic energy that can be transferred in the elastic collision. In other words, in order to reduce the speed of neutrons (i.e., to moderate them) with the fewest number of elastic collisions, target nuclei with low atomic number should be used. Biological tissues and other materials containing a large proportion of hydrogen or deuterium (such as light or heavy water) are thus favored for slowing down of neutrons. In
fact, for \( A = 1 \) (scattering from hydrogen), the average energy loss has its largest value of \( E_n/2 \).

II.1.2.2 Average logarithmic energy decrement per collision

Consider a series of moderating collisions \( 1 \to k \) for a single neutron. Suppose that the initial neutron kinetic energy is \( (E_n)_0 \) and the final value is \( (E_n)_k \). Intermediate kinetic energies are \( (E_n)_1, (E_n)_2, \ldots, (E_n)_i, \ldots \), and so forth. After \( k \) individual elastic scattering collisions, the average value of \( \ln(E_n)_k \) is\(^{22} \) \(^{147} \)

\[
\ln \left( \frac{(E_n)_k}{(E_n)_0} \right) = \ln \left( \frac{(E_n)_0}{E_n} \right) - k\xi, \tag{28}
\]

where

\[
\xi = \ln \left[ \frac{(E_n)_i}{(E_n)_i-1} \right] \tag{29}
\]

is defined as the "average change in the natural logarithm of the neutron energy after a single collision". It can be shown that \( \xi \) is independent of the initial energy and expressed as (for a derivation, see refs. 144, 147, 149)

\[
\xi = 1 + \frac{(A-1)^2}{2A} \ln \left( \frac{A-1}{A+1} \right). \tag{30}
\]

It follows that the average value of \( \ln(E_n) \) is decreased after each collision by an amount \( \xi \).

For collisions with protons (\( A = 1 \)) \( \xi \) becomes unity.\(^{23} \) For oxygen (\( A = 16 \)), \( \xi = 0.120 \). When \( A \) is large (\( A \gg 1 \)), for heavy elements: \( \xi \approx 2/A \). Equations (28) and (30) will be used copiously in the present study.

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\(^{22}\) Average kinetic energy values are desired since one usually deals with a beam of many neutrons.

\(^{23}\) Note that Eq. (30) is not defined when \( A = 1 \), but the limit as \( A \) approaches unity is valid in this case.
II.1.2.3 Viewpoint of the radiation chemist, radiobiologist, and radiation therapist

The study of the action of fast neutrons is highly relevant to the various fields of radiation chemistry, radiobiology, and clinical radiation oncology. For radiation chemists, the scattering of neutrons by elastic collisions with atomic nuclei is a process of most interest since the recoil nuclei so generated will be charged and will deposit their ionizing energy into the stopping material in a similar manner to other (high-LET) heavy charged particles (see Sect. I.1.4). For the fast neutron radiolysis of water and aqueous systems and the incident neutron energies of interest to us here, the neutrons are stopped mainly by both protons and oxygen nuclei, producing a spectrum of recoil-ion energies from which the LET along the track of each densely ionizing heavy charged particle recoil released can be assigned and the chemical yields for the various species formed can be obtained (see Sects. III and IV).

From the viewpoint of the radiation biologist, because of the predominance of hydrogen in tissue, 85% of the energy of fast neutrons is transferred to hydrogen nuclei resulting in the emission of recoil protons. In other words, the n-p collision is by far the most important mechanism for energy transfer under these conditions. The remaining 15% of the absorbed dose is due to additional elastic scattering of neutrons with the light elements oxygen, carbon, and nitrogen (representing the major constituents of tissue), in that order of importance (150-153). As mentioned above (see Tables 2 and 4), fast neutrons are indirectly ionizing radiations, generating at a site of interaction charged particle recoils of high LET (>10 keV/μm). The biological properties of neutron beams are thus directly correlated to those of

24 In general, nuclear reactions and capture, the latter giving an isotope of the target element, tend to be an embarrassment in radiation-chemical applications because of the possibility that the product nuclei will be radioactive, introducing handling and disposal problems; e.g., see ref. 7).
these high-LET recoiling nuclei produced. Compared to low-LET X- or γ-ray photons and fast electrons, the main radiobiological effects of fast neutron radiation are (for reviews, see refs. 151, 154-157):

(i) The cytotoxic effectiveness is less dependent on oxygen concentration or, in other words, the “oxygen effect” is less dominant. Recall here that a measure of the degree of cellular radiosensitization by $O_2$ is given by the “oxygen enhancement ratio” or OER, defined as the ratio of doses without and with oxygen needed to produce the same biological effect. For most cellular organisms, the value of OER decreases with increasing LET (47, 65, 158, 159). While the OER for cell killing is generally found between 2.5 and 3 for low-LET radiations with conventional dose rates, fast neutrons exhibit much lower OER values in the range from 1.5 to 1.8. Thus tumors containing hypoxic cells are, in principle, less protected against neutrons.

(ii) DNA damage is less repairable by tumor cells than that induced by photons or fast electrons and the efficiency of cell killing per unit dose is increased. In fact, low-LET γ or X rays will cause mostly single strand breaks of the DNA helix, as the ionization density is low and no target is likely to be hit more than once. Single strand breaks of DNA molecules can be readily repaired, and so the effect on the target cell is not necessarily lethal. By contrast, the high-LET charged particles produced from neutron irradiation cause many ionizations and excitations in close proximity as they traverse a cell, and so double-strand breaks (DSB) of the DNA molecule and other more complex clustered DNA lesions, in which DSB lesions are associated with different types of DNA damage (such as base and sugar modifications, base losses, and DNA-DNA and DNA-protein crosslinks), are possible (160-163). These “clustered” types of lesions, whose complexity increases with increasing LET, are much more difficult for a cell to repair, and more likely lead to cell death.

This increased efficiency of cell killing by high-LET neutron beams compared with photons per unit of absorbed dose can be quantified by the "relative biological
effectiveness" or RBE, defined as the ratio of the dose of a "reference radiation" (normally 250-kV X-rays or $^{60}\text{Co}$ $\gamma$-rays) to the dose of the radiation under study that is necessary to produce the same level of biological effect. Because of the high LET, the RBE of fast neutrons is 2-6 times that of X-ray photons, with a mean value of about 4 (164-166). This means that 1 Gy of fast neutrons is equal to 4 Gy of X-rays. These RBE values were found in many biological systems, including bacteria, plants, transplanted animal cancers, and human tumor cell lines spanning a wide range of radiosensitivities. It should be noted here that the RBE of fast neutrons depends not only on the dose level or fractionation and the specific biological endpoint used, but also on the LET distribution of charged recoil particles and on neutron energy. Therefore, fast neutron beams produced with different energy spectra at different facilities generally have different RBE values (167, 168). Actual evaluations must also account for the low-LET gamma-ray component always present in a neutron radiation field or generated by nuclear reactions in the system. As will be discussed in Sect. IV, these mixed-field situations usually lead to complications due to the difficulty in assessing the energy deposited by each of the qualitatively different radiation types, or in other words, in determining the separate absorbed doses of neutrons and of photons (37, 82, 152).

(iii) The variation in cell response with the phase of the mitotic cell cycle has a less pronounced influence on cell killing (e.g., see ref. 169).

Because of the basic radiobiological advantages of high-LET radiation, fast neutron therapy is, for the radiation therapist, an alternative to conventional photon (or electron) therapy in clinical radiation oncology (for a historical background, see ref. 170). However, previous multicentric clinical trials comparing neutron and photon beams have failed to show clear indications of the suggested therapeutic advantages. While local/regional tumor control may be more efficiently achieved for some tumors, the degree of side effects and late complications seem to be more severe for neutron radiotherapy. One reason for these hitherto inconclusive findings may be the poorer physical dose distributions achievable with the neutron
beams used in the randomized trials (171). With the recent development of more sophisticated beam delivery and collimation systems, the most promising reported results for the future use of fast-neutron beams as a therapeutic modality appear to be in the treatment of large, slowly-growing or photon-resistant tumors such as inoperable salivary gland tumors, locally advanced prostatic adenocarcinomas, low-grade soft-tissue sarcomas and some sarcomas of bone (e.g., see refs. 166, 172).

II.2 Interaction of fast neutrons with water

II.2.1 Scattering cross sections

By definition, the "cross section" represents a measure of the probability of any particular event occurring between a neutron and a single nucleus. This quantity is usually given the symbol $\sigma$ and is expressed in area units. The practical unit is a barn (1 barn $= 10^{-24}$ cm$^2$). As seen above, a neutron can have many types of (competing) interactions (scattering or absorption) with a nucleus, each of them having its own probability and cross section. The probability of occurrence for each type of event is independent of the probability of the others, so the sum of all the possible individual interaction cross sections defines what we call the "total cross section".

All of the cross sections are critically dependent on the energy of the neutron involved and on the type of the target nucleus (for reviews, see refs. 144, 146, 148, 173). Note that, as a general rule the cross section is a lot larger at low energies than at high energies. At energies usually less than 1 keV, the elastic cross section is nearly constant, whereas the inelastic scattering cross section and absorption (capture) cross sections exhibit a $1/\sqrt{E_n}$ behavior (this inverse proportionality is also called the $1/v$ law, where $v$ is the neutron velocity; e.g., see ref. 174). So at low energies the total cross section can be nearly constant or decreasing with increasing energy, depending on which type of event dominates. At higher energies the cross section may have large peaks superimposed on the $1/v$. 

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background. These peaks are called "resonances" and occur at neutron kinetic energies where reactions with nuclei are enhanced. For example, a resonance will occur if the target nucleus and the captured neutron form a "compound nucleus", and the excitation energy brought by the incident neutron corresponds to a quantum state of the resulting compound system. Scattering and absorption cross sections exhibit resonance peaks at neutron kinetic energies corresponding to those quantum nuclear states. In general, resonances occur at lower energies for heavy nuclei than for light nuclei. In heavy nuclei, large and narrow resonances appear in the slow neutron region. For intermediate energies the resonances can be too close together to evaluate. As we move to energies in the MeV range, the resonances are sparser and have very broad shapes. For light nuclear targets, resonances appear only in the MeV region and are broad and relatively small. Of all the nuclides, only hydrogen and its isotope deuterium exhibit no resonances at all. Exceptions to the general trends also exist in some nuclei with "magic" numbers of protons or neutrons\(^{25}\) where the behavior may be similar to that of light nuclei despite the actual atomic weight. In practice, we rely on tables of cross sections for the nuclei of interest [e.g., see: Nucl. Data Sheets 107, 2931 (2006), a special issue ("Evaluated nuclear data file ENDF/B-VII.0") on evaluations of neutron cross sections from the U.S. Cross Section Evaluation Working Group of the National Nuclear Data Center of Brookhaven National Laboratory (http://www.nndc.bnl.gov/csewg/); see also the T-2 Nuclear Information Service of the Los Alamos National Laboratory (http://t2.lanl.gov/data/data.html), which provides access to a variety of nuclear data, including the ENDF/B-VII.0 library of evaluated neutron data with links to PDF plots of the cross sections and angular distributions for most nuclides over the neutron energy range up to 200 MeV].

\(^{25}\) Those nuclei have a completely filled shell of either protons or neutrons; they are said to be "magic" because they are relatively more stable than nuclei with either a larger or a smaller number of nucleons.
II.2.2 Elastic scattering interactions of fast neutrons in water

As already pointed out, fast neutrons at incident energies less than about 10 MeV cause radiation effects primarily through the generation of elastically scattered charged nuclei of the absorbing medium. In the case of the fast-neutron radiolysis of water, the ionizing particles involved are thus proton and oxygen ion recoils. It is in fact important to note that, in this energy range, the contributions resulting from the $^{16}\text{O}(n,\alpha)^{13}\text{C}$ reaction (threshold at ~3.8 MeV), producing $\alpha$-particles and recoiling carbon ions, and especially from the inelastic scattering with oxygen (first level at ~6.05 MeV), producing gamma radiation, can be neglected to a very good approximation. From the radiolysis point of view and as long as the energy is less than ~10 MeV, we therefore need only consider elastic neutron-proton ($n$-$p$ collisions) and to a smaller extent (see below) neutron-oxygen scattering interactions.

Figure 1 shows a comparison of the elastic cross sections for $n$-$p$ scattering and for neutrons incident on oxygen nuclei in the energy range from 5 keV to 10 MeV. As can be seen, the cross-section curve for neutrons incident on $^1\text{H}$ is featureless (no resonances are present) and decreases continuously with increasing neutron energy. For neutrons incident on $^{16}\text{O}$, the cross section is quite flat in the region below ~0.3 MeV but shows resonance peaks at higher energies. Moreover, below about 0.3 MeV, the scattering for proton recoils is very high and largely dominates the oxygen elastic scattering; however, in the energy range ~0.3-10 MeV, because of the occurrence of the various resonances in oxygen, the

---

26 This is because the cross sections for these nuclear reactions are about an order of magnitude less than the cross sections for hydrogen and oxygen elastic scattering for most of the energies that interest us here. Notice that they rise steeply, however, as neutron energy increases, but become significant only at neutron energies around or greater than 10 MeV [data from the Brookhaven ENDF/B-VII.0 library (2006); see also ref. 145].
cross section for oxygen elastic scattering tends to become more or less the same as that for $n-p$ collisions.

It is worth noting that the (elastic) scattering cross sections shown in Fig. 1 describe the interactions of a neutron with a single nucleus, hydrogen or oxygen. These cross sections, referring to an individual element, are often called "microscopic" cross sections (146). If the studied sample is now a compound containing several elements instead of a simple element, the cross section is simply the sum of the cross sections of the individual target nuclei. For example, for the case of the water molecule ($H_2O$), which contains two hydrogen atoms and one oxygen atom, the cross section describing the interaction of a neutron with the molecule is

$$\sigma_{H_2O} = 2\sigma_H + \sigma_O,$$

where $\sigma_H$ and $\sigma_O$ are the microscopic cross sections for hydrogen and oxygen, respectively. More generally, for bulk materials containing a mixture of elements $i$ with density $N_i$ and individual cross section $\sigma_i$, we can define the so-called "macroscopic" cross section (denoted here by the symbol $\mu$ and with dimensions of cm$^{-1}$), given by (146)

$$\mu = \sum_i N_i \sigma_i .$$

As an illustration of Eq. (32), the macroscopic cross section for neutrons in water is

$$\mu_{\text{water}} = \frac{N_{\text{Av}} \rho}{M} \left( n_H \sigma_H + n_O \sigma_O \right),$$

where $\rho$ is the density of water, $M = 18$ is its molecular weight, $N_{\text{Av}}$ is Avogadro's number, and $n_H = 2$ and $n_O = 1$ are the numbers of atoms of hydrogen and oxygen in one molecule, respectively. Interestingly, the fact that there are twice as many hydrogen atoms as oxygen atoms per given volume of water also contributes to making oxygen ion recoils of minor importance in the fast-neutron radiolysis of water. In fact, Edwards et al. (82) estimated that, in the energy range below 10
MeV, 88% of the neutron energy is absorbed by protons and 12% by oxygen recoils.

II.2.3 Neutron mean free path and ranges of recoil protons and oxygen ions in water: information on track structure

A very descriptive feature of the transmission of neutrons through bulk matter is the "mean free path" \( \lambda \), which is the average distance a neutron travels between two consecutive interactions. It is defined as the reciprocal of the macroscopic cross section \( \mu \) given in Eq. (32):

\[
\lambda = \frac{1}{\mu}.
\]  

(34)

\( \lambda \) is a key parameter in the study of neutron transport and interactions in matter and has many qualitative applications in assay instruments and shielding. For example, it is found that, under the conditions of the transmission of a pencil beam of monoenergetic neutrons incident normally (along the direction \( z \)) on a thick sample of infinite lateral extent, the relative number of neutrons that travel a distance \( z \) in the sample (the origin being at the point where the neutrons enter the sample) without experiencing a collision falls off exponentially as \( \exp(-z/\lambda) \) \((146, 174)\). Mathematically, this is a representation of the Poisson distribution and corresponds to the probability of no event when, on the average, \( z/\lambda \) events should occur \((175)\). Importantly, \( \lambda \) also determines the free flight distances of individual neutrons in Monte-Carlo procedures that are used to simulate how neutrons are transported through matter. In those computer calculations, individual free flight distances for a large number of simulated neutrons must be selected randomly so as to give the observed \( \exp(-z/\lambda) \) distribution \((176)\).

