



**PEACEFUL USES  
OF ATOMIC ENERGY**

# **Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy**

**Held in Geneva  
1 September - 13 September 1958**

**Volume 29  
Chemical Effects of Radiation**



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**1958**



## PREFACE

More than 2,100 papers were submitted by the nations, the specialized agencies, and the International Atomic Energy Agency, which participated in the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. The number of papers was thus about twice that involved in the First Conference. Provision was therefore made to hold five concurrent technical sessions in comparison with the three that were held in 1955. Even so, the percentage of orally presented papers was less in 1958 than in 1955.

In arranging the programme, the Conference Secretariat aimed at achieving a balance, allowing adequate time for presentation of as many papers as possible and, nevertheless, leaving time for discussion of the data presented. Three afternoons were left free of programme activities so that informal meetings and discussions among smaller groups could be arranged. No records of these informal meetings were made.

A scientific editorial team assembled by the United Nations checked and edited all of the material included in these volumes. This team consisted of: Mr. John H. Martens, Miss L. Ourom, Dr. Walter M. Barss, Dr. Lewis G. Bassett, Mr. K. R. E. Smith, Martha Gerrard, Mr. F. Hudswell, Betty Guttman, Dr. John H. Pomeroy, Mr. W. B. Woollen,

Dr. K. S. Singwi, Mr. T. E. F. Carr, Dr. A. C. Kolb, Dr. A. H. S. Matterson, Mr. S. Peter Welgos, Dr. I. D. Rojanski and Dr. David Finkelstein.

The speedy publication of such a vast bulk of literature obviously presents considerable problems. The efforts of the editors have therefore been primarily directed towards scientific accuracy. Editing for style has of necessity been kept to a minimum, and this should be noted particularly in connection with the English translations of certain papers from French, Russian and Spanish.

The Governments of the Union of Soviet Socialist Republics and of Czechoslovakia provided English translations of the papers submitted by them. Similarly, the Government of Canada provided French-language versions of the Canadian papers selected for the French edition. Such assistance from Governments has helped greatly to speed publication.

The task of printing this very large collection of scientific information has been shared by printers in Canada, France, Switzerland, the United Kingdom and the United States of America.

The complete Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy are published in a 33-volume English-language edition as follows:

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# Recent Studies on Reactions in Irradiated Water

By Edwin J. Hart \*

Ionizing radiations create free hydrogen atoms and hydroxyl radicals in liquid water. All phases of this net dissociation reaction from the ionization act to the final stages of complex chemical reaction are under investigation. In particular much progress has been made in the establishment of free radical and molecular product yields for  $\gamma$  rays and for a group of heavy particle radiations. The precise determination of these yields paves the way for the development of diffusion kinetics and for the unravelling of complex hydrogen atom and hydroxyl radical reactions. This survey paper deals with recent research on diffusion theory, free radical yields, new radical species, chemical dosimetry and the chemistry of some simple aqueous inorganic and organic reactions.

## FREE RADICAL DIFFUSION THEORY

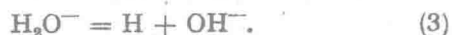
Studies in irradiated water at both theoretical and experimental levels support the dissociation of liquid water into free radicals,



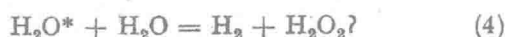
Almost nothing is known about the detailed mechanism of reaction (1), but the process giving rise to the hydroxyl radical is written as:



Then capture of the secondary electron by water gives  $\text{H}_2\text{O}^-$  which produces hydrogen atoms:



The net reaction of (2) and (3) is (1). Reaction (1) is so simple that one wonders if it is the only net primary process. Can there be other reactions leading directly to the "molecular products", hydrogen and hydrogen peroxide? Is it possible that excited water molecules react with neighboring water molecules in the "spur" by a reaction such as:



The answer to these questions is no. However, hydrogen and hydrogen peroxide appear as primary irradiation products in dilute aqueous solutions. Their yields,  $G(\text{H}_2)$  and  $G(\text{H}_2\text{O}_2)$ , decrease with

increasing concentration of solute. In the case of hydrogen, the solute,  $\text{S}_1$ , scavenges hydrogen atoms and thereby decreases  $G(\text{H}_2)$ .



and an oxidizable solute,  $\text{S}_2$ , decreases  $G(\text{H}_2\text{O}_2)$  because of reaction (8):



Qualitatively, experimental results covering a wide variety of scavengers are in accord with free radical dissociation reaction (1). As the molecular yield decreases with increasing concentrations of  $\text{S}_1$  or  $\text{S}_2$ , the free radical yields increase in the manner expected from reactions (5)–(8).

