## **Fundamentals of Water Radiolysis**

## Subjects: Others

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Radiolysis of water and aqueous solutions refers to the decomposition of water and its solutions under exposure to ionizing radiation, such as  $\gamma$ -rays, X-rays, accelerated particles, or fast neutrons. This exposure leads to the formation of highly reactive species, including free radicals like hydroxyl radicals (°OH), hydrated electrons (e<sup>-</sup><sub>aq</sub>), and hydrogen atoms (H<sup>•</sup>), as well as molecular products like molecular hydrogen (H<sub>2</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). These species may further react with each other or with solutes in the solution. The yield and behavior of these radiolytic products depend on various factors, including pH, radiation type and energy, dose rate, and the presence of dissolved solutes such as oxygen or ferrous ions, as in the case of the ferrous sulfate (Fricke) dosimeter. Aqueous radiation chemistry has been pivotal for over a century, driving advancements in diverse fields, including nuclear science and technology—particularly in water-cooled reactors—radiobiology, bioradical chemistry, radiotherapy, food preservation, wastewater treatment, and the long-term management of nuclear waste. This field is also vital for understanding radiation effects in space.

water and aqueous solutionsradiolysistime scale of radiolysis eventslinear energy transfer (LET)radical and molecular yieldspHdissolved oxygendose rateFricke chemical dosimeter

Radiation chemistry research focuses heavily on water and aqueous solutions, emphasizing their critical importance in biological systems and a variety of practical applications. This research spans fundamental scientific aspects and extends into areas such as nuclear science and technology—especially in water-cooled nuclear power reactors, where controlling radiolytic processes is crucial to prevent deleterious (corrosion) effects, radiation effects in space, radiotherapy, diagnostic radiology, and the long-term environmental management of nuclear waste materials (for a selection of articles and books published since 1980, see <sup>[1][2][3][4][5][6][7][8][9][10][11][12][13][14][15][16][17]</sup> <sup>[18][19][20][21][22][23][24][25][26][27][28][29][30]</sup>). Additionally, water is the standard reference material in clinical radiation therapy, chosen for its ionizing radiation absorption properties, which closely mimic those of biological tissue <sup>[31]</sup>.

Water radiolysis, the decomposition of water under ionizing radiation, has been an active research area for over a century. In fact, it is known that only a few months after the discovery of X-rays by Wilhelm C. Röntgen at the University of Würzburg, Germany, natural radioactivity was, in turn, discovered in February–May 1896 by Henri Becquerel in Paris. Following this, polonium <sup>[32]</sup> and radium <sup>[33]</sup> were identified in 1898 by Pierre and Marie Sklodowska Curie, along with Gustave Bémont. The Curies and Becquerel were awarded the Nobel Prize in Physics in 1903 for these discoveries. Early observations by Curie and Debierne <sup>[34]</sup>, Giesel <sup>[35][36]</sup>, and Ramsay and Soddy <sup>[37]</sup> revealed that dissolved radium salts continuously decompose aqueous solutions, releasing hydrogen and oxygen gases primarily due to the emission of  $\alpha$ -particles from radium, a process Marie Curie <sup>[38]</sup>

compared to "electrolysis without electrodes". Notably, the pivotal experiment by Rutherford and Royds <sup>[39]</sup> providing direct evidence that alpha particles are ionized helium atoms dates from 1909.

Various other studies on the gaseous emissions resulting from the action of radon on water were subsequently conducted by Ramsay and Cameron <sup>[40][41]</sup> and by Usher <sup>[42]</sup>. These authors demonstrated that  $\alpha$ -particles are primarily responsible for the observed chemical effects. Conversely, Kernbaum <sup>[43]</sup> found that X-rays do not produce any observable gas release under similar conditions, a finding later corroborated by Risse <sup>[44]</sup> and Fricke and Brownscombe <sup>[45]</sup>. In fact, it is now well established that  $\alpha$ -rays induce the radiolysis of water into measurable stable products, whereas X-ray-induced radiolysis in the absence of air is notably weak due to significant and rapid reverse reactions.

Most importantly, André Debierne <sup>[46]</sup>, in 1914, first suggested that water radiolysis produces hydrogen atoms (H<sup>•</sup>) and hydroxyl radicals (<sup>•</sup>OH), a hypothesis that predated the general acceptance of such reactive intermediates by about 30 years. Debierne proposed, "*On peut supposer que chaque molécule d'eau est décomposée en un atome H et un radical hydroxyl OH, deux atomes d'hydrogène se soudant pour faire une molécule d'hydrogène, et deux radicaux hydroxyls donnant lieu à la production d'une molécule d'eau oxygénée*" [One can suppose that each water molecule is decomposed into one hydrogen atom and one hydroxyl radical OH, with two hydrogen atoms bonding to form a hydrogen molecule, and two hydroxyl radicals resulting in the production of a hydrogen peroxide molecule]. Such an interpretation, founded in solid principles, was overlooked for years until Risse <sup>[47]</sup>, the group led by M. Burton and J. Franck (see, e.g., <sup>[48][49]</sup>), and Weiss <sup>[50]</sup> independently stated it.

With these brief reminders in mind, we direct readers to comprehensive historical accounts of aqueous radiation chemistry published in the last few decades [51][52][53][54][55][56][57][58][59][60] for further details.

This review investigates the effects of ionizing radiation on water and dilute aqueous solutions, starting with the basics of water radiolysis. Given the breadth of this topic and space limitations, a comprehensive analysis is beyond the scope of a single manuscript. Instead, we provide a concise assessment of key parameters, including pH, radiation type and energy, dissolved solutes (e.g., oxygen), and dose rate. The review concludes with an examination of the radiolysis of the ferrous sulfate (Fricke) dosimeter under various experimental conditions. Much of the content aligns with the curriculum of the author's graduate-level *Introduction to Radiation Chemistry* course at the Université de Sherbrooke.

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