The mean free path depends on both the type of material and the energy of the neutron. For the case of 100-keV incident neutrons in water, \( \lambda \) can easily be calculated from Eqs. (33) and (34) to be \( \sim 1.04 \) cm, using the microscopic cross section values \( \sigma_H \approx 12.5 \) and \( \sigma_O \approx 3.65 \) barns \((60)\). The mean free path of neutrons in water as a function of neutron energy is shown in Fig. 2. After each
collision, the neutron's energy is decreased and the cross section changes, thereby affecting the mean free path accordingly. For the range of the energies that interest us here, $\lambda$ decreases as the neutron's energy decreases.

Table 5 gives some values for the mean free path and secondary-particle (recoil proton and oxygen ion) maximum range for several neutron energies in water. As can be seen, the elastically scattered proton and oxygen ion recoils generated by the passage of the incident neutron are widely separated from one another along the path of the neutron.\(^{27}\) Moreover, these recoil nuclei have maximum ranges (i.e., track lengths) much less than the average separation between two successive neutron interactions ($\lambda$), so that they can be considered as behaving independently of each other: their ionizing energy is deposited locally in dense tracks in the water in the immediate vicinity of the collision sites (the points of generation of the recoil particles) with virtually no allowance for overlap of the reaction zones of neighboring tracks.\(^{28}\) As a consequence, under normal irradiation conditions, fast neutrons deposit their energy in water primarily through the generation of "isolated" tracks of recoil nuclei and the observed water radiolysis chemistry should tend to be much like that induced by independent, high-LET protons and oxygen ions.

This track structure information for the elastically scattered proton and oxygen ion recoils strongly supports the procedure used in the present study to calculate the radiolysis G-values for fast neutrons by simply summing the yields for each of these recoil ions after allowance has been made for the appropriate weighting according to energy (see Sects. I.1.5, III, and IV).

\(^{27}\) Like photons, neutrons are uncharged and hence can travel appreciable distances without interacting.

\(^{28}\) This approximation would not necessarily be correct at very high neutron intensities or dose rates.
III. METHODOLOGY

III.1 Monte-Carlo simulations

The complex sequence of events that are generated in liquid water and dilute aqueous solutions under irradiation can be modeled successfully by the use of Monte-Carlo simulation methods. Such a procedure is particularly well-suited to account for the stochastic nature of the phenomena. Turner et al. (178) at the Oak Ridge National Laboratory (Oak Ridge, Tennessee, U.S.A.) and Lawrence Berkeley Laboratory (Berkeley, California, U.S.A.) were the first to use Monte-Carlo calculations to derive computer-plot representations of the chemical evolution of a few keV electron tracks in liquid water at times from $10^{-12}$ to $10^{-7}$ s. Zaider and Brenner (179) also described such an approach, and their calculated time-dependent yields of $e^{-aq}$ and $\cdot OH$ radicals were somewhat similar to values measured or derived in pulse-radiolysis studies of pure water. Following these pioneering works, stochastic simulation codes employing Monte-Carlo procedures were developed independently by different researchers to study the relationship between the initial track structure and the ensuing chemistry (e.g., see refs. 141, 180). In a program begun in the summer of 1988, Prof. Jean-Paul Jay-Gerin's group at the Université de Sherbrooke, in collaboration with Prof. Jean Paul Patau (Université Paul-Sabatier, Toulouse) and Prof. Christiane Ferradini (Université René-Descartes, Paris) in France, has also developed and progressively refined with very high levels of detail several Monte-Carlo codes that simulate, in a three-dimensional (3D) geometrical environment, the track structure of ionizing particles in liquid water, the production of the various reactive species in the radiation track,

29 The so-called "Monte-Carlo method" is a general term (named after the famous European gambling center) used to describe any algorithm or computational method that employs random numbers. Simulation methods are used to estimate means of random variables or probabilistic features of models that we cannot compute analytically.

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and the subsequent chemical reactions of these species with themselves (owing to
diffusion from their initial positions) or with any dissolved solutes present at the
time of irradiation (13, 24, 25, 35, 36, 62, 64, 72, 92, 115, 181, 182). A most recent
version of the Sherbrooke codes, called IONLYS-IRT, has been used in the
present work. The detailed description and implementation of IONLYS-IRT has
already been given (13, 24, 64, 92, 115), and will not be reproduced here. Only a
brief overview of the most essential features of the simulation methodology and
reaction scheme, pertinent to the current calculations, is given below.

III.1.1 The IONLYS simulation code

The IONLYS simulation code is used to cover the early "physical" and
"physicochemical" stages of radiation action up to \(-10^{-12}\) s. It is actually composed
of two modules, one (named TRACPRO) for transporting the investigated incident
charged particle (proton or any other heavy ion projectile) and one (named
TRACELE) for transporting all of the energetic electrons (collectively named
"secondary electrons") that result from the ionization of the water molecules. The
code models, event by event, all the basic physical interactions (energy deposition)
and the subsequent establishment of thermal equilibrium in the system (conversion
of the physical products created locally after completion of the physical stage into
the various "initial" chemical species of the radiolysis). For a detailed description of
these events as well as their time scales, see Sect. 1.1.2 (see also ref. 47).

In particular, IONLYS provides the detailed distribution of coordinates of all
physical events (ionization, excitation of electronic, vibrational and rotational levels
of single water molecules, excitation of plasmon-type collective modes, and elastic
scattering) that occur locally during the slowing-down of the irradiating charged
particle and of all the secondary electrons that it has generated. The energy-
dependent cross sections for the various elastic and inelastic processes involved,
together with their angular distributions, are entered as input data in the code,
based on direct measurements (where available, as cross-section data in the case
of liquid water are scarce) or on theoretical estimations. These collision cross
sections are needed to follow the history of an energetic charged particle and its products, covering all ranges of energy transferred in individual collisions. Most importantly, they provide the mean free path used to determine the distance to the next interaction, the type of interaction at each event, energy loss, and the angle of emission of the scattered particle (e.g., see refs. 180, 183). Full details of the cross-section database used in the IONLYS code can be found in the references cited (13, 24, 184). It is worth mentioning that this code, which uses protons or heavy ions as the primary particles, is particularly well adapted to the study of the fast-neutron radiolysis of water, since the ionizing particles involved in this case are proton and oxygen ion recoils. Interestingly, the choice of proton impact in the Sherbrooke code was originally adopted owing to the fact that protons represent, by far, the most comprehensive database of cross sections for bare ion collisions (not only on water but also on a number of different target atoms or molecules; e.g., see refs. 185-188), and also because they constitute a valuable tool for studying LET effects on radiolytic yields (13). Another great advantage of the code is that, while it was devised for protons, it can also be used for heavier ion projectiles by assuming that the interaction cross sections scale as $Z^2$, where $Z$ is the projectile charge number. In this scaling procedure, based on the lowest-order (or first Born) approximation of perturbation theories, the cross sections for bare ion impact are approximately $Z^2$ times the cross sections for proton impact at the same velocity. This simple $Z^2$ scaling rule, which holds at sufficiently high impact energies (say above ~1 MeV/nucleon) where the interactions are not too strong, is particularly useful for providing cross sections for ionization and excitation by ion projectiles, especially as there are only limited experimental data available involving ions heavier than proton or helium in collision with water molecules (24, 47, 189-191). In practice, the stochastic selection of the scattering events is done with various sampling techniques (direct inversion, etc.; e.g., see ref. 192) in accordance to the appropriate scattering cross sections for each process induced by the considered
charged particle. These techniques all use pseudo-random numbers uniformly distributed on the interval between 0 and 1.

The simulations performed with IONLYS consist in the generation of short high-energy proton (ion) track segments in water. The primary particle is simulated until it has penetrated the chosen length of the track segment into the medium. Note that, due to its large mass, the proton (or the impacting heavy ion) is almost not deflected by collisions with the target electrons. In the present simulations, these deflections are simply neglected. The use of small path segments is particularly useful as the instantaneous LET of the incident particle is nearly constant over such segments and can be varied simply by changing its energy. Figure 3 shows our simulated LET for protons in liquid water as a function of proton energy in the range ~15 keV-300 MeV, together with the recommendations of Watt (60) and the compilation of ICRU Report 49 (69). It is seen that, while our calculated LET values are slightly lower than the published data at energies near the Bragg peak (~80 keV) and below, there is a good overall agreement among the three independent assessments. To reproduce the effects of fast electron or $^{60}$Co γ-radiolysis, we use short (~100 μm) track segments of 300-MeV protons over which the average LET value obtained in the simulations is essentially constant and equal to ~0.3 keV/μm at 25 °C.

All of the produced energetic (dry) secondary electrons are explicitly transported spatially from their initial energies until they reach the subexcitation energy region below ~7.3 eV, the threshold assumed for electronic excitation in liquid water (see Sect. 1.1.2). The location, type of collision, specific quantum

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30 For comparison, a 300-MeV proton has a range in water of ~52.1 cm (60).
31 Recall here that most energy-loss events by the fast primary charged particle involve small transfers of energy. In fact, Monte-Carlo simulations have shown that the most probable energy loss for liquid water is 15-20 eV, while the track-averaged mean energy loss is around 50-60 eV, depending on the authors (13,
transition, and energy transferred are determined by the IONLYS code, event by event. All physical details about the various elastic and energy-loss processes involved and the corresponding scattering cross sections employed by IONLYS for the simulation can be found in refs. 13, 24, and 184. The time that a secondary electron takes to reach a subexcitation energy is $<10^{-15}$ s.

The thermalization of subexcitation electrons is treated by IONLYS using the distribution of thermalization distances obtained from Monte-Carlo track-structure calculations (195, 196) based on experimental scattering cross sections of slow ($\sim$1-100 eV) electrons in amorphous ice films at 14 K (197) with corrections to account for the liquid phase. Given the initial position of the subexcitation electron, its position is simply displaced in a randomly selected, isotropic direction by the corresponding, energy-dependent mean penetration distance. At this new position, the electron is regarded as thermalized and subsequently trapped and hydrated where it is, an approximation likely to be valid in a highly polar medium such as liquid water in which very-low energy (e.g., “subvibrational”) electrons have a strong tendency – due to the presence of a large density of possible electron trapping sites – to get instantly trapped prior to thermalization (18). As mentioned in Sect. I.1.2, the time scale of thermalization, trapping, and hydration of a subexcitation electron in liquid water at 25 °C is less than $\sim10^{-12}$ s. Finally, it is worth recalling here that a certain proportion of subexcitation electrons will actually never get thermalized, but will instead undergo prompt recombination\(^{32}\) with their

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193, 194). Cobut et al. (13) also calculated that, if we sum all the electrons ejected directly by the primary particle and by the successive generations of secondary electrons, 88% of them have kinetic energies less than 20 eV.\(^{32}\) About 25.5% of the subexcitation electrons are found to initially recombine with $\text{H}_2\text{O}^+$ (24), with an average recombination time as short as a few femtoseconds (195). This average recombination time shows that the recombination process mainly occurs on the water cation and not on $\text{H}_3\text{O}^+$, that is, before the proton
positive parent ion $H_2O^{+}$ or dissociative attachment (DEA) onto a surrounding $H_2O$ molecule. All details about the various parameters intervening in the IONLYS code to describe this competition between thermalization, geminate recombination, and dissociative attachment, as well as the values of the branching ratios used in the code for the different dissociative decay channels of the electronically and vibrationally excited $H_2O$ molecules, can be found in ref. 24.

III.1.2 The IRT simulation code

The complex spatial distribution of reactants at the end of the physicochemical stage (~$10^{-12}$ s; we assume that this time also marks the beginning of diffusion), which is provided as an output of the IONLYS program, is then used directly as the starting point for the subsequent nonhomogeneous chemical stage. This third and final stage, during which the individual reactive species diffuse randomly at rates determined by their diffusion coefficients and react with one another (or with any added solutes present at the time of irradiation) until all spur/track processes are complete (~$10^{-7}$-$10^{-6}$ s), is covered by the IRT program. This program employs the “independent reaction times” (IRT) method (198, 199), a computer efficient stochastic simulation technique that is used to simulate reaction times without following the trajectories of the diffusing species.
The IRT method relies on the approximation that the distances between pairs of reactants evolve independently of each other, and therefore the reaction times of the various potentially reactive pairs are independent of the presence of other reactants in the system. In essence, the simulation begins by considering the initial, or "zero-time", spatial distribution of the reactants (given by the IONLYS program). The separations between all the pairs of reactants are first calculated. Overlapping pairs (i.e., pairs formed in a reactive configuration) are assumed to combine immediately. For each remaining pair, a reaction time is stochastically sampled according to the reaction time probability distribution function (115, 199, 200) that is appropriate for the type of reaction considered. This function depends upon the initial distance separating the species, their diffusion coefficients, their Coulomb interaction (for reactions between ionic species), their encounter distance, and the probability of reaction during one of their encounters. The competition between the various reactions is taken into account by realizing them in the ascending order of sampled reaction times. In other words, the first reaction time is found by taking the minimum of the resulting ensemble of reaction times and allowing the corresponding pair of species to react at this time. When a reaction occurs, the reactants become unavailable for the competing reactions that are sampled to occur at longer times but one must then consider the possible reactions of the newly formed products with the species that have survived up to that point. The minimum of the new ensemble of reaction times is the next reaction time. The simulation proceeds in this manner until a pre-defined cut-off time is reached or all the potentially reactive pairs have reacted. Since the IRT method is solely based on a comparison of reaction times, it does not follow the diffusive motion of the species within the spur/track. The model must therefore be supplemented by including an approximation which allows the calculation of either new inter-particle

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33 The "encounter (or reaction) distance" \( a_{AB} \) for each pair of interacting species A and B can be derived from the Smoluchowski equation (see Sect. I.1.5).
distances at the time when a new product is formed, or reaction times without inter-particle distances. Several alternative procedures, which incorporate varying degrees of spatial information about the system, have been devised and discussed in detail previously (198, 199). The procedure adopted in our IRT code to account for the subsequent reactions of reactive products is described in ref. 115.

The IRT program also allows one to incorporate in a simple way pseudo first-order reactions of the radiolytic products with various scavengers that are homogeneously distributed in the solution, such as $\text{H}^+$, $\text{OH}^-$, and $\text{H}_2\text{O}$ itself, or more generally any solutes for which the relevant reaction rates are known. Similarly, the truly first-order fragmentations of the species are easily simulated. Finally, the IRT method is very well suited for the description of reactions that are only partially diffusion-controlled, in which the species do not react instantaneously on encounter but experience, on the average, many encounters and separations before they actually react with each other.

The IRT simulation of nonhomogeneous kinetics has been found to be particularly accurate in solvents of high static dielectric constant (such as is the case for liquid water, $\varepsilon_s \sim 78$) where the Coulomb forces between the ions are weak (e.g., see ref. 201). Indeed, the time-dependent yields of water radicals and molecular products obtained with the IRT method under different irradiation conditions have been shown to compare very well to those calculated using full

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34 Most reactions that occur in irradiated water are not diffusion-controlled even at room temperature; as mentioned in Sect. I.1.5, an adequate description of the activation processes that are involved in those reactions is a prerequisite for the modeling of the effects of high temperature on water radiolysis.
random flights (or "step-by-step") Monte-Carlo simulations, which do follow the reactant trajectories in detail (198, 202, 203).\(^{35}\)

Compared to the original version of our IRT program, only slight adjustments have been made in some reaction rate constants (see Table 1 for the list of the main spur/track chemical reactions and values of reaction rate constants considered in our pure liquid water radiolysis simulations at room temperature) and diffusion coefficients of reactive species (Table 6 shows the values of diffusion coefficients for the various track species involved in our simulations) to take account of the latest data available from the literature (24, 64, 194).