Substantially complete suppression of hydrogen in calcium nitrate solutions clinches the argument against the primary molecular product reaction (4).  $G(\text{H}_2)$  for reactor irradiated 15.9 M calcium nitrate solutions is only 0.011.<sup>1</sup> If only energy absorbed in the water is considered,  $G(\text{H}_2)$  is 0.025. Thus for mixed  $\gamma$ -ray and recoil proton radiation from the  $\text{N}^{14}(\text{n},\text{p})\text{C}^{14}$  reaction, molecular hydrogen is essentially absent. Therefore, reaction (4) is unimportant.

The theory of the track effect is being developed in a number of laboratories,<sup>2-7</sup> and even with a one-radical model, by assuming an original Gaussian distribution of free radicals and simultaneous diffusion of radicals with radical-radical and radical-solute reactions, the theoretical fraction of radicals scavenged agrees well with the experimental fraction. A serious shortcoming of these studies is the absence of reliable absolute radical-radical and radical-solute rate constants, free radical diffusion constants and constants relating to the number and distribution of free radicals in a spur. However, by choosing reasonable values for these constants, relatively good agreement is found between experiment and theory for the case of spherical diffusion.<sup>2-8</sup>

Recently, a numerical solution of the equation

$$\frac{\partial n}{\partial t} = D \left[ \frac{\partial^2 n}{\partial r^2} + \frac{\varepsilon}{r} \frac{\partial n}{\partial r} \right] - 2\alpha n^2 - \beta c n \quad (9)$$

\* Argonne National Laboratory, Lemont, Illinois.

with boundary conditions suitable to several spherical and cylindrical diffusion cases has been obtained using an electronic computer.<sup>7</sup> Equation (9) represents the reaction kinetics of a one-radical model with a single scavenger.  $D$  is the diffusion constant,  $r$  is the distance from the center of symmetry of the radicals of concentration  $n$ ,  $\alpha$  and  $\beta$  are rate constants, and  $c$  is the concentration of solute.  $\epsilon$  equals two for spherical diffusion and one for cylindrical diffusion. The number of radicals reacting with solute is reported as a function of two dimensionless parameters that define the problem. This work enables comparison of experiment with theory for a great variety of ionizing radiations. The advent of high speed multi-channel computers into radiation chemistry augurs well for the future of diffusion kinetics. A more realistic model incorporating such parameters as several free radicals, different rate and diffusion constants and local depletion of solute into the diffusion kinetic picture can now be treated.

Scavenger studies with aqueous potassium iodide irradiated by 3.4 Mev  $\alpha$  particles show a sharp decrease in  $G(\text{H}_2\text{O}_2)$  in the concentration range 0.01 to 0.1  $M$  solutions.<sup>8</sup> The functional decrease in  $G(\text{H}_2\text{O}_2)$  agrees with the results predicted by the cylindrical diffusion model. Thus for densely ionizing  $\alpha$  particles, our primary dissociation reaction (1) holds.

### FREE RADICAL YIELDS

A knowledge of free radical yields is of great practical value to chemists. These yields enable us to predict quantitative chemical changes taking place during irradiation. Besides, they help to untangle mechanisms of reactions. Two important aspects are: (1) effect of charge and velocity of ionizing particles on the radical yields,  $G(\text{H})$  and  $G(\text{OH})$ , and (2) effect of pH on these yields.

Chemical systems that measure radiation yields are given in Table 1. The simplified equations, applicable only under conditions where competitive reactions are minimized, appear also. In these equations the experimental yield,  $G(\text{Product})$ , is equated to the free radical and molecular product yields denoted by lower case  $g$ 's. Only rarely does a single system differentiate between the four principal species generated.

The sum or the difference of certain systems gives these basic yields. Starting with the oxygen reactions, note that  $g(\text{OH})$  is obtained as the difference between the two peroxide yields, (II-I), and that  $g(\text{H})$  is given by the difference between the two ferric yields, (III-IV);  $g(\text{H})$  is also obtained from the dissolved deuterium system, V;  $g(\text{H}_2\text{O}_2)$  is uniquely measured by the ceric system VI and  $g(\text{HO}_2)$  by the ferrous-cupric system VII. (Evidence for the hydroperoxy radical,  $\text{HO}_2$ , is presented in the "New Radical Species" section.) Systems VIII, IX and X, involving ferric ion and formic acid or methyl alcohol, give us the sum,  $g(\text{H}) + g(\text{OH})$ . And the formic acid-oxygen system, XI, enables one to measure each of the molecular product and free radical yields. If hydrogen is determined, each of the systems, including XII, boiling water, provides  $g(\text{H}_2)$ . Unless each of the yields can be measured separately, the equation of material balance, XIII, helps to derive these product yields. These systems are limited to acid solutions except for I, II, V, XI and XII which may be used over the entire pH range.