As mentioned in Sect. II, fast neutrons impinging on liquid water at incident energies less than \(~10\) MeV generate primarily energetic protons and to a smaller extent oxygen ion recoils. For example, the first four recoil protons generated by a 0.8-MeV neutron have energies of 0.505, 0.186, 0.069, and 0.025 MeV with LET values of \(~41, 69, 82,\) and \(62\) keV/\(\mu\)m, respectively. To reproduce the effects of fast-neutron radiolysis on the yields of the various radiation-induced species in neutral or acidic water, as well as on the yield of ferric ions in the Fricke dosimeter, we simulate short \((\sim 15-100\ \mu\)m\) track segments of each of those generated recoil protons (in the range of incident energies from \(~0.015\) to 300 MeV; see Fig. 3).

\(^{35}\) The full step-by-step Monte-Carlo description of the diffusion and encounters of the various species of the system is certainly the most reliable and is generally considered as a measure of reality. Unfortunately, this method can be exceedingly consuming in computer time when large systems (such as complete radiation tracks or track segments) are studied. The IRT method has been devised to achieve much faster realizations than are possible with the full Monte-Carlo model. For example, depending on the LET of the track segment considered and on the timescale over which the reaction kinetics is simulated, the IRT technique is of the order of a few hundred times faster than a full step-by-step Monte-Carlo calculation.
Over such simulated track segments, the energy and LET of the protons are well defined and remain nearly constant. Such model calculations thus give track segment yields at a well-defined LET. The number of proton histories (usually ~10-150, depending on the proton energy) is chosen so as to ensure only small statistical fluctuations in the computed averages of chemical yields, while keeping acceptable computer time limits.

III.2 Modeling the effects of acidity

To model the radiolysis of the ferrous sulfate (Fricke) dosimeter (see Sect. 1.2), we have used aqueous solutions of 0.4 \textit{M} sulfuric acid (pH ~ 0.46). For aqueous \( \text{H}_2\text{SO}_4 \) (a diprotic acid), we have:

\[
\text{H}_2\text{SO}_4 \overset{\text{H}^+}{\underset{\text{pK}_{a1}}{\rightleftharpoons}} \text{HSO}_4^- \overset{\text{H}^+}{\underset{\text{pK}_{a2}}{\rightarrow}} \text{SO}_4^{2-}
\]  

(35)

with \( \text{pK}_{a1} \approx -3 \) and \( \text{pK}_{a2} = 1.987 \) at 25 °C (205). Hence, \( \text{H}_2\text{SO}_4 \) is virtually completely dissociated when dissolved in water above pH ~ 0, and the solution contains mainly \( \text{H}^+ \), \( \text{HSO}_4^- \), and a certain amount of \( \text{SO}_4^{2-} \).

The model assumptions and procedures employed to carry out the Monte-Carlo simulations of the radiolysis of 0.4 \textit{M} \( \text{H}_2\text{SO}_4 \) aqueous solutions with IONLYS-IRT have already been given (35, 36, 64). In brief, as noted before, the effects of the background concentration of \( \text{H}^+ \) in solutions are added to the IRT program as pseudo first-order reactions. We have also supplemented the pure-water reaction scheme (Table 1) to include the reactions listed in Table 7, which account for the species present in irradiated sulfuric acid solutions. The diffusion coefficients of \( \text{HSO}_4^- \), \( \text{SO}_4^{2-} \), \( \text{SO}_4^{2-} \), and \( \text{S}_2\text{O}_8^{2-} \), employed in the simulations are taken to be (in units of \( 10^{-9} \text{ m}^2 \text{ s}^{-1} \)) 1.385 (for both \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \)), 1.065, and 1.145, respectively (206).
In addition, we have introduced, in the IRT program, the effects due ionic strength in 0.4 \( M \) H\(_2\)SO\(_4\) solutions (e.g., see ref. 207) for reaction (13) \((e^{-}_{aq} + H^+ \rightarrow H^+)\) and for the recombination of the proton with the hydroxyl ion (24, 35):

\[
{\text{OH}^-} + {\text{H}}^+ \rightarrow \text{H}_2\text{O}
\]  

(36)
as well as for all reactions between ions,\(^{36}\) including those given in Table 7. To relate rate constant and ionic strength of the solution, we used the following equation, obtained from the Brönsted-Bjerrum model of ionic reactions and the extended Debye-Hückel theory of ionic solutions (209-211):

\[
\log\left(\frac{k}{k_0}\right) = 3.64 \times 10^6 \frac{Z_a Z_b}{(\varepsilon T)^{\frac{1}{2}}} \left( \frac{l^{\frac{1}{2}}}{1 + l^{\frac{1}{2}}} \right),
\]  

(37)

where \(k\) is the rate constant at ionic strength \(l\), \(k_0\) is the rate constant at infinite dilution of ions (i.e., in the limit of zero ionic strength), \(Z_a\) and \(Z_b\) are the algebraic numbers of charges on the reactants (positive for cations and negative for anions), \(T\) is the absolute temperature (in K), and \(\varepsilon\) is the dielectric constant of the medium (for water, \(\varepsilon = 78.5\) at 25 °C and 13.0 at 350 °C). The ionic strength of the solution (in M) is defined as (212):

\[
l = \frac{1}{2} \sum_i Z_i^2 C_i,
\]  

(38)

where \(Z_i\) is the charge number of the \(i\)th ion and \(C_i\) is its molar concentration. The sum extends over all ionic species present in the solution. According to Eq. (37), the rate constant will increase, decrease, or remain the same with increasing ionic strength, depending on whether the reactants have the same sign, opposite signs, or whether one reactant is neutral. For example, in 0.4 \( M \) H\(_2\)SO\(_4\) solutions, the rate constants for reactions (13) and (36), corrected for these effects, are \(k_{13} = 1.12 \times \)

\(^{36}\)Except for the peculiar bimolecular self-recombination of \(e^{-}_{aq}\) for which there is no evidence of any ionic strength effect (208).
$10^{10} \text{ M}^{-1} \text{s}^{-1}$ (see Sect. 1.1.3) and $k_{36} = 5.97 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ (instead of $2.11 \times 10^{10}$ and $11.3 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ in neutral water at 25 °C, respectively; see Table 1) (36).

Finally, in our simulations the "direct" action of ionizing radiation on the sulfuric acid anions (mainly HSO$_4^-$) is neglected, which is a reasonably good approximation for 0.4 M sulfuric acid solutions. In fact, at this concentration of H$_2$SO$_4$, only about 3.5% of the total energy expended in the solution is initially absorbed by direct action on HSO$_4^-$ ions (rather than on H$_2$O) (assuming that the energy absorbed by each component is proportional to its electron fraction) (213).

### III.3 Modeling the effects of temperature

In this work, we use an extended version of our Monte-Carlo computer code which was developed previously to include the effects of high temperature (from 25 up to 300 °C) on water radiolysis at low (15, 92) and high (107, 214, 215) LET.

Briefly, the scattering cross sections are independent of the medium's temperature because the energy of the ionizing particles is much larger than the thermal energies and because the motion of the target (water) molecules can be neglected. The influence of temperature on the physical stage of radiation action is thus mainly due to the fact that temperature brings the water molecules further apart without changing their ability to interact with the ionizing particles. For example, the density ($\rho$) of pressurized water varies with temperature from $\rho = 1$ g/cm$^3$ at room temperature to $\rho = 0.712$ g/cm$^3$ at 300 °C. This influences the particle's scattering mean free paths (MFP) which are related to the scattering cross sections (see Sect. II) through the simple relation $\text{MFP} = 1/(\sigma N)$, where $\sigma$ is the total cross section and $N$ is the number of scatterers per unit volume. As a result of the invariance of the scattering cross sections, this dilatation is proportional to the inverse of the density. Since very little is known about the influence of the temperature on the early physicochemical processes, the simulations were performed using a number of assumptions for the temperature dependences of the initial distributions of the reactive species. For example, the
possible decay channels for H\(_2\)O\(^{**}\) and for vibrationally and electronically excited H\(_2\)O molecules are likely to be essentially independent of temperature since those primary processes are not thermally activated.\(^{37}\) As for the migration of the cations H\(_2\)O\(^{**}\) (hole transfer) and of the subexcitation electrons, it is likely to be sensitive to temperature. In fact, the variations of density would act as they did in the physical stage, increasing (on average) each step of the random walk. Most importantly, electrons in the subexcitation energy range (\(<7.3\) eV) are known to be sensitive to the structural order of the surrounding medium, owing to their nonnegligible delocalized character. In various media, as well as for water, their scattering cross-sections have been shown to increase rapidly when the degree of order diminishes (92). On this physical basis, one could expect the scattering cross sections of subexcitation electrons to increase with temperature in the range 25-300 °C, since the diminution of hydrogen bonding gives rise to a decrease of the structural order. As a result, this effect could affect the thermalization distances (\(r_{th}\)) of those electrons, in reducing them significantly with increasing temperature. It is difficult, however, to estimate to what extent this could affect \(r_{th}\), but this effect could overcome the \(~30\%\) decrease in the density as temperature rises from 25 to 300 °C and in turn reduce those distances appreciably. In the present simulations, \(r_{th}\) is assumed to decrease linearly with temperature by a factor of 2 between 25 and 300 °C. This choice was shown to offer the best agreement with experiment of \(G_{e^-_{aq}}\) and \(G_{H_2}\) at elevated temperature in the case of low-LET radiation (92, 107). Similar conclusion was also suggested previously by Hochanadel and Ghormley (216), who pointed out that, at higher temperature, "subexcitation electrons are thermalized more rapidly".

\(^{37}\) We should mention here that other authors, such as Swiatla-Wojcik and Buxton (23), have suggested that the temperature, through a diminution of hydrogen bonding in liquid water, could possibly change the relative contributions of the dissociative decay channels for H\(_2\)O\(*\).
It should be noted that the temperature effects mentioned above do not modify the initial yields of the radiolytic species. In contrast, they have an impact on the spatial distribution of the energy deposition events, and consequently on the initial distribution of primary radiolytic species (broader at higher temperature) and the subsequent reaction kinetics. As mentioned above (see Sects. I.1.5 and III.1.2), the important parameters in the kinetic modelling following irradiation are the diffusion coefficients of the different reactive species and their reaction rate constants. The values used in the computer simulations, including their temperature dependences (up to 300 °C), are essentially the same as those reported by Elliot (76) and Elliot et al. (77), and also those recently compiled by Elliot and Bartels (97). Room-temperature values of the rate constants of the spur/track reactions and diffusion coefficients are listed in Tables 1 and 6, respectively.

III.4 Simulation of the Fricke dosimeter

The ferrous-sulfate Fricke dosimeter is an air-saturated solution of 1-10 mM FeSO₄ in aqueous 0.4 M H₂SO₄ (pH 0.46) (see Sect. 1.2). To stochastically model the chemistry of the Fricke dosimeter, we have added to the IRT program the reactions of Fe²⁺ ions with the oxidizing species 'OH, HO₂*, and H₂O₂ that are formed in the water of the irradiated solutions under aerated conditions. The mechanism for the radiolytic oxidation of Fe²⁺ ions to Fe³⁺ is well-understood and the rate constants at 25 °C of the individual reactions taking place are known. The reaction scheme is as follows (4, 7, 40, 97, 124, 217):

\[
\begin{align*}
e^-_{\text{aq}} + H^+ & \rightarrow H^+ & k_{13} = 1.12 \times 10^{10} M^{-1} s^{-1} & (13) \\
pK_a (H^+/e^-_{\text{aq}}) & = 9.74 \\
H^+ + O_2 & \rightarrow HO_2^* & k_{39} = 2.1 \times 10^{10} M^{-1} s^{-1} & (39) \\
Fe^{2+} + 'OH & \rightarrow Fe^{3+} + OH^- & k_{40} = 3.4 \times 10^8 M^{-1} s^{-1} & (40) \\
Fe^{2+} + HO_2^* & \rightarrow Fe^{3+} + HO_2^- & k_{41} = 7.9 \times 10^5 M^{-1} s^{-1} & (41)
\end{align*}
\]
\[ \text{HO}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]  
\[ k_{42} = 2.66 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]  
\[ \text{pK}_a (\text{H}_2\text{O}_2/\text{HO}_2^-) = 11.84 \]  

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{^}{\text{HO}} + \text{OH}^- + \text{Fe}^{3+} \]  
\[ k_{43} = 52 \text{ M}^{-1} \text{ s}^{-1} \]  

\[ \text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \]  
\[ k_{36} = 5.97 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]  
\[ \text{pK}_a (\text{H}_2\text{O}/\text{OH}^-) = 14.17 \]  

At the acid concentration of 0.4 \( \text{M} \) \( \text{H}_2\text{SO}_4 \), \( \text{e}^-_{\text{aq}} \) is rapidly converted to \( \text{H}^+ \) (see Sect. I.1.3). The \( \text{H}^+ \) atoms created directly by radiolysis and by reaction (13) react with oxygen in aerated solutions to form hydroperoxyl radicals (\( \text{HO}_2^- \)). Each of these radicals oxidizes three \( \text{Fe}^{2+} \) ions, one by reaction (41) and two by the reaction sequence (42), (43), and (40). Each \( ^{\text{OH}} \) radical oxidizes one \( \text{Fe}^{2+} \) ion, and each molecule of \( \text{H}_2\text{O}_2 \) oxidizes two \( \text{Fe}^{2+} \) ions. Summing all sources of \( \text{Fe}^{3+} \) ions, the yield of ferric ions in an aerated solution \( G(\text{Fe}^{3+}) \) is related to the escape yields of the free radicals and molecular species of (acidic) water radiolysis by Eq. (22).

Note that the values of \( k_{13}, k_{36}, \) and \( k_{42} \) used in the simulations have been corrected using Eqs. (37) and (38) for the effects due to the ionic strength in the case (under study here) of a solution made of 0.4 \( \text{M} \) \( \text{H}_2\text{SO}_4 \) and 5 \( \text{mM} \) \( \text{FeSO}_4 \). Note also that, as we have mentioned above, for solutions of 0.4 \( \text{M} \) in \( \text{H}_2\text{SO}_4 \) there is a small amount of \( ^{\text{OH}} \) radicals that react with \( \text{HSO}_4^- \) to form \( \text{SO}_4^{2-} \) [reaction (14)]. However, the overall ferric ion yield remains the same as given by Eq. (22) since the sulfate radical reacts with \( \text{Fe}^{2+} \) in the same way as \( ^{\text{OH}} \) (124, 138):

\[ \text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \]  
\[ k_{44} = 2.79 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \]  

Under normal irradiation conditions, the radical concentrations are low compared with the background concentrations of acid, \( \text{Fe}^{2+} \) ions, and oxygen (2.5 \( \times 10^{-4} \text{ M} \)) in solution, and the reactions are treated in the IRT program as pseudo first-order (see Sect. III.1.2). In modeling the Fricke dosimeter, the fastest reaction of \( \text{Fe}^{2+} \) ions is with \( ^{\text{OH}} \) radicals. The slowest component of the kinetics of \( \text{Fe}^{3+} \)
formation is due to the Fenton-type reaction (43). For example, in the case of 5 mM FeSO₄ solutions considered here, this reaction takes several seconds to go to completion (36), which increases significantly the computer time usually chosen for modeling the radiolysis of water (typically, the nonhomogeneous spur/track expansion is complete by ~1 μs). In the simulations reported here, the time evolution of G(Fe³⁺) has been followed until ~200 s.

The temperature dependences of the rate constants for the ferrous ion reactions (40), (41), and (43) were scaled from their values at 25 °C using simple Arrhenius equations with activation energies of 9.2, 42, and 42 kJ mol⁻¹, respectively (217-220). Finally, as there are no experimental data available on the temperature dependences of the diffusion coefficients of the Fe²⁺ and Fe³⁺ ions, the procedure adopted here was to scale the 25 °C values (0.719 × 10⁻⁹ m² s⁻¹ and 0.604 × 10⁻⁹ m² s⁻¹, respectively; see ref. 206) according to the self-diffusion in liquid water (92; see also Sect. III.1.2).

IV. RESULTS AND DISCUSSION
IV.1 Time evolution of G(Fe³⁺) in aerated Fricke solutions over the range of temperature from 25 to 300 °C

IV.1.1 Kinetics of Fe³⁺ formation in the radiolysis of the Fricke dosimeter with 300-MeV irradiating protons (LET ~ 0.3 keV/μm) at 25 °C

As seen in Sect. III.4, the mechanism of oxidation of Fe²⁺ ions to Fe³⁺ in an aerated Fricke solution involves reactions of Fe²⁺ ions with the oxidizing species ·OH, HO₂⁻, and H₂O₂ that are produced in the radiolytic decomposition of water. These reactions take place on different time scales. The fastest component of Fe³⁺ formation is due to Fe²⁺ oxidation by ·OH radicals, and the slowest is due to the

³⁸ Note that thermal decomposition of H₂O₂ is not taken into account in the simulations. However, this process may not necessarily be negligible at temperatures above 150 °C (e.g., see refs. 87, 142).
reaction of Fe$^{2+}$ with H$_2$O$_2$. As a result of the differences in the lifetimes of the reactions making up the radiolysis mechanism, $G(\text{Fe}^{3+})$ is time dependent (7, 36, 142, 221). This time evolution of $G(\text{Fe}^{3+})$ is illustrated in Fig. 4 for aerated solutions of 5 mM FeSO$_4$ in aqueous 0.4 M H$_2$SO$_4$ irradiated with 300-MeV protons (LET $\sim$ 0.3 keV/$\mu$m) at 25 °C. As can be seen from this figure, three temporal stages are clearly identified:

- Stage 1 (at $\sim$4 $\mu$s)
  
  \[ G(\text{Fe}^{3+}) = G_{OH} \]
  
  \[ G(\text{Fe}^{3+}) \approx 3.1 \text{ molec./100 eV} \]

- Stage 2 (at $\sim$2 ms)
  
  \[ G(\text{Fe}^{3+}) = G_{OH} + G_{\text{aq}^-\text{+H}^+} + G_{\text{HO}_2}. \]
  
  \[ G(\text{Fe}^{3+}) \approx 6.7 \text{ molec./100 eV} \]

- Stage 3 (at times $>$30 s)
  
  \[ G(\text{Fe}^{3+}) = G_{OH} + 3 \left( G_{\text{aq}^-\text{+H}^+} + G_{\text{HO}_2}. \right) + 2 G_{\text{H}_2\text{O}_2} \]
  
  \[ G(\text{Fe}^{3+}) \approx 15.45 \text{ molec./100 eV}. \]

As shown in Fig. 4 and as mentioned above, the fastest reaction of Fe$^{2+}$ ions is with 'OH radicals. It is completed on a microsecond time scale. The oxidation of Fe$^{2+}$ by HO$_2.$ is slower and requires a few milliseconds for completion. Finally, the slowest component in the formation of Fe$^{3+}$ is due to Fe$^{2+}$ oxidation by H$_2$O$_2$ [both the molecular product yield and that formed by reaction (42)]. This latter reaction takes place at times longer than $\sim$0.1 s and is completed by about 30 s. The standard value of the ferric ion yield in the Fricke dosimeter, obtained for $^{60}$Co $\gamma$-rays, high-energy X radiation or fast electrons, is $G(\text{Fe}^{3+}) = 15.6 \pm 0.2 \text{ molec./100 eV}$ (e.g., see refs. 4, 7, 126, 128, 130). Under the same low-LET conditions, our computed value of $G(\text{Fe}^{3+})$ at $\sim$30 s is equal to $\sim$15.45 (see Fig. 4), in very good agreement with the standard value.
IV.1.2 Kinetics of Fe$^{3+}$ formation in the radiolysis of the Fricke dosimeter with 0.8-MeV neutrons at different temperatures from 25 to 300 °C

Figure 5 shows the kinetics of Fe$^{3+}$ formation as obtained from our simulations of the radiolysis of the Fricke dosimeter by 0.8-MeV incident neutrons$^{39}$ at different temperatures in the range 25-300 °C. The corresponding time evolution of $G(\text{Fe}^{3+})$ simulated for 300-MeV irradiating protons at the same temperatures is presented in Fig. 6 for the sake of comparison. The $G$-values for Fe$^{3+}$ formed from a 0.8-MeV neutron in the FeSO$_4$ medium are calculated here on the basis of the first four collisions that generate recoil protons of 0.505, 0.186, 0.069, and 0.025 MeV (see Sect. III.1.2).$^{40}$ The yields are estimated as the sum of the $G$-values for these four recoil protons (obtained from our Monte-Carlo simulations) after appropriate weighting is made according to the energy deposited by each of these protons (see Sect. I.1.5) (139, 140, 222):

$$G(\text{Fe}^{3+}) = \sum_{i=1}^{4} \frac{G_i(\text{Fe}^{3+})E_i}{E_T}, \quad (45)$$

where

$$E_T = \sum_{i=1}^{4} E_i \quad \quad (46)$$

is the sum of all recoil proton energies.

All reactions take place faster at higher temperature. As can be seen from Fig. 5, the kinetics of Fe$^{3+}$ formation at 300 °C is several orders of magnitude faster than at room temperature. Also, an interesting feature shown in this figure is the

---

$^{39}$ Recall that this 0.8-MeV energy corresponds to the average energy of fast neutrons from the "YAYOI" reactor of the University of Tokyo (38, 39, 121).

$^{40}$ Further recoil protons are generated from the neutron, but their average energies are low and only have a relatively little effect on the radiolysis. In the calculations, the radiation effects due to oxygen recoils are also neglected here.
increase of $G(\text{Fe}^{3+})$ with temperature. In fact, the yield of $\text{Fe}^{3+}$ (in molec./100 eV) increases from $\sim 8.9$ at 25 °C to 11.6 at 300 °C (Fig. 5), which corresponds to a temperature coefficient of $\sim 0.97\%$ per degree.\textsuperscript{41} According to Eq. (22), which relates $G(\text{Fe}^{3+})$ to the primary radical and molecular yields of the radiolysis of the solution:

$$G(\text{Fe}^{3+}) = 3 \left( G_{\text{aq}^-} \cdot H^+ + G_{\text{HO}_2} \right) + G_{\text{OH}} + 2 \ G_{\text{H}_2\text{O}_2} ,$$

\hspace{1cm} (22)

this increase is a reflection of the fact that $G_{\text{aq}^-}, G_{H^+},$ and $G_{\text{OH}}$ continuously increase with increasing temperature (see Sect. I.1.5).\textsuperscript{42}

\hspace{1cm} IV.2 The effect of LET on the chemistry and the yields of the Fricke dosimeter

It has been known since very early studies with internal and external $^{210}\text{Po}$ $\alpha$-particle sources that the yield for oxidation of ferrous ions in the Fricke dosimeter is appreciably less for high-LET radiations, such as accelerated ions and neutrons, than for low-LET radiations, that is $^{60}\text{Co}$ $\gamma$-rays, high-energy X-rays, fast electrons or energetic protons (e.g., see refs. 36, 40, 223, 224). In recent studies, our laboratory has carried out Monte-Carlo simulations of the radiolysis of the Fricke dosimeter in the low-LET regime from $\sim 0.3$ to 15 keV/μm (using protons of various initial energies in the range $\sim 300$-2.1 MeV) at ambient temperature (36, 194). The general trend of the experimental variation of $G(\text{Fe}^{3+})$ with radiation quality was well reproduced by our computed $\text{Fe}^{3+}$ ion yield values.

\textsuperscript{41} This value is to be compared with the temperature coefficient of $\sim 1.09\%$ per degree obtained from Fig. 6 for the 300-MeV proton radiolysis of the Fricke dosimeter over the range of temperature from 25 to 300 °C (see Sect. IV.3.1).

\textsuperscript{42} Recall here that the production of $\text{Fe}^{3+}$ ions is highly sensitive to the primary free-radical yields, especially the yield of $H^+$ atoms (see Sect. I.2). The contribution of hydrogen peroxide to the oxidation of $\text{Fe}^{2+}$ ions to $\text{Fe}^{3+}$ only slightly decreases on going from 25 to 300 °C (see Sect. I.1.5).
In the present study, our aim is to model the action of fast neutron radiation on the chemistry and the yields in the Fricke dosimeter. As emphasized in Sects. I and II, *neutrons can be regarded as high-LET particles* because they are stopped by nuclei (both protons and oxygen nuclei), which become recoil ions, losing their energy in dense tracks. However, in the neutron energy range of interest here (below 10 MeV), the greatest energy deposition in the solution comes from recoil protons. In fact, summing over all events, Edwards et al. (82) estimated that 88% of the neutron energy is absorbed by protons and 12% by oxygen nuclei. Given the minor fraction of energy in oxygen recoil, and the small anticipated yield, we begin below with the proton radiolysis problem, extending the previously reported simulations of Autsavapromporn et al. (36) to higher LET values up to ~70 keV/μm corresponding to the Bragg peak region (~0.15 MeV) (see Fig. 3). As a logical subsequent step, we then calculate the fast neutron radiolysis yields in the Fricke dosimeter as a function of neutron energy, using our simulated proton radiolysis yields and taking into account the contribution of recoil oxygen ions.

IV.2.1 Variation of $G(\text{Fe}^{3+})$ with LET using irradiating protons of various initial energies at 25 °C

Figure 7 shows the values of $G(\text{Fe}^{3+})$ calculated from our Monte-Carlo simulations of the radiolysis of aerated solutions of 5 mM FeSO$_4$ in 0.4 M H$_2$SO$_4$ as a function of LET for incident protons of initial energies in the range ~300-0.15 MeV (~0.3-70 keV/μm) at 25 °C. It is seen that as the LET increases the yield diminishes (see also Table 4). Our computed values are compared with experimental data of ferric ion yields versus LET obtained by a number of different workers (4, 41, 42, 50, 87, 127-131, 133, 223-235) using a variety of methods for radiations of different energies. Despite the relatively large uncertainties of the reported measurements, there is a good agreement between theory and experiment, especially for LET below ~10-15 keV/μm.

As already mentioned above, this dependence of $G(\text{Fe}^{3+})$ on LET is explained by the fact that the production of ferric ions in the Fricke system is *most sensitive* to
free-radical yields, especially $H^+$ atoms (see Sect. 1.2). Indeed, according to Eq. (22), the lower the yield of radicals which escape the radiation track, the lower the Fricke $G$-values. Since the $G$-values for radicals do show a marked decrease with increasing LET (see Sect. 1.1.4 and Table 2), it follows that $G(\text{Fe}^{3+})$ also decreases as the LET increases. This behavior directly results from the increased importance of intratrack processes at higher LET which enhance radical-radical recombination reactions producing molecular products.$^{43}$

IV.2.2 Variation of $G(\text{Fe}^{3+})$ with neutron energy for irradiating fast (~0.5-10 MeV) neutrons at 25 °C

As noted earlier, in the fast neutron energy range below ~10 MeV, approximately 88% of the neutron energy is absorbed by recoil protons and the remaining 12% by oxygen nuclei (82). Those particles released by neutron interactions in the medium create the primary free radical and molecular product yields, which subsequently lead to the oxidation of ferrous ions in the Fricke solution according to the radiolysis mechanism previously described in Sects. 1.2 and III.4. The integrated yields of ferric ions produced by both recoil protons and oxygen ions can be derived using the general relationship:

$^{43}$ Note that, at high particle LET, the production of $\text{Fe}^{3+}$ is not uniquely determined by LET but rather increases with increasing particle charge because of differences in the local energy density. In fact, at the same LET, the impinging particle with higher charge has a smaller local energy density because of its higher velocity [see Eq. (16)] so that more radicals escape the particle track to oxidize ferrous ions (e.g., see refs. 24, 223, 224). However, in the range of relatively low LET considered in this study, $G(\text{Fe}^{3+})$ remains a nearly singular function of LET, which can therefore be considered as a useful specifier to compare $G(\text{Fe}^{3+})$ for different radiation beam qualities.
\[
G(\text{Fe}^{3+}) = \left[ \frac{\sum \left( 2 \sigma_H(E_{ni}) G_{pi}(\text{Fe}^{3+}) E_{pi} + \sigma_O(E_{ni}) G_{Oi}(\text{Fe}^{3+}) E_{Oi} \right)}{\sum \left( 2 \sigma_H(E_{ni}) E_{pi} + \sigma_O(E_{ni}) E_{Oi} \right)} \right],
\]

(47)

where the index \(i\) corresponds to the number of fast neutron interactions that take place in the solution, \(G_{pi}\) and \(G_{Oi}\) are the yields of \(\text{Fe}^{3+}\) for the recoil proton (p) and oxygen ion (O) released by the \(i\)th interaction of the neutron, \(E_{pi}\) and \(E_{Oi}\) are the energies of those two charged particle recoils, respectively, and \(\sigma_H(E_{ni})\) and \(\sigma_O(E_{ni})\) are, respectively, the elastic scattering cross sections for a fast neutron incident on hydrogen and oxygen with kinetic energy \(E_{ni}\) just before the \(i\)th collision (see Fig. 1). This expression also takes explicitly into account the fact that a water molecule contains two hydrogen atoms and one oxygen atom.

In the range of neutron energies investigated here, Eq. (47) can be well approximated by the simplified expression:

\[
G(\text{Fe}^{3+}) = \left[ \frac{\sum \left( 2 G_{pi}(\text{Fe}^{3+}) E_{pi} + G_{Oi}(\text{Fe}^{3+}) E_{Oi} \right)}{\sum \left( 2 E_{pi} + E_{Oi} \right)} \right],
\]

(48)

where it is assumed that the neutron scattering cross sections \(\sigma_H\) and \(\sigma_O\) are all equal whatever the value of \(E_n\). Indeed, as is illustrated in Fig. 8, the two curves of \(G(\text{Fe}^{3+})\) versus the incident neutron energy, calculated from Eqs. (47) and (48) (solid and dash-dot lines, respectively), are more or less superposed. The relative superposition of these curves results from the fact that only the first few terms of the summation over \(i\) in Eq. (47) play a dominant role in the determination of \(G(\text{Fe}^{3+})\) and that for those terms the intervening cross sections \(\sigma_H(E_{ni})\) and \(\sigma_O(E_{ni})\) are more or less the same in the range of energy considered and vary

\[44\] In fact, only the first 4 neutron collisions are considered in the present calculations \((i = 1 \text{ to } 4)\), as further recoil protons and/or oxygen ions generated by the neutron as it is further moderated do not contribute significantly to the radiolysis owing to their low average energies.
slowly with the neutron energy (see Fig. 1). It should be noted here that Eq. (48) reduces to Eqs. (45) and (46) (assuming \( i = 1 \) to 4) if the contribution due to recoil oxygen ions is ignored.

Figure 8 also shows our results of \( G(\text{Fe}^{3+}) \) calculated from Eq. (48) for recoil protons only (i.e., ignoring the contribution of oxygen ion recoils) (dot line) and for recoil oxygen ions only (i.e., assuming all the neutron energy is absorbed by oxygen nuclei) (dash-dot-dot line), for incident fast neutrons with energies between \( \sim 0.5 \) and 10 MeV. In the calculations, the intervening ferric ion yields \( G_p(\text{Fe}^{3+}) \) produced by recoil protons are directly obtained from our Monte-Carlo simulations (see Fig. 7). However, for the values of \( G_O(\text{Fe}^{3+}) \) produced by oxygen ions, only estimates can be derived. This results from the fact that our IONLYS simulation code cannot be employed because the energies with which those ions are ejected are, over all the fast neutron energy range considered, too low\(^{45}\) for the \( Z^2 \) scaling law (used in the code to provide interaction cross sections for bare ion impact from proton impact cross sections) to be applicable. In the absence of simulated (and experimental) data, the \( G(\text{Fe}^{3+}) \) values produced by recoil oxygen ions (\( O_q^{eff+} \), with an average effective charge \( q_{eff} \leq 8 \), depending on the velocity)\(^{46}\) are roughly approximated here by the Fricke yield measurements of LaVerne and Schuler (223, 4).

\(^{45}\) For example, in this range, \( E_{O_f} \) varies between \( \sim 0.0035 \) and 0.071 MeV/nucleon, while the applicability of the \( Z^2 \) scaling rule requires impact energies above, say, 1 MeV/nucleon (see Sect. III.1.1).