Light particle radiations such as X rays,  $\gamma$  rays and electrons generate free radicals mainly. The sum,  $G(\text{H}) + G(\text{OH})$ , varies between 6 and 7, gradually increasing as the scavenger concentration increases from 0.0001  $M$  to 1.0  $M$ .<sup>9, 10</sup> Molecular hydrogen and hydrogen peroxide yields are 0.4-0.5. Heavy particle radiations produce molecular hydrogen

Table 1. Systems for Measuring Yields in Irradiated Water

System	Simplified equation
I $\text{O}_2, \text{Br}^-$	$G(\text{H}_2\text{O}_2) = g(\text{H}_2\text{O}_2) + \frac{1}{2}[g(\text{H}) - g(\text{OH})]$
II $\text{O}_2, \text{H}_2$	$G(\text{H}_2\text{O}_2) = g(\text{H}_2\text{O}_2) + \frac{1}{2}[g(\text{H}) + g(\text{OH})]$
III $\text{Fe}^{++}, \text{O}_2$	$G(\text{Fe}^{+++}) = 2g(\text{H}_2\text{O}_2) + 3g(\text{H}) + g(\text{OH})$
IV $\text{Fe}^{++}$	$G(\text{Fe}^{+++}) = 2g(\text{H}_2\text{O}_2) + g(\text{H}) + g(\text{OH})$
V $\text{D}_2$	$G(\text{HD}) = g(\text{H})$
VI $\text{Ce}^{4+}$	$\begin{cases} G(\text{Ce}^{3+}) = 2g(\text{H}_2\text{O}_2) + g(\text{H}) - g(\text{OH}) \\ G(\text{O}_2) = g(\text{H}_2\text{O}_2) \end{cases}$
VII $\text{Fe}^{++}, \text{Cu}^{++}$	$\begin{cases} G(\text{Fe}^{+++}) = 2g(\text{H}_2\text{O}_2) - g(\text{H}) - g(\text{HO}_2) + g(\text{OH}) \\ G(\text{O}_2) = g(\text{HO}_2) \end{cases}$
VIII $\text{Fe}^{+++}, \text{HCOOH}$	$G(\text{Fe}^{++}) = g(\text{H}) + g(\text{OH})$
IX $\text{Fe}^{+++}, \text{CH}_3\text{OH}$	
X $\text{Fe}^{+++}, \text{Cu}^{++}, \text{HCOOH}, \text{O}_2$	
XI $\text{HCOOH}, \text{O}_2$	$\begin{cases} G(\text{H}_2\text{O}_2) = g(\text{H}_2\text{O}_2) + \frac{1}{2}[g(\text{H}) + g(\text{OH})] \\ G(\text{CO}_2) = g(\text{OH}) \\ G(-\text{O}_2) = \frac{1}{2}[g(\text{H}) + g(\text{OH})] \\ G(\text{H}_2) = g(\text{H}_2) \end{cases}$
XII Boiling water	$G(\text{H}_2) = g(\text{H}_2)$
XIII	Material balance equation $g(\text{H}) + 2g(\text{H}_2) = g(\text{OH}) + 2g(\text{H}_2\text{O}_2)$



and hydrogen peroxide principally. The limit is reached with fission recoils where  $G(\text{H}_2)$  equals 1.83.<sup>11</sup> For all practical purposes  $g(\text{H})$  and  $g(\text{OH})$  are zero for these fission recoils. Work has been reported on protons,<sup>12</sup> deuterons,<sup>12, 13</sup>  $\alpha$  particles,<sup>13</sup>  $\text{B}^{10}(\text{n}, \alpha) \text{Li}^7$  and  $\text{Li}^6(\text{n}, \alpha) \text{H}^3$ .<sup>14, 15</sup> Over this entire range of radiations the number of water molecules decomposed (in acid solutions) varies only from 4.5 for  $\gamma$  rays to 3.6 for fission recoils whereas the sum,  $g(\text{H}) + g(\text{OH})$  decreases from 6.0 to 0.

Besides ionization processes, dissociation processes contribute to free radical yields in water. Light at 1849 and 1960 Å dissociates liquid water with a quantum yield,  $\phi(-\text{H}_2\text{O})$ , of 0.44.<sup>16</sup> Dilute formic acid solutions are decomposed by these radiations into hydrogen and carbon dioxide. These radiations also form hydrogen deuteride in the system, dissolved deuterium gas-liquid water. Thus quantum yields as high as 0.44 show the importance of dissociation processes in radiation chemistry.