\(^{46}\) Such slow ions are usually incompletely stripped and can undergo successive electron capture and loss events contributing to a changing equilibrium charge state that depends on the velocity (e.g., see refs. 3, 190). On the average, the net positive (or "effective") charge on an incident ion decreases when the speed decreases. This charge exchange also complicates the derivation of relevant cross sections for heavy charged, partially "dressed" particles in the low-velocity regime.
236) for $^{12}$C$^{6+}$ ions for the corresponding range of oxygen ion energies. Given the minor fraction of energy in oxygen recoil and the small contribution of the oxygen nuclei to the final $G$(Fe$^{3+}$) values (on the order of 10% at 10 MeV; see Fig. 8), the uncertainty introduced by this approximation is considered to represent a relatively small error only.

As can be seen from Fig. 8, the agreement between our calculated neutron $G$(Fe$^{3+}$) values and those obtained by experiment (38, 134-137, 139) is reasonably satisfactory taking into account the relatively large uncertainties in the experimental measurements and the various approximations included in the model. Over the whole ~0.5-10 MeV range of neutron energies studied here, the computed yields of ferric ions (slightly) increase with neutron energy. Such an energy dependence of $G$(Fe$^{3+}$) is a reflection of the fact that the greater the energy of the neutrons, the less the LET, and the larger the values of $G$(Fe$^{3+}$) (see, for example, Table 4). In this respect, even if neutrons cannot produce ionization or excitation directly, the radiation chemistry of fast neutron irradiations, determined by the charged particle radiations they produce, parallels that of other ionizing radiations.

An additional remark should be made from Fig. 8 regarding the predicted $G$(Fe$^{3+}$) values obtained from our Monte-Carlo simulations assuming that neutrons are stopped by protons only. These values (shown as the dot line in Fig. 8) are found to be ~20% larger than the corresponding experimental data obtained in fast neutron radiolysis. This result agrees very well with the measurements of Katsumura et al. (39)$^{47}$ who reported, in the vicinity of room temperature, $G$(Fe$^{3+}$) values comprised in the range ~7-10 molec./100 eV for an irradiation with 3.3 MeV protons,$^{48}$ while they found a ferric ion yield of 6.95 molec./100 eV for an irradiation

$^{47}$ This result also agrees with the compilation of $G$(Fe$^{3+}$)-versus-particle energy data for protons and deuterons of Lawson and Porter (139).

$^{48}$ These authors carried out proton beam radiolysis as a model experiment of the fast neutron radiolysis.
with 0.8 MeV incident neutrons (see Table 4). From the present simulations, it can clearly be inferred that this difference originates from the high-LET oxygen recoil ions whose radiolysis chemistry induces a decrease in the Fricke yield arising from the hydrogen recoil ions only. From a strict quantitative standpoint, we can conclude that, even if the anticipated yield is relatively small, the contribution of recoil oxygen ions should be accounted for when we calculate the fast neutron radiolysis yields in the Fricke dosimeter. In this respect, there is a need for a better characterization of the chemistry induced by oxygen ions in the energy range below ~1-2 MeV\(^{49}\) and of the \(G(\text{Fe}^{3+})\) values produced by these recoil ions.

**IV.3 The influence of temperature on the yields of the Fricke dosimeter**

**IV.3.1 Variation of \(G(\text{Fe}^{3+})\) for \(\gamma\)-irradiation in the Fricke dosimeter as a function of temperature**

Early measurements of the temperature dependence of \(G(\text{Fe}^{3+})\) for the Fricke dosimeter were reported prior to 1970 (e.g., see refs. 216, 230, 237-241). The values then found for the temperature coefficient of the ferric-ion yield indicated that this coefficient was positive but small. However, the reported values were rather scattered (from zero to ~0.5% per degree between 4 and 20 °C, depending on the authors), due mainly to relatively large uncertainties in the measurements. The availability in the 1980s of precision spectrophotometers allowed new, more accurate determinations of the influence of the irradiation temperature on the Fricke yield. For example, Shortt (242) reported a value for the change in \(G(\text{Fe}^{3+})\) of \((0.121 \pm 0.005)\)% per °C for a standard \(^{60}\text{Co}\ \gamma\)-ray source and an irradiation temperature range of 15-35 °C, in agreement with values now commonly used in most laboratories. Experiments on the effect of temperature on \(G(\text{Fe}^{3+})\) were also extended to cover a larger range of temperatures up to 250 °C (e.g., see refs. 243-

\(^{49}\) For the first three collisions, a 10-MeV fast neutron generates recoil oxygen ions having energies of 1.13, 1.00, and 0.89 MeV.
As can be seen from Fig. 9, \( G(\text{Fe}^{3+}) \) rises slightly with increasing temperature. This increase in the \( \text{Fe}^{3+} \) yields with temperature was already noted in Sect. IV.1.2 (see Fig. 6).

The \( \gamma \)-ray radiolysis of the (aerated) Fricke dosimeter at elevated temperatures was modeled using our Monte-Carlo IONLYS-IRT code for 300-MeV incident protons (LET \( \sim 0.3 \) keV/\( \mu \)m), following the simulation methodology described in Sects. III.3 and III.4. As shown in Fig. 9, the predicted \( G \)-values (in molec./100 eV) for \( \text{Fe}^{2+} \) oxidation increase from \( \sim 15.4 \) to 18.4 over the temperature range from 25 to 300 °C (i.e., an \( \sim 19\% \) increase), which corresponds to a temperature coefficient of \( \sim 1.05\% \) per degree.

A good agreement is obtained between our computed \( \text{Fe}^{3+} \) yields and the available experimental data. Our \( G \)-values also compare well with those predicted theoretically by Bęgusová and Pimblott (142) using stochastic simulation methods. As discussed in Sect. IV.1.2, this increase in \( G(\text{Fe}^{3+}) \) is readily explained by an increase in the yields of free radicals on going from 25 to 300 °C (97).

IV.3.2 Variation of \( G(\text{Fe}^{3+}) \) for the 0.8-MeV neutron radiolysis in the Fricke dosimeter as a function of temperature

Our calculated yields of \( \text{Fe}^{2+} \) oxidation in the (aerated) Fricke dosimeter irradiated by 0.8-MeV incident neutrons over the range of temperature from 25 to 300 °C are shown in Fig. 10, along with the experimental data of Katsumura et al. (38, 39). In fact, as far as we know, Katsumura et al.’s data (acquired with the University of Tokyo neutron source reactor “YAYOI” whose average energy of the neutrons is \( \sim 0.8 \) MeV; see Sects. I.1.5 and IV.1.2) are, up until now, the only data available in the literature with which to compare our results on the temperature dependence of the \( \text{Fe}^{3+} \) yields for the Fricke dosimeter irradiated by fast neutrons.

50 This value compares well with that (0.6% per degree) predicted by Bęgusová and Pimblott (142) from their stochastic IRT simulations of the \( \gamma \)-radiolysis of the aerated Fricke solution over this same temperature range.
As can be seen from Fig. 10 (see also Fig. 5), \( G(\text{Fe}^{3+}) \) increases with increasing temperature, which is attributed to the fact that the free-radical escape yields (especially the yield of H* atoms) increase as the temperature increases (see Sect. I.1.5). An increase in the Fe\(^{3+}\) yield (in molec./100 eV) of ~29% from ~8.9 at 25 °C to 11.5 at 300 °C is predicted. Experimentally, the yield of Fe\(^{3+}\) increases from ~7.0 at 25 °C to ~10.5 at 250 °C, which corresponds to the temperature coefficient of ~1.5% per degree over this range of temperature. Our \( G(\text{Fe}^{3+}) \) values, calculated from Eq. (48) assuming only recoil protons (i.e., with no corrections being made for oxygen-recoil-ion contributions), agree well with experiment above 75 °C. At temperatures lower than 75 °C, however, they are higher than the experimental data, by about 1.9 G-unit at room temperature. The reasons for such a difference between Katsumura et al.'s experimental results and our model predictions below 75 °C are not clear. Of course, the incorporation in our calculations of the contributions originating from the high-LET oxygen recoil ions would clearly induce a (slight) decrease in the Fricke yields (see Sect. IV.2.2). This effect due to oxygen ions should also be present, more or less equally, over the whole temperature range studied. As a result, the agreement observed at temperatures above 75 °C between experiment and calculations should be expected to be even better, not to say excellent. Another possible reason to explain the discrepancy below 75 °C could simply be of experimental origin, as the neutron \( G \)-values reported by Katsumura et al. (38, 39) were obtained in a nuclear reactor, that is, under a mixed high-LET neutron and low-LET gamma-ray irradiation field. Assessing the chemistry yields induced by the neutrons alone under such mixed LET irradiation conditions is difficult (e.g., see refs. 37, 82, 87), even if the authors estimate that more than 95% of the total dose in the sample solutions comes from fast neutrons. In the absence of other information about possible overlap and chemical interaction between fast-neutron and \( \gamma \)-ray tracks, this leads us to believe that the true situation is uncertain. More experimental data would be greatly needed in order to compare in a more critical fashion our Monte-
Carlo modeling calculations of the effect of temperature on the Fe$^{3+}$ ion yields in the radiolysis of the Fricke solution by fast neutrons (especially for different incident neutron energies).

V. Conclusion

In this study, Monte-Carlo simulations have been successfully used to investigate the radiolysis of the ferrous sulfate (Fricke) dosimeter by fast (0.5-10 MeV) neutrons at 25 °C and also as a function of temperature over the range 25-300 °C. The radiation effects due to fast neutrons are estimated on the basis of track segment yields calculated for the first four recoil protons with appropriate weighting according to the energy deposited by each of these protons. In so doing, we consider that further recoils make only a negligible contribution to the radiolysis.

Our results show that the radiolysis of dilute aqueous solutions by fast neutrons generates smaller radical yields and larger molecular product yields (with respect to corresponding values for $^{60}$Co $\gamma$-rays or fast electrons), due to the high LET associated with fast neutrons. The effect of recoil oxygen ions, which are taken into account in our calculations, is shown to decrease $G$(Fe$^{3+}$) by about 10%. A reasonably good agreement has been obtained between the available experimental data and our calculated values of $G$(Fe$^{3+}$), which are found to increase slightly with neutron energy over the energy range covered in this study. This agreement between experiment and modeling validates a posteriori the assumptions employed in the calculations.

We have also simulated the effects of temperature on the oxidation of Fe$^{2+}$ in the fast neutron radiolysis of the Fricke dosimeter from 25 to 300 °C. The results obtained from our simulation studies show that the kinetics of Fe$^{3+}$ formation accelerates when the temperature increases. Our results also show an increase of $G$(Fe$^{3+}$) with increasing temperature, which is readily explained by an increase in the yields of free radicals (especially the yield of H$^+$ atoms). For 0.8-MeV incident neutrons (the only case for which experimental data are available in the literature),
there is a ~29% increase in $G(\text{Fe}^{3+})$ on going from 25 to 300 °C. Although such changes compare relatively well with experiment, additional experimental data, especially for different incident neutron energies, would be needed to more critically compare our results with respect to the yields of $\text{Fe}^{3+}$ ions at elevated temperatures.

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References

45. J.L. Magee and A. Chatterjee. *In Kinetics of nonhomogeneous processes.*
55. M.H. Mariano and M.L. Santos. *RADIAT. Res. 32, 905 (1967).*


Table 1: Main spur/track reactions and rate constants ($k$) for the radiolysis of pure liquid water at 25 °C (from ref. 24).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ ($M^{-1}$ s$^{-1}$)</th>
<th>Reaction</th>
<th>$k$ ($M^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + H^+ \rightarrow H_2$</td>
<td>$5.03 \times 10^9$</td>
<td>$\bar{e}<em>{aq} + \bar{e}</em>{aq} \rightarrow H_2 + 2 \text{OH}^-$</td>
<td>$5.0 \times 10^9$</td>
</tr>
<tr>
<td>$H^+ + \cdot \text{OH} \rightarrow H_2O$</td>
<td>$1.55 \times 10^{10}$</td>
<td>$\bar{e}_{aq} + H^+ \rightarrow H^+$</td>
<td>$2.11 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + H_2O_2 \rightarrow H_2O + \cdot \text{OH}$</td>
<td>$3.5 \times 10^7$</td>
<td>$\bar{e}_{aq} + O_2^- \rightarrow H_2O_2 + 2 \text{OH}^-$</td>
<td>$1.3 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + \bar{e}_{aq} \rightarrow H_2 + \text{OH}^-$</td>
<td>$2.5 \times 10^9$</td>
<td>$\bar{e}_{aq} + \text{HO}_2^- \rightarrow \text{O}^- + \text{OH}^-$</td>
<td>$3.51 \times 10^9$</td>
</tr>
<tr>
<td>$H^+ + \text{OH}^- \rightarrow H_2O + \bar{e}_{aq}$</td>
<td>$2.51 \times 10^7$</td>
<td>$\bar{e}_{aq} + \text{O}^- \rightarrow 2 \text{OH}^-$</td>
<td>$2.31 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + O_2 \rightarrow \text{HO}_2^-$</td>
<td>$2.1 \times 10^{10}$</td>
<td>$\bar{e}_{aq} + \text{H}_2O \rightarrow H^- + \text{OH}^-$</td>
<td>15.8</td>
</tr>
<tr>
<td>$H^+ + \text{HO}_2^- \rightarrow H_2O_2$</td>
<td>$1.0 \times 10^9$</td>
<td>$\bar{e}_{aq} + O_2^- \rightarrow O_2^-$</td>
<td>$1.74 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + \text{O}_2^- \rightarrow \text{HO}_2^-$</td>
<td>$1.0 \times 10^7$</td>
<td>$\bar{e}_{aq} + \text{HO}_2^- \rightarrow \text{HO}_2^-$</td>
<td>$1.28 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + \text{HO}_2^- \rightarrow \text{OH} + \text{OH}^-$</td>
<td>$1.46 \times 10^8$</td>
<td>$\bar{e}_{aq} + O(P) \rightarrow O^-$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + O(P) \rightarrow \text{OH}^-$</td>
<td>$2.02 \times 10^{10}$</td>
<td>$\bar{e}_{aq} + O_2 \rightarrow O_2^-$</td>
<td>$3.6 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + \text{O}^- \rightarrow \text{OH}^-$</td>
<td>$2.0 \times 10^{10}$</td>
<td>$\bar{H}^+ + O^- \rightarrow \text{OH}^-$</td>
<td>$4.78 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + O_2 \rightarrow O_2 + \cdot \text{OH}$</td>
<td>$3.7 \times 10^9$</td>
<td>$\bar{H}^+ + O_2^- \rightarrow \text{OH}^-$</td>
<td>$4.78 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + \text{O}_2^- \rightarrow \text{OH} + O_2$</td>
<td>$1.0 \times 10^9$</td>
<td>$\bar{H}^+ + \text{OH}^- \rightarrow \text{H}_2O$</td>
<td>$11.3 \times 10^{10}$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2O_2$</td>
<td>$5.5 \times 10^9$</td>
<td>$\bar{H}^+ + \text{O}_2^- \rightarrow \cdot \text{OH} + O_2$</td>
<td>$9.0 \times 10^{10}$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \text{H}_2O_2 \rightarrow \text{HO}_2^- + \text{H}_2O$</td>
<td>$2.87 \times 10^7$</td>
<td>$\bar{H}^+ + \text{HO}_2^- \rightarrow \text{H}_2O_2$</td>
<td>$5.0 \times 10^9$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \text{H}_2 \rightarrow \bar{H}^+ + \text{H}_2O$</td>
<td>$3.28 \times 10^7$</td>
<td>$\text{OH}^- + O(P) \rightarrow \text{HO}_2^-$</td>
<td>$4.2 \times 10^8$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \bar{e}_{aq} \rightarrow \text{OH}^-$</td>
<td>$2.95 \times 10^9$</td>
<td>$\text{OH}^- + \text{HO}_2^- \rightarrow O_2^- + \text{H}_2O$</td>
<td>$6.3 \times 10^8$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \text{OH} \rightarrow \text{O}^- + \text{H}_2O$</td>
<td>$6.3 \times 10^9$</td>
<td>$O_2 + O^- \rightarrow O_2^-$</td>
<td>$3.7 \times 10^8$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \text{HO}_2^- \rightarrow O_2 + \text{H}_2O$</td>
<td>$7.9 \times 10^9$</td>
<td>$O_2 + O(P) \rightarrow O_3$</td>
<td>$4.0 \times 10^9$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + O_2^- \rightarrow O_2 + \text{OH}^-$</td>
<td>$1.07 \times 10^9$</td>
<td>$\text{HO}_2^- + O_2^- \rightarrow \text{HO}_2^+ + O_2$</td>
<td>$9.7 \times 10^7$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + \text{HO}_2^- \rightarrow \text{HO}_2^+ + \text{OH}^-$</td>
<td>$8.32 \times 10^9$</td>
<td>$\text{HO}_2^- + \text{HO}_2^- \rightarrow \text{O}_2 + \text{OH}^-$</td>
<td>$8.3 \times 10^8$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + O(P) \rightarrow \text{HO}_2^-$</td>
<td>$2.02 \times 10^9$</td>
<td>$\text{HO}_2^- + O(P) \rightarrow O_2^- + \text{OH}^-$</td>
<td>$2.02 \times 10^{10}$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + O^- \rightarrow \text{HO}_2^-$</td>
<td>$1.0 \times 10^9$</td>
<td>$\text{HO}_2^- + \text{H}_2O \rightarrow \text{HO}_2^- + \text{OH}^-$</td>
<td>$1.29 \times 10^4$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + O_2^- \rightarrow O_2^- + \text{HO}_2^-$</td>
<td>$8.5 \times 10^9$</td>
<td>$O_2^- + O^- \rightarrow O_2 + 2 \text{OH}^-$</td>
<td>$6.0 \times 10^8$</td>
</tr>
<tr>
<td>$\cdot \text{OH} + O_2 \rightarrow O_2 + \text{HO}_2^-$</td>
<td>$1.11 \times 10^9$</td>
<td>$O_2^- + \text{H}_2O \rightarrow \text{HO}_2^- + \text{OH}^-$</td>
<td>$0.075$</td>
</tr>
<tr>
<td>$\text{H}<em>2O_2 + \bar{e}</em>{aq} \rightarrow \text{OH}^- + \text{OH}^-$</td>
<td>$1.1 \times 10^9$</td>
<td>$O_2^- + O_2 \rightarrow O_2^- + O_2$</td>
<td>$1.5 \times 10^9$</td>
</tr>
<tr>
<td>$\text{H}_2O_2 + \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2O$</td>
<td>$4.75 \times 10^9$</td>
<td>$\text{HO}_2^- + \text{H}_2O \rightarrow \text{HO}_2^- + \text{OH}^-$</td>
<td>$3.83 \times 10^4$</td>
</tr>
<tr>
<td>$\text{H}_2O_2 + O(P) \rightarrow \text{HO}_2^+ + \text{OH}$</td>
<td>$1.6 \times 10^9$</td>
<td>$\text{HO}_2^- + O^- \rightarrow O_2^- + \text{OH}^-$</td>
<td>$3.5 \times 10^6$</td>
</tr>
<tr>
<td>$\text{H}_2O_2 + O^- \rightarrow \text{HO}_2^- + \text{OH}^-$</td>
<td>$5.55 \times 10^9$</td>
<td>$\text{HO}_2^- + O(P) \rightarrow O_2^- + ^\prime \text{OH}$</td>
<td>$5.3 \times 10^8$</td>
</tr>
<tr>
<td>$\text{H}_2 + O(P) \rightarrow \text{H}^+ + \text{OH}$</td>
<td>$4.77 \times 10^8$</td>
<td>$O^- + O^- \rightarrow \text{H}_2O_2 + 2 \text{OH}^-$</td>
<td>$1.0 \times 10^6$</td>
</tr>
<tr>
<td>$\text{H}_2 + O^- \rightarrow \text{H}^+ + \text{OH}^-$</td>
<td>$1.21 \times 10^8$</td>
<td>$O^- + O_2^- \rightarrow 2 \text{O}_2^-$</td>
<td>$7.0 \times 10^8$</td>
</tr>
<tr>
<td>$O(P) + O(P) \rightarrow O_2$</td>
<td>$2.2 \times 10^9$</td>
<td>$\text{O}^- + \text{H}_2O \rightarrow \cdot \text{OH} + \text{OH}^-$</td>
<td>$1.02 \times 10^9$</td>
</tr>
<tr>
<td>$O(P) + \text{H}_2O \rightarrow 2 \cdot \text{OH}$</td>
<td>$1.9 \times 10^3$</td>
<td>$O_2^- + \text{H}_2O \rightarrow \text{O}^- + O_2$</td>
<td>$48.0$</td>
</tr>
</tbody>
</table>
Table 2: Dependence of the primary yields (in molec./100 eV) of free radical and molecular products from irradiated 0.4 M H₂SO₄ aqueous solutions on LET, at room temperature.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>LET (^{(a)}) (keV/μm)</th>
<th>(G_{e^-_{aq} + H^+})</th>
<th>(G_{OH})</th>
<th>(G_{H_2})</th>
<th>(G_{H_2O_2})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{60})Co γ-rays</td>
<td>~0.2</td>
<td>3.7</td>
<td>2.9</td>
<td>0.4</td>
<td>0.8</td>
<td>Hochanadel and Lind (30); Ferradini and Pucheault (31)</td>
</tr>
<tr>
<td>8-kV X-rays (Cu)</td>
<td>3.1</td>
<td>2.55</td>
<td>1.9</td>
<td>0.7</td>
<td>1.05</td>
<td>Lefort (50)</td>
</tr>
<tr>
<td>(^3)H(^+) β-particles (mean energy: (~5.7) keV(^{(b)})</td>
<td>3.5</td>
<td>2.91</td>
<td>2</td>
<td>0.53</td>
<td>0.97</td>
<td>Collinson et al. (51)</td>
</tr>
<tr>
<td>18-MeV deuterons</td>
<td>5</td>
<td>2.39</td>
<td>1.75</td>
<td>0.71</td>
<td>1.03</td>
<td>Barr and Schuler (52)</td>
</tr>
<tr>
<td>8-MeV deuterons</td>
<td>9.5</td>
<td>1.71</td>
<td>1.45</td>
<td>1.05</td>
<td>1.17</td>
<td>Barr and Schuler (52)</td>
</tr>
<tr>
<td>32-MeV (^4)He(^{++}) ions</td>
<td>22</td>
<td>1.28</td>
<td>1.06</td>
<td>1.14</td>
<td>1.25</td>
<td>Barr and Schuler (52)</td>
</tr>
<tr>
<td>0.8-MeV neutrons</td>
<td>~60</td>
<td>1.25</td>
<td>0.68</td>
<td>0.99</td>
<td>1.27</td>
<td>Katsumura et al. (38, 39)</td>
</tr>
<tr>
<td>(^5.3)MeV α-particles ((^{210})Po)</td>
<td>88</td>
<td>0.6</td>
<td>0.3</td>
<td>1.4</td>
<td>1.25</td>
<td>Vladimirova (53)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6</td>
<td>0.5</td>
<td>1.57</td>
<td>1.45</td>
<td>Lefort and Tarrago (54)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49</td>
<td>0.5</td>
<td>1.57</td>
<td>1.25</td>
<td>Mariano and Santos (55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.77</td>
<td>0.67</td>
<td>1.51</td>
<td>1.56</td>
<td>Burch (56)</td>
</tr>
<tr>
<td>(^{10})B((n, \alpha))(^7)Li recoils</td>
<td>~250</td>
<td>0.23</td>
<td>0.41</td>
<td>1.66</td>
<td>1.57</td>
<td>Barr and Schuler (52)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.69</td>
<td>0.37</td>
<td>1.08</td>
<td>1.24</td>
<td>Pucheault and Sigli (57)</td>
</tr>
<tr>
<td>20-MeV (^{12})C(^{6+}) ions</td>
<td>535</td>
<td>0.29</td>
<td>0.19</td>
<td>1.48</td>
<td>1.18</td>
<td>LaVerne (58)</td>
</tr>
<tr>
<td>Fission fragments from dissolved (^{252})Cf</td>
<td>~4000</td>
<td>0</td>
<td>0</td>
<td>2.1</td>
<td>0.96</td>
<td>Bibler (59) (^{(c)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) "Incident" LET values, taken from Watt (60).

\(^{(b)}\) In 0.05 M H₂SO₄ solutions (pH ~ 1.3).

\(^{(c)}\) The author also includes a yield of HO₂\(^+\) radicals of 0.5 molec./100 eV.
Table 3: Dependence of the primary yields (in molec./100 eV) of radical and molecular products for neutral water irradiated with fast neutrons on temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$G_{e^-_{aq}}$</th>
<th>$G_{H^+}$</th>
<th>$G_{H_2}$</th>
<th>$G_{*OH}$</th>
<th>$G_{H_2O_2}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.52</td>
<td>0.34</td>
<td>0.97</td>
<td>0.72</td>
<td>0.92</td>
<td>Elliot et al. (87)</td>
</tr>
<tr>
<td></td>
<td>0.43</td>
<td>0.58</td>
<td>1.07</td>
<td>0.86-0.70</td>
<td>1.14-1.22</td>
<td>Katsumura et al. (91)</td>
</tr>
<tr>
<td>100</td>
<td>0.49</td>
<td>0.78</td>
<td>1.2</td>
<td>0.89-1.68</td>
<td>1.39-1.0</td>
<td>Ishigure et al. (90)</td>
</tr>
<tr>
<td>200</td>
<td>0.72</td>
<td>0.64</td>
<td>1.26</td>
<td>1.1</td>
<td>1.37</td>
<td>Ishigure et al. (90)</td>
</tr>
<tr>
<td>250</td>
<td>0.60</td>
<td>0.34</td>
<td>1.16</td>
<td>2.39</td>
<td>0.33</td>
<td>Elliot et al. (87)</td>
</tr>
<tr>
<td></td>
<td>0.68</td>
<td>0.52</td>
<td>1.52</td>
<td>1.66</td>
<td>1.29</td>
<td>Sunaryo et al. (89)</td>
</tr>
<tr>
<td>300</td>
<td>0.61</td>
<td>0.34</td>
<td>1.21</td>
<td>2.76</td>
<td>0.19</td>
<td>Elliot et al. (87)</td>
</tr>
</tbody>
</table>

(a) The authors also include a yield of HO$_2^*$ radicals of 0.05 molec./100 eV.
Table 4: Values of ferric-ion yields $G(\text{Fe}^{3+})$ (in molec./100 eV) for the Fricke dosimeter irradiated with different types of radiation, at room temperature.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>LET (^{(a)}) (keV/\mu m)</th>
<th>$G(\text{Fe}^{3+})$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}\text{Co}$ (\gamma)-rays</td>
<td>(-0.3)</td>
<td>15.6 ± 0.3</td>
<td>Hochanadel &amp; Ghormley (125)</td>
</tr>
<tr>
<td>2-MeV cathode rays (electrons)</td>
<td>(-0.3)</td>
<td>15.45 ± 0.11</td>
<td>Schuler &amp; Allen (126)</td>
</tr>
<tr>
<td>20-MV X-rays</td>
<td>(-0.3)</td>
<td>15.55 ± 0.1</td>
<td>Klassen et al. (127)</td>
</tr>
<tr>
<td>$^{137}\text{Cs}$ (\gamma)-rays</td>
<td>(-0.91) (^{(b)})</td>
<td>15.3 ± 0.3</td>
<td>ICRU Report 34 (128)</td>
</tr>
<tr>
<td>250-kV X-rays</td>
<td>1.9</td>
<td>14.9 ± 0.8</td>
<td>Back &amp; Miller (129)</td>
</tr>
<tr>
<td>60-kV(_p) X-rays (^{(c)})</td>
<td>2.6</td>
<td>14.1 ± 0.3</td>
<td>Fregene (130)</td>
</tr>
<tr>
<td>8-kV X-rays (Cu)</td>
<td>6.5</td>
<td>13.4 ± 0.6</td>
<td>Lefort (50)</td>
</tr>
<tr>
<td>$^3\text{H}^+$ (\beta)-particles (mean energy: (-5.7) keV)</td>
<td>9.5</td>
<td>12.7 ± 0.3</td>
<td>Hart (131)</td>
</tr>
<tr>
<td>23-MeV deuterons</td>
<td>11.9</td>
<td>12.15 ± 0.45</td>
<td>Elliot et al. (87)</td>
</tr>
<tr>
<td>2.466-keV monochromatic synchrotron X-rays</td>
<td>(-14)</td>
<td>9.36 ± 0.48</td>
<td>Watanabe et al. (132)</td>
</tr>
<tr>
<td>12-MeV deuterons</td>
<td>17.7</td>
<td>9.81</td>
<td>Hart et al. (133)</td>
</tr>
<tr>
<td>7.6-MeV neutrons</td>
<td>(-21)</td>
<td>9.4 ± 0.6</td>
<td>Greene et al. (134)</td>
</tr>
<tr>
<td>3-MeV neutrons</td>
<td>(-34.5)</td>
<td>7.2 ± 0.6</td>
<td>Pejuan &amp; Kühn (135)</td>
</tr>
<tr>
<td>2.3-MeV neutrons (^{252}\text{Cf})</td>
<td>(-39.5)</td>
<td>7.5 ± 1.1</td>
<td>Greene et al. (136)</td>
</tr>
<tr>
<td>1.5-MeV neutrons</td>
<td>(-47)</td>
<td>7.6 ± 0.9</td>
<td>Law et al. (137)</td>
</tr>
<tr>
<td>0.8-MeV neutrons (reactor YAYOI)</td>
<td>(-60)</td>
<td>6.95</td>
<td>Katsumura et al. (38, 39)</td>
</tr>
</tbody>
</table>

\(^{(a)}\) "Mean" LET values, taken from Watt (60) and Autsavapromporn et al. (36).

\(^{(b)}\) Meesungnoen et al. (35).

\(^{(c)}\) In 0.05 \(M\) \(\text{H}_2\text{SO}_4\) solutions (pH \(-1.3\)).
Table 5: Neutron mean free path (taken from Fig. 2) and maximum ranges for elastically scattered protons and oxygen ions in water (60).

<table>
<thead>
<tr>
<th>Neutron energy (MeV)</th>
<th>Neutron mean free path ($\lambda$) (cm)</th>
<th>Secondary-proton maximum range (nm)</th>
<th>Secondary-oxygen-ion maximum range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.04</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>2.01</td>
<td>8.9</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>2.43</td>
<td>24.6</td>
<td>0.9</td>
</tr>
<tr>
<td>3.0</td>
<td>5.58</td>
<td>149</td>
<td>1.9</td>
</tr>
<tr>
<td>5.0</td>
<td>7.77</td>
<td>362</td>
<td>2.7</td>
</tr>
<tr>
<td>10.0</td>
<td>11.8</td>
<td>1230</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Table 6: Values at 25 °C of the diffusion coefficients ($D$) of the various reactive species involved in our IRT simulations.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D \left( 10^{-9} \text{ m}^2 \text{ s}^{-1} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.299$^{(a)}$</td>
</tr>
<tr>
<td>$\text{e}_{\text{aq}}^-$</td>
<td>4.9</td>
</tr>
<tr>
<td>$\text{H}^+$</td>
<td>9.46</td>
</tr>
<tr>
<td>$\text{H}^-$</td>
<td>7.0</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>2.2</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>2.3</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>4.8</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>5.3</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>2.4</td>
</tr>
<tr>
<td>$\text{O}_2^{2-}$</td>
<td>1.75</td>
</tr>
<tr>
<td>$\text{HO}_2^-$</td>
<td>2.3</td>
</tr>
<tr>
<td>$\text{HO}_2^{2-}$</td>
<td>1.4</td>
</tr>
<tr>
<td>$\text{O}^\left(3P\right)$</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{O}^-$</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{O}_3^{2-}$</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^{(a)}$ Self-diffusion coefficient of water at 25 °C (204).
Table 7: Reactions added to the pure water reaction scheme to simulate the radiolysis of aqueous H₂SO₄ solutions, at 25 °C (from ref. 36). (a)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k (M^{-1} s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + SO_4^{2-} \rightarrow HSO_4^-$</td>
<td>$1.0 \times 10^{10}$</td>
</tr>
<tr>
<td>$H^+ + S_2O_8^{2-} \rightarrow SO_4^{2-} + HSO_4^-$</td>
<td>$2.5 \times 10^7$</td>
</tr>
<tr>
<td>$^\cdot$OH + HSO$_4$(^{-}) \rightarrow H_2O + SO$_4$(^{-})</td>
<td>$1.5 \times 10^5$</td>
</tr>
<tr>
<td>$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{2-}$</td>
<td>$1.2 \times 10^{10}$</td>
</tr>
<tr>
<td>$H_2O_2 + SO_4^{2-} \rightarrow HO_2^\cdot + HSO_4^-$</td>
<td>$1.2 \times 10^7$</td>
</tr>
<tr>
<td>$OH^- + SO_4^{2-} \rightarrow ^\cdot$OH + SO$_4^{2-}$</td>
<td>$8.3 \times 10^7$</td>
</tr>
<tr>
<td>$SO_4^{2-} + SO_4^{2-} \rightarrow S_2O_8^{2-}$</td>
<td>$4.4 \times 10^8$</td>
</tr>
</tbody>
</table>

(a) Note that the rate constants given here for the reactions between ions are at ionic strength equal to zero.
FIGURE CAPTIONS

**Figure 1:** Comparison of elastic scattering cross sections (in barn) for fast neutrons incident on hydrogen (solid line) and oxygen (dash-dot line) targets as a function of neutron energy (from ref. 60).