More hydrogen atoms than hydroxyl radicals appear in  $\gamma$ -ray irradiated acid solutions. In 0.8 *N* sulfuric acid  $g(\text{H})$  is 3.65 and  $g(\text{OH})$  is 2.95.<sup>17</sup> As the pH increases above 3, the difference,  $g(\text{H}) - g(\text{OH})$ , decreases. In neutral solutions, the evidence is conflicting; in formic acid-oxygen systems,  $g(\text{H})$  nearly equals  $g(\text{OH})$ ; in oxygen-bromide ion solutions,  $g(\text{H}) - g(\text{OH})$  is 0.6.<sup>38</sup> Over the entire pH range,  $g(-\text{H}_2\text{O})$  remains constant at 4.0 to 4.5.<sup>18</sup> The exact value depends on the effectiveness of the scavenger used to measure the yields.

The cage effect prevents efficient dissociation of water molecules in liquid water. As expected, free radical yields in water vapor are high compared to yields in liquid water.  $g(-\text{H}_2\text{O})$  equals 11.7 for tritiated steam containing scavenger concentrations of deuterium.<sup>19</sup> Here the electron liberated in the tritium atom decay ionizes the water molecules. The simple mechanism explains the stoichiometry:



$G(\text{HD})$  equals 11.7 and so  $g(-\text{H}_2\text{O})$  equals 11.7. This is a nonchain reaction at temperatures below 150°C. Above this temperature a chain reaction sets in with an activation energy of 18 kcal. The chain propagating step is



### NEW RADICAL SPECIES

Evidence accumulates that species other than hydrogen atoms and hydroxyl radicals exist in irradiated water. Suggested species are the hydroperoxy radical,  $\text{HO}_2$ , hydrogen molecule ion,  $\text{H}_2^+$ , oxygen atom ion,  $\text{O}^-$  and subexcitation electrons.

Recent experimental work supports the inclusion of the hydroperoxy radical ( $\text{HO}_2$ ) among the species

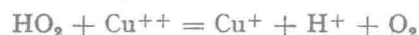
present in the track of ionizing particles. Thus the general radiolysis equation becomes:



$g(\text{HO}_2)$  is low, being 0.026 for  $\gamma$  rays but increasing to 0.15 for low energy  $\alpha$  rays. This hydroperoxy radical behaves like a primary radical. At high solute concentrations, this radical is not found. For this reason, it is probably formed in the spur by the reaction



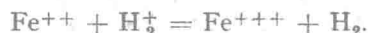
When hydroxyl radicals are removed by high scavenger concentrations, reaction (11) cannot take place. Experimental evidence for  $\text{HO}_2$  stems from (a) oxygen formation in air-free  $\text{FeSO}_4$ - $\text{CuSO}_4$ <sup>9</sup> by the reaction:



(b) a lower than predicted  $G(\text{Ce}^{++})$  in the  $\text{Ce}^{++}$ - $\text{Tl}^+$  system<sup>20</sup> and (c) oxygen formation in the  $\text{Fe}^{+++}$ - $\text{Cu}^{++}$ - $\text{HCOOH}$  system.<sup>10</sup>

Rotating sector experiments using electrons irradiating deaerated water show a species with a half-life of 0.01 sec.<sup>21</sup>  $G(\text{H}_2\text{O}_2)$  depends on (Intensity)<sup>1</sup>. This species may be the hydroperoxy radical generated to some extent in the track but to a much greater extent by hydroxyl radical reaction with hydrogen peroxide outside the track.

Ferric ion and hydrogen yields in deaerated acid solution are explained by the  $\text{H}_2^+$  reaction



But a three body reaction accounts for this oxidation reaction



as well as participation of the polarized hydrogen atoms in the hydration layer of the ferrous ion by the reaction



The absence of a chain reaction in the water-deuterium system, the absence of a pH effect in the hydrogen atom-ferrous sulfate reaction and the existence of an isotope in the  $\text{H}$  (or  $\text{D}$ ) +  $\text{Fe}^{++}$  reaction in light and heavy water support the oxidation by hydrogen atoms plus hydrogen ions rather than by the  $\text{H}_2^+$  intermediate.<sup>22-24</sup>

pH studies reveal an ionization of the hydroxyl radical at pH's above 9.0:<sup>25</sup>



In water containing dissolved isotopically labelled oxygen,  $\text{O}^*_2$ , normal oxygen,  $\text{O}_2$ , is a product. The over-all reaction is:



In solutions up to a pH of about 9,  $G(\text{O}_2)$  is 1.0. Above this pH, a chain reaction sets in increasing