**Figure 2:** Neutron mean free path for water as a function of neutron energy (from ref. 177).

**Figure 3:** Variation of LET as a function of the impact energy of protons calculated using the IONLYS code for liquid water at 25 °C. The data reported by Watt (60) and in the compilation of ICRU Report 49 (69) for liquid water (density 1 g/cm³) are also shown for the sake of comparison.

**Figure 4:** Time evolution of $G(\text{Fe}^{3+})$ (in molec./100 eV) in the radiolysis of air-saturated solution of 5 mM FeSO₄ in aqueous 0.4 M H₂SO₄ as obtained from our simulations for 300-MeV incident protons (LET ~ 0.3 keV/μm) at 25 °C. The concentration of dissolved oxygen used in the calculations is ~2.5 x 10⁻⁴ M. The solid line corresponds to our simulated kinetics of Fe³⁺ ion formation. The arrow on the right of the figure shows the yield of the Fricke dosimeter recommended for ⁶⁰Co γ-rays and fast electrons (15.6 molec./100 eV).

**Figure 5:** Time evolution of $G(\text{Fe}^{3+})$ (in molec./100 eV) for 0.8-MeV irradiating neutrons in aerated solutions of 5 mM FeSO₄ in aqueous 0.4 M H₂SO₄ at different temperatures in the range 25-300 °C. Yields of Fe³⁺ were obtained from Eqs. (45) and (46) taking into account the first four recoil protons only (see text). The different lines correspond to our theoretical simulations at 25 (—), 50 (—–), 100 (—–), 200 (—–), and 300 (—–) °C.
Figure 6: Time evolution of $G(\text{Fe}^{3+})$ (in molec./100 eV) for 300-MeV incident protons in aerated solutions of 5 mM FeSO$_4$ in aqueous 0.4 M H$_2$SO$_4$ at different temperatures in the range 25-300 °C. The different lines correspond to our theoretical simulations at 25 (——), 50 (-----), 100 (--------), 200 (------), and 300 (-------) °C.

Figure 7: Plot of the ferric ion yield $G(\text{Fe}^{3+})$ (in molec./100 eV) for the aerated Fricke solution at 25 °C against LET in the range ~0.3-70 keV/μm. The solid curve represents the values of $G(\text{Fe}^{3+})$ calculated from our Monte-Carlo simulations using incident protons of various initial energies between ~300 and 0.15 MeV. The dashed line corresponds to the Fricke $G$-values calculated by Autsavaprompon et al. (36) for LET varying from ~0.3 to 15 keV/μm. Experimental data: ($\psi$), ref. 41; ($\Omega$), ref. 42; ($t$), ref. 50; ($\gamma$), ref. 87; ($\omega$), ref. 127; ($\xi$), ref. 128; ($\delta$), ref. 129; ($\alpha$), ref. 130; ($\mu$), ref. 133; ($\nu$), ref. 223; ($\chi$), ref. 225; ($\%$), ref. 226; ($\theta$), ref. 227; ($\Xi$), ref. 229; ($\Box$), ref. 230; ($\nu$), ref. 231; ($\chi$), ref. 232; and ($\sim$), ref. 235. Dose-average LET values used here for the various radiation types considered are taken from Watt (60). Note that, for X-rays, there are in certain cases insufficient experimental details for an estimate of the average energy of electrons resulting from photon absorption in the solution to be made. This results in some uncertainty in assigning an average LET value to the corresponding reported $G(\text{Fe}^{3+})$ results.

Figure 8: Yield of ferric ions $G(\text{Fe}^{3+})$ (in molec./100 eV) for fast neutrons in the aerated Fricke solution at 25 °C as a function of incident neutron energy in the range ~0.5-10 MeV. The solid line shows our $G(\text{Fe}^{3+})$ values for neutrons calculated from Eq. (47) taking into account 4 neutron collisions in the medium and using the elastic scattering cross sections $\sigma_H$ and $\sigma_O$ shown in Fig. 1. The dash-dot line represents our neutron $G(\text{Fe}^{3+})$ values calculated from Eq. (48) also considering 4
neutron collisions in the solution but assuming that $\sigma_H$ and $\sigma_O$ are all equal over all the neutron energy range considered. The dot line represents the $G(\text{Fe}^{3+})$ values obtained from our Monte-Carlo simulations taking into account recoil protons only. The dash-dot-dot line represents the $G(\text{Fe}^{3+})$ values assuming that the neutrons are stopped only by oxygen nuclei (see text). The dash line shows the neutron $G$-values for the Fricke dosimeter predicted by Lawson and Porter (139) using a semi-empirical method based on published charged particle $G$-values along with neutron-induced particle spectra calculated for monoenergetic neutron interactions with the dosimeter medium. Experiment (at 25 °C): (Q), ref. 38; (7), ref. 134; (β), ref. 135; (!), ref. 136; (µ), ref. 137; and (B), ref. 139.

**Figure 9:** Yield of Fe$^{3+}$ in aerated Fricke solution as a function of temperature, for 300-MeV irradiating protons (LET ~ 0.3 keV/μm). The solid line shows the values of $G(\text{Fe}^{3+})$ obtained from our Monte-Carlo simulations. The dot line shows the $G$-values for the Fricke dosimeter predicted by Běgusová and Pimblott (142) from stochastic IRT simulations employing simulated electron track structures. Experiment: (ψ), ref. 216; (,), ref. 243; (X), ref. 244; (7), ref. 245; and (−), ref. 246.

**Figure 10:** Yield of Fe$^{3+}$ in the aerated Fricke solution as a function of temperature for 0.8-MeV incident neutrons. The solid line shows our simulated results for $G(\text{Fe}^{3+})$, calculated from Eq. (48) taking into account four neutron collisions and assuming all the neutron energy is absorbed by protons only (i.e., ignoring the contribution due to recoil oxygen ions). The symbol (−) refers to the experimental data of Katsumura et al. (38, 39).
Figure 1
Figure 2
Figure 3
\[ \text{Figure 4} \]

- \(5 \text{ mM FeSO}_4\)
- \(0.4 \text{ M H}_2\text{SO}_4 (\text{pH } 0.46)\)
- \([\text{O}_2]\) = \(2.5 \times 10^{-4} \text{ M}\)
- LET \(\sim 0.3 \text{ keV/\mu m}\)
- \(25^\circ \text{C}\)

**Reaction Equations:**

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \cdot \text{OH} + \text{OH}^- + \text{Fe}^{3+} \]

- \(k = 52 \text{ M}^{-1}\text{s}^{-1}\)

\[ \text{H}^+ + \text{O}_2 \rightarrow \cdot \text{HO}_2^- \]

\[ \cdot \text{HO}_2^- + \text{Fe}^{2+} \rightarrow \text{H}_2\text{O}_2 + \text{Fe}^{3+} \]

- \(k = 7.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}\)

\[ \cdot \text{OH} + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+} \]

- \(k = 3.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}\)

**Graph:**
- \(G(\text{Fe}^{3+})\) in molecules/(100 eV)
- \(25^\circ \text{C}\)
- \(10^{-12} \rightarrow 10^2\) Time (s)
Figure 5
Figure 6

\[ \mathrm{H}_2\mathrm{O}_2 + \mathrm{Fe}^{2+} \rightarrow \cdot \mathrm{OH} + \mathrm{OH} + \mathrm{Fe}^{3+} \]

\[ \mathrm{H}^+ + \mathrm{O}_2 \rightarrow \cdot \mathrm{HO}_2^- \]

\[ \cdot \mathrm{HO}_2^- + \mathrm{Fe}^{2+} \rightarrow \cdot \mathrm{OH} + \mathrm{Fe}^{3+} \]

\[ \cdot \mathrm{OH} + \mathrm{Fe}^{2+} \rightarrow \mathrm{OH}^- + \mathrm{Fe}^{3+} \]
Figure 7
Figure 8

Incident neutron energy (MeV)

G(Fe\(^{3+}\)) (molec./100 eV)

H
H+O
O

Lawson and Porter, 1975

25 \(^{\circ}\)C
Figure 9
APPENDIX 2 – LIST OF PRESENTATIONS IN INTERNATIONAL/NATIONAL CONFERENCES

1. 4th Meeting of the Thai Academy of Science and Technology on “Coordinate Intelligence of the Future” for reducing global warming and energy crisis, 20-21 March 2009, Bangkok, Thailand.
   - Presentation of a poster:
     “The efficiency of ureal thiourea-based anion receptor with halide anions: B3LYP/6-31+G(d)”, M. Kuno, S. Sanguanmith, and N. Supaphimon.

   - Presentation of two conferences:
     (a) “Monte-Carlo simulations of the radiolysis of water at elevated temperatures up to 350 °C”, S. Sanguanmith, J. Meesungnoen, and J.-P. Jay-Gerin

   - Oral presentation:

4. 2nd Canada-China Joint Workshop on Supercritical Water-Cooled Reactors (CCSC-2010), Toronto, Ontario, Canada, April 25-28, 2010.
   - Oral presentation:

   - Oral presentation:
"Radiolysis of water at elevated temperature up to 350 °C and application to the Fricke dosimeter: Monte-Carlo simulations", S. Sanguanmith, J. Meesungnoen, and J.-P. Jay-Gerin.

   • Oral Presentation:

7. "Special Lecture on Radiation Chemistry and Radiobiology"
   Srinakharin Wirot University, Bangkok, Thailand, June 15, 2011.
   • Oral Presentation:

   • Oral Presentation:

9. Radiation Laboratory, Notre Dame University, Indiana, USA, November 11, 2011.
   • Seminar:
APPENDIX 3 – TEMPERATURE DEPENDENCE OF THE REACTION RATE CONSTANTS THAT HAVE BEEN UPDATED IN OUR IRT PROGRAM

Temperature dependence of reaction rate constants which intervene in the chemical stage of radiolysis of pure liquid water in 25-350 °C temperature range.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) H' + H' → H₂</td>
<td>5.20E+09</td>
<td>8.43E+09</td>
<td>1.83E+10</td>
<td>3.30E+10</td>
<td>5.25E+10</td>
<td>7.65E+10</td>
<td>1.04E+11</td>
<td>1.36E+11</td>
</tr>
<tr>
<td>2) H' + 'OH → H₂O</td>
<td>1.61E+10</td>
<td>2.14E+10</td>
<td>3.37E+10</td>
<td>4.77E+10</td>
<td>6.26E+10</td>
<td>7.80E+10</td>
<td>9.36E+10</td>
<td>1.09E+11</td>
</tr>
<tr>
<td>3) H' + H₂O₂ → 'OH + H₂O</td>
<td>3.60E+07</td>
<td>6.95E+07</td>
<td>1.99E+08</td>
<td>4.45E+08</td>
<td>8.39E+08</td>
<td>1.40E+09</td>
<td>2.14E+09</td>
<td>3.05E+09</td>
</tr>
<tr>
<td>4) H' + eₐq → H₂ + OH'</td>
<td>2.76E+10</td>
<td>4.28E+10</td>
<td>9.33E+10</td>
<td>1.69E+11</td>
<td>2.48E+11</td>
<td>2.99E+11</td>
<td>3.14E+11</td>
<td>3.17E+11</td>
</tr>
<tr>
<td>5) H' + OH' → e₋aq + H₂O</td>
<td>2.44E+07</td>
<td>8.46E+07</td>
<td>3.99E+08</td>
<td>1.44E+09</td>
<td>2.86E+09</td>
<td>4.91E+09</td>
<td>8.03E+09</td>
<td>1.32E+10</td>
</tr>
<tr>
<td>6) H' + O₂ → HO₂</td>
<td>1.31E+10</td>
<td>1.87E+10</td>
<td>3.03E+10</td>
<td>4.08E+10</td>
<td>4.93E+10</td>
<td>5.88E+10</td>
<td>6.07E+10</td>
<td>6.42E+10</td>
</tr>
<tr>
<td>7) H' + HO₂ → H₂O₂</td>
<td>1.12E+10</td>
<td>1.81E+10</td>
<td>3.85E+10</td>
<td>6.87E+10</td>
<td>1.09E+11</td>
<td>1.57E+11</td>
<td>2.13E+11</td>
<td>2.75E+11</td>
</tr>
<tr>
<td>8) H' + O₂ → HO₂</td>
<td>1.12E+10</td>
<td>1.81E+10</td>
<td>3.85E+10</td>
<td>6.87E+10</td>
<td>1.09E+11</td>
<td>1.57E+11</td>
<td>2.13E+11</td>
<td>2.75E+11</td>
</tr>
<tr>
<td>9) H' + H₂O₂ → 'OH + OH'</td>
<td>1.47E+09</td>
<td>3.26E+09</td>
<td>1.17E+10</td>
<td>3.06E+10</td>
<td>6.61E+10</td>
<td>1.26E+11</td>
<td>2.03E+11</td>
<td>2.77E+11</td>
</tr>
<tr>
<td>10) H' + O₂(P) → 'OH</td>
<td>2.02E+10</td>
<td>3.28E+10</td>
<td>7.14E+10</td>
<td>1.29E+11</td>
<td>2.07E+11</td>
<td>3.02E+11</td>
<td>4.13E+11</td>
<td>5.37E+11</td>
</tr>
<tr>
<td>11) H' + O₂ → OH'</td>
<td>2.00E+10</td>
<td>3.39E+10</td>
<td>6.84E+10</td>
<td>1.11E+11</td>
<td>1.62E+11</td>
<td>2.26E+11</td>
<td>3.04E+11</td>
<td>3.99E+11</td>
</tr>
<tr>
<td>12) H' + O₂ → O₂ + 'OH</td>
<td>3.67E+10</td>
<td>5.40E+10</td>
<td>9.24E+10</td>
<td>1.35E+11</td>
<td>1.79E+11</td>
<td>2.24E+11</td>
<td>2.67E+11</td>
<td>3.12E+11</td>
</tr>
<tr>
<td>13) H' + H₂O → e₋aq + H₂</td>
<td>4.58E-05</td>
<td>1.01E-03</td>
<td>1.43E-01</td>
<td>6.27E+00</td>
<td>1.24E+02</td>
<td>1.38E+03</td>
<td>1.00E+04</td>
<td>5.36E+04</td>
</tr>
<tr>
<td>14) H' + SO₄²⁻ → HSO₄⁻</td>
<td>9.96E+09</td>
<td>1.54E+10</td>
<td>3.12E+10</td>
<td>5.33E+10</td>
<td>8.10E+10</td>
<td>1.14E+11</td>
<td>1.50E+11</td>
<td>1.91E+11</td>
</tr>
<tr>
<td>15) H' + SO₂ → SO₃²⁻</td>
<td>1.40E+07</td>
<td>1.94E+07</td>
<td>3.32E+07</td>
<td>4.98E+07</td>
<td>6.83E+07</td>
<td>8.82E+07</td>
<td>1.09E+08</td>
<td>1.31E+08</td>
</tr>
<tr>
<td>16) H' → e₋aq + H₂</td>
<td>1.07E+01</td>
<td>9.20E-01</td>
<td>2.45E+01</td>
<td>2.13E+02</td>
<td>9.50E+02</td>
<td>2.63E+03</td>
<td>4.16E+03</td>
<td>2.78E+03</td>
</tr>
<tr>
<td>17) 'OH + 'OH → H₂O ∆</td>
<td>6.31E+09</td>
<td>7.56E+09</td>
<td>1.15E+10</td>
<td>1.35E+10</td>
<td>1.42E+10</td>
<td>1.39E+10</td>
<td>1.30E+10</td>
<td>1.18E+10</td>
</tr>
<tr>
<td>18) 'OH + H₂O₂ → HO₂⁻ + H₂O</td>
<td>2.94E+07</td>
<td>4.52E+07</td>
<td>8.99E+07</td>
<td>1.52E+08</td>
<td>2.30E+08</td>
<td>3.22E+08</td>
<td>4.24E+08</td>
<td>5.35E+08</td>
</tr>
<tr>
<td>19) 'OH + H₂ → H₂ + H₂O</td>
<td>3.95E+07</td>
<td>7.10E+07</td>
<td>1.27E+08</td>
<td>3.62E+08</td>
<td>6.11E+08</td>
<td>7.88E+08</td>
<td>7.83E+08</td>
<td>6.19E+08</td>
</tr>
<tr>
<td>20) 'OH + e₋aq → OH'</td>
<td>3.55E+10</td>
<td>4.88E+10</td>
<td>8.50E+10</td>
<td>1.36E+11</td>
<td>2.01E+11</td>
<td>2.80E+11</td>
<td>3.72E+11</td>
<td>4.77E+11</td>
</tr>
<tr>
<td>21) 'OH + OH' → O₂⁻ + H₂O</td>
<td>1.33E+10</td>
<td>2.17E+10</td>
<td>4.04E+10</td>
<td>6.06E+10</td>
<td>8.27E+10</td>
<td>1.07E+11</td>
<td>1.36E+11</td>
<td>1.68E+11</td>
</tr>
<tr>
<td>22) 'OH + HO₂ → O₂ + H₂O</td>
<td>9.00E+09</td>
<td>1.11E+10</td>
<td>1.54E+10</td>
<td>1.98E+10</td>
<td>2.41E+10</td>
<td>2.83E+10</td>
<td>3.23E+10</td>
<td>3.61E+10</td>
</tr>
<tr>
<td>23) 'OH + O₂⁻ → O₂ + OH'</td>
<td>1.08E+10</td>
<td>1.52E+10</td>
<td>2.61E+10</td>
<td>3.96E+10</td>
<td>5.49E+10</td>
<td>7.16E+10</td>
<td>8.91E+10</td>
<td>1.07E+11</td>
</tr>
<tr>
<td>24) 'OH + HO₂ → HO₂⁻ + OH'</td>
<td>8.32E+09</td>
<td>1.35E+10</td>
<td>2.95E+10</td>
<td>5.34E+10</td>
<td>8.53E+10</td>
<td>1.25E+11</td>
<td>1.70E+11</td>
<td>2.22E+11</td>
</tr>
<tr>
<td>25) 'OH + O₂(P) → HO₂</td>
<td>2.02E+10</td>
<td>3.28E+10</td>
<td>7.14E+10</td>
<td>1.29E+11</td>
<td>2.07E+11</td>
<td>3.02E+11</td>
<td>4.13E+11</td>
<td>5.37E+11</td>
</tr>
</tbody>
</table>
Temperature(°C)
Reactions
26) "OH + o" -> H02-

27) "OH + O," -> 02'" + H02'
28) "OH + O, -> H02' + 02
29) "OH + H20 O- + H+
30) "OH + HS04" -> SO/"
31) H202 + e",0 -> 'OH + OH"
32) H202 + OH' -> H02' +H20
33) H202 + 0(JP) -> "OH + H02"
34) H202 + O" -> H02* + OH'
35) H202 + H20
H+ + H02'
36) H2Oz + S04" S04"' + H02"
37) H2 + 0(JP) -> H' + "OH
38) H2 + 0" -» H' + OH'
39) eM + eM->H2 + 20H'
40) e"atl + H+ -> H*
41) e",0 + 02 -> 02"
42) e"aa + H02" -> HOz"
43) e"ao + 02" -> H202+ 20H'
44) e-aq + H02" O" + OH'
45) e"ao + 0(3P) -> 0"
46) e"aQ + 0- OH" + OH'
47) e"a„ + 03 -> 03"
48) e'ao + HzO -» H' + OH'
49) e'aa + S208'" SO/' + SO;'
50) H+ + OH' -> H20
51) H+ + 02" -> H02"
52) H+ + H02" H202
53) H+ + O" -» 'OH
54) H+ + 03" -> 'OH + 02
55) OH' + H02' -> 02" + H20
56) OH' + 0(3P) -> H02'
57) OH" + S04" -> S042" + 'OH
58) 02 + 0(JP) 03
59) 02 + O" -> 03"

25

50

100

150

200

250

300

350

1.00E+09
8.50E+09
1.11E+08
1.70E-03
1.50E+05
1.10E+10
1.33E+10
1.60E+09
5.55E+08
1.70E-03
1.19E+07
4.77E+03
1.28E+08
7.26E+09
2.13E+10
2.34E+10
1.30E+10
1.30E+10
3.51E+09
1.98E+10
2.31E+10
3.57E+10
1.58E+01
7.78E+10
1.18E+11
5.02E+10
5.02E+10
5.02E+10
9.00E+10
1.33E+10
4.20E+08
2.12E+08
4.00E+09
3.72E+09

1.27E+09
1.15E+10
1.81E+08
7.94E-03
2.48E+05
1.79E+10
2.17E+10
2.78E+09
9.03E+08
7.94E-03
1.92E+07
1.42E+04
1.91E+08
1.44E+10
2.89E+10
3.36E+10
1.95E+10
1.95E+10
5.67E+09
3.17E+10
2.96E+10
5.71E+10
4.71E+01
1.15E+11
1.83E+11
7.55E+10
7.55E+10
7:55E+10
1.36E+11
2.17E+10
4.22E+08
3.13E+08
4.62E+09
5.28E+09

1.87E+09
1.55E+10
3.93E+08
5.74E-02
5.54E+05
3.91E+10
4.04E+10
6.73E+09
1.97E+09
5.74E-02
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8.07E+04
3.63E+08
3.85E+10
5.40E+10
5.99E+10
3.73E+10
3.73E+10
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4.39E+10
1.13E+11
2.01E+02
2.16E+11
3.22E+11
1.27E+11
1.27E+11
1.27E+11
2.36E+11
4.04 E+10
4.24E+08
5.87E+08
5.19E+09
9.23E+09

2.51E+09
1.78E+10
7.13E+08
1.88E-01
1.02E+06
7.11E+10
6.06E+10
1.32E+10
3.56E+09
1.88E-01
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3.05E+05
5.93E+08
7.52E+10
8.91E+10
9.32E+10
6.11E+10
6.11E+10
2.20E+10
1.04E+11
5.93E+10
1.87E+11
4.38E+02
3.49E+11
4.54E+11
1.87E+11
1.87E+11
1.87E+11
3.50E+11
6.06E+10
4.25E+08
9.49E+08
5.45E+09
1.41E+10

3.16E+09
1.92E+10
1.14E+09
4.12E-01
1.66E+06
1.14E+11
8.27E+10
2.25E+10
5.69E+09
4.12E-01
8.42E+07
8.70E+05
8.74E+08
1.50E+10
1.54E+11
1.32E+11
9.03E+10
9.03E+10
3.49E+10
1.54E+11
7.52E+10
2.77E+11
7.30E+02
5.10E+11
6.05E+11
2.71E+11
2.71E+11
2.71E+11
4.87E+11
8.27E+10
4.25E+08
1.39E+09
5.59E+09
I.98E+10

3.81E+09
2.03E+10
1.67E+09
6.56E-01
2.46E+06
1.67E+11
1.07E+11
3.46E+10
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6.56E-01
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2.03E+06
1.20E+09
4.57E+08
3.05E+11
1.75E+11
1.24E+11
1.24E+11
5.08E+10
2.09E+11
9.11E+10
3.76E+11
1.18E+03
6.92E+11
8.14E+11
3.92E+11
3.92E+11
3.92E+11
6.62E+11
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1.88E+09
5.68E+09
2.60E+10

4.45E+09
2.10E+10
2.28E+09
6.39E-01
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3.25E+10

5.06E+09
2.15E+10
2.96E+09
2.58E-01
4.46E+06
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1.68E+11
6.64E+10
1.48E+10
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1.73E+08
7.36E+06
1.92E+09
5.53E+04
1.93E+12
2.69E+11
2.00E+11
2.00E+11
8.96E+10
3.26E+11
1.22E+11
5.87E+11
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1.63E+12
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8.22E+11
8.22E+11
1.25E+12
1.68E+11
4.26E+08
2.99E+09
5.78E+09
3.93E+10


<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60) H$_2$O$^+$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$</td>
<td>1.94E+08</td>
<td>2.38E+08</td>
<td>3.31E+08</td>
<td>4.26E+08</td>
<td>5.19E+08</td>
<td>6.10E+08</td>
<td>6.96E+08</td>
<td>7.78E+08</td>
</tr>
<tr>
<td>61) HO$_2$ + O$_2$ $\rightarrow$ O$_3$ + HO$_2$</td>
<td>9.70E+07</td>
<td>1.27E+08</td>
<td>1.95E+08</td>
<td>2.70E+08</td>
<td>3.49E+08</td>
<td>4.30E+08</td>
<td>5.11E+08</td>
<td>5.90E+08</td>
</tr>
<tr>
<td>62) HO$_2$ + O($^3$P) $\rightarrow$ O$_2$ + OH</td>
<td>2.02E+10</td>
<td>3.28E+10</td>
<td>7.14E+10</td>
<td>1.29E+11</td>
<td>2.07E+11</td>
<td>3.02E+11</td>
<td>4.13E+11</td>
<td>5.37E+11</td>
</tr>
<tr>
<td>63) HO$_2$ + H$_2$O $\rightarrow$ O$_3$ + H$^+$</td>
<td>1.40E+04</td>
<td>2.54E+04</td>
<td>4.49E+04</td>
<td>4.54E+04</td>
<td>2.95E+04</td>
<td>1.29E+04</td>
<td>3.92E+03</td>
<td>8.78E+02</td>
</tr>
<tr>
<td>64) O$_2$ + O$^-$ $\rightarrow$ O$_3$ + 2OH$^-$</td>
<td>6.00E+08</td>
<td>6.28E+08</td>
<td>6.55E+08</td>
<td>6.74E+08</td>
<td>6.97E+08</td>
<td>7.35E+08</td>
<td>8.10E+08</td>
<td>1.03E+09</td>
</tr>
<tr>
<td>65) O$_2$ + O$_3$ $\rightarrow$ O$_3$ + O$_2$</td>
<td>1.50E+09</td>
<td>2.13E+09</td>
<td>3.73E+09</td>
<td>5.71E+09</td>
<td>7.99E+09</td>
<td>1.05E+10</td>
<td>1.31E+10</td>
<td>1.59E+10</td>
</tr>
<tr>
<td>66) O$_2$ + H$_2$O $\rightarrow$ HO$_2$ + 'OH</td>
<td>1.55E-01</td>
<td>1.14E+00</td>
<td>2.09E+01</td>
<td>1.82E+02</td>
<td>1.20E+03</td>
<td>6.78E+03</td>
<td>2.87E+04</td>
<td>6.10E+04</td>
</tr>
<tr>
<td>67) HO$_2$ + O($^3$P) $\rightarrow$ 'OH + O$_3$</td>
<td>5.30E+09</td>
<td>6.53E+09</td>
<td>7.84E+09</td>
<td>8.48E+09</td>
<td>8.85E+09</td>
<td>9.09E+09</td>
<td>9.26E+09</td>
<td>9.38E+09</td>
</tr>
<tr>
<td>68) HO$_2$ + O$^-$ $\rightarrow$ OH + O$_2^-$</td>
<td>8.02E+08</td>
<td>1.71E+09</td>
<td>5.75E+09</td>
<td>1.45E+10</td>
<td>3.01E+10</td>
<td>5.43E+10</td>
<td>8.85E+10</td>
<td>1.33E+11</td>
</tr>
<tr>
<td>69) HO$_2$ + H$_2$O $\rightarrow$ H$_2$O$_2$ + OH$^-$</td>
<td>1.27E+06</td>
<td>3.65E+06</td>
<td>1.63E+07</td>
<td>4.40E+07</td>
<td>8.56E+07</td>
<td>1.33E+08</td>
<td>1.76E+08</td>
<td>2.08E+08</td>
</tr>
<tr>
<td>70) O($^3$P) + O($^3$P) $\rightarrow$ O$_2$</td>
<td>2.20E+10</td>
<td>3.58E+10</td>
<td>7.80E+10</td>
<td>1.41E+11</td>
<td>2.26E+11</td>
<td>3.30E+11</td>
<td>4.51E+11</td>
<td>5.86E+11</td>
</tr>
<tr>
<td>71) O($^3$P) + H$_2$O $\rightarrow$ 'OH + 'OH</td>
<td>1.90E+03</td>
<td>6.84E+03</td>
<td>5.31E+04</td>
<td>2.54E+05</td>
<td>8.74E+05</td>
<td>2.37E+06</td>
<td>5.41E+06</td>
<td>1.08E+07</td>
</tr>
<tr>
<td>72) O$^+$ + O$^-$ $\rightarrow$ H$_2$O$_2$ + 2OH</td>
<td>1.00E+08</td>
<td>1.11E+08</td>
<td>1.19E+08</td>
<td>1.21E+08</td>
<td>1.21E+08</td>
<td>1.20E+08</td>
<td>1.20E+08</td>
<td>1.19E+08</td>
</tr>
<tr>
<td>73) O$^+$ + O$_3$ $\rightarrow$ 2O$_2$</td>
<td>7.00E+08</td>
<td>7.39E+08</td>
<td>7.78E+08</td>
<td>8.07E+08</td>
<td>8.44E+08</td>
<td>9.05E+08</td>
<td>1.04E+09</td>
<td>1.51E+09</td>
</tr>
<tr>
<td>74) O$^+$ + H$_2$O $\rightarrow$ 'OH + OH</td>
<td>1.27E+06</td>
<td>3.65E+06</td>
<td>1.63E+07</td>
<td>4.40E+07</td>
<td>8.56E+07</td>
<td>1.33E+08</td>
<td>1.76E+08</td>
<td>2.08E+08</td>
</tr>
<tr>
<td>75) O$_3$ + H$_2$O $\rightarrow$ O$^+$ + O$_2$</td>
<td>4.65E+01</td>
<td>1.98E+02</td>
<td>2.05E+03</td>
<td>1.25E+04</td>
<td>5.29E+04</td>
<td>1.76E+05</td>
<td>4.99E+05</td>
<td>1.34E+06</td>
</tr>
<tr>
<td>76) H$_2$O $\rightarrow$ H$^+$ + OH$^-$</td>
<td>2.12E-05</td>
<td>1.78E-04</td>
<td>3.14E-03</td>
<td>1.68E-02</td>
<td>4.58E-02</td>
<td>7.50E-02</td>
<td>6.33E-02</td>
<td>2.04E-02</td>
</tr>
<tr>
<td>77) SO$_4$ + SO$_3$ $\rightarrow$ S$_2$O$_8$</td>
<td>1.12E+09</td>
<td>1.66E+09</td>
<td>3.12E+09</td>
<td>5.04E+09</td>
<td>7.34E+09</td>
<td>9.97E+09</td>
<td>1.29E+10</td>
<td>1.59E+10</td>
</tr>
</tbody>
</